The photogalvanic effect in media lacking a center of symmetry

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This review presents the fundamental theoretical concepts concerning the photogalvanic effect (PGE)—the phenomenon of appearance of a direct current in a homogeneous medium under uniform illumination. This effect can occur in all media lacking a center of symmetry, in particular, in ferroelectrics, piezoelectrics, gyrotropic crystals, and in gases and liquid possessing natural optical activity. The starting point of a systematic microscopic theory is the asymmetry of the elementary electronic processes—their noninvariance with respect to spatial reflection. Within the framework of the theory, we study the most important mechanisms of the PGE in the regions of impurity, interband, and intraband light absorption. Possible observable manifestations of the PGE are discussed. Theoretical results are compared with experimental data.

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CONTENTS

1. INTRODUCTION

An electric current in a medium usually stems either from applied fields (electric and magnetic) or from spatial inhomogeneity (gradient of temperature or illumination).[1,2]

It has become evident in recent years that currents of another type can occur under thermodynamic nonequilibrium conditions that are due to lack of a center of symmetry in the medium. The most important effect of this class is the photogalvanic effects (PGE)—the appearance of a direct electric current in homogeneous crystals under uniform illumination.

The PGE has been observed in many of its manifestations during the period 1969–1974 by a number of authors.[1)] Thus, in experiments[5-7] performed on crystals of the ferroelectrics $LiNbC_3$ and $BaTiO_3$, constant pho-

[1)]It is not ruled out that the PGE had been observed considerably earlier, e.g., in the experiments of Refs. 3 and 4. However, systematic studies of the photoelectric properties of crystals whose results allow one to speak with assurance of observing the effect began only with development of laser technology.

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tocurrents $j_{ph} \sim 10^{-10}$ A/cm^2, and photovoltages that substantially exceeded the width of the forbidden band were observed. These phenomena were attributed to relaxation of the internal fields in the crystals. In studies[8,9] of the effect of entrainment of electrons by light in the piezoelectric Te, an additional contribution to the current was observed. This current showed a strong dependence on the polarization of the light, and was interpreted as an optical rectification effect (alteration by light of the polarization of the crystal[10,11]). Thus the explanations presented could pertain only to a transition current; they contradicted the observations.

Results analogous to Refs. 5–7 were obtained in 1974 by A. M. Glass and his associates with the ferroelectrics $LiNbO_3$, $BaTiO_3$, and $LiTaO_3$.[12,13] Moreover, these studies showed that the direct photocurrents (the measurements were performed over a period of 20 hours) depend linearly on the light intensity. In insulated $LiNbO_3$ crystals they give rise to anomalously large photovoltages, $U \sim 10^3 - 10^5$ V/cm. Here the electric field intensity in the crystal satisfied the relationship $j_{ph} + \sigma E = 0$ (σ is the conductivity of the crystal), which reflects the fact that the total current equals zero under stationary conditions.

The experimental data discussed above seriously contradicted the then prevailing ideas concerning the mechanisms of origin of currents and emf's in crystals. The effect of transition processes caused by heating of the crystals by the light or relaxation of some internal fields was ruled out by the long time of observation of the currents. The anomalously large values of the photovoltages and the dependence of their sign on the frequency and polarization of the light[14] ruled out Dember effects,[1] entrainment of electrons by photons,[15] microinhomogeneities of the crystals,[16] and other known photovoltaic phenomena.[2] The authors of Refs. 12 and 13 for the first time attributed the photoinduced direct currents to the existence in the ferroelectric of an intrinsic unique direction—the polar axis. They proposed that light can cause a directional current of electrons along the polar axis of the crystal. This idea, together with the unusual character of the observed regularities stimulated development of theoretical and experimental studies.[2)]

We should note that the possibility of a photogalvanic effect in semiconductors lacking a center of symmetry had been pointed out as early as 1969.[17,18] In studying nonlinear optical phenomena, these authors noted that the current $\mathbf{j}(\omega_1 - \omega_2)$ at the difference frequency of two waves $\mathbf{E}(\omega_1)$ and $\mathbf{E}(\omega_2)$ formally does not vanish in the limit as $\omega_1 - \omega_2 \to 0$. Thus a direct current can arise that cannot be described in terms of conductivity and photoconductivity. However, the theory developed in Refs. 17 and 18 remained valid only when $|\omega_1 - \omega_2| \gg \Gamma$, where Γ is the characteristic rate of electronic collisions.[19] As has been shown subsequently (see Sec. 7), the mechanisms treated in Refs. 17 and 18 do not give rise to a direct current when collisions are taken into account.

A theory of the PGE originated in Refs. 20 and 21. First of all, the theory had to resolve two problems of principle. Starting from first principles, it was necessary to establish the reason for the existence of direct currents of particles in the absence of macroscopic forces. Second, it was necessary to understand why the PGE cannot arise from "blackbody radiation," i.e., thermal photons distributed according to Planck's law. The existence of uniform currents in thermodynamic equilibrium would imply the existence of a perpetual-motion machine of the second kind. The solution of the stated problems has shown that the PGE differs substantially from the known kinetic and nonlinear-optical phenomena. It amounts to a striking macroscopic manifestation of asymmetry of the elementary electronic processes—their noninvariance under spatial inversion. In view of its importance in the subsequent treatment, it is expedient to take up this point in greater detail.

The simplest example of asymmetry of electronic processes is provided by the process of elastic scattering of a particle by a potential lacking central symmetry. As is known,[22,23] the properties of the scattering centers are characterized by the probability $W_{\mathbf{kk}'}$ of transition of a particle from the state with the momentum $\mathbf{k}'$ to the state $\mathbf{k}$. This approach can be applied to both a quantum and a classical description of scattering and also in treating inelastic scattering. In elastic scattering the probability $W_{\mathbf{kk}'}$ satisfies the symmetry relationship:

$$W_{\mathbf{k},\mathbf{k}'} = W_{-\mathbf{k}',-\mathbf{k}}. \tag{1.1}$$

This is implied by the invariance of the equations of motion under time inversion (T-invariance) and is called the reciprocity theorem.[22] As is equally well known, for noncentral potentials the probability $W_{\mathbf{kk}'}$ is not invariant under the substitution $\mathbf{k}, \mathbf{k}' \to -\mathbf{k}, -\mathbf{k}'$. That is, it possesses the asymmetry

$$W_{\mathbf{kk}'} \neq W_{-\mathbf{k},-\mathbf{k}'}. \tag{1.2}$$

The asymmetry of scattering (1.2) and the relationship (1.1) are pictorially demonstrated by the example of elastic scattering of a particle by a wedge-shaped potential (Fig. 1).

The concept of asymmetry extends also to other elementary processes, in particular, processes of excitation and recombination of electrons. If $w_{\mathbf{k}}^{i}$ and $w_{\mathbf{k}}^{r}$

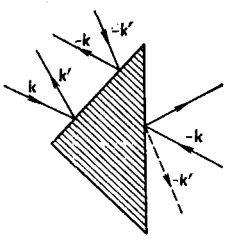

FIG. 1. Asymmetry of elastic scattering by a wedge. The reciprocity theorem is satisfied.

[2)]The original studies[12,13] employed the term "high-voltage bulk photovoltaic effect" for the new phenomenon. The literature in our country has employed this term alongside the term PGE.

are respectively the probabilities of transition of an electron from an impurity to the conduction band and of recombination with the impurity, then an asymmetry of these processes implies that:

$$w_{\mathbf{k}}^{\mathrm{i,r}} \neq w_{-\mathbf{k}}^{\mathrm{i,r}}. \tag{1.3}$$

At the same time, owing to T-invariance (reciprocity theorem), we have

$$w_{\mathbf{k}}^{\mathrm{i}} = w_{-\mathbf{k}}^{\mathrm{r}}. \tag{1.4}$$

The relationships (1.3) and (1.4) are illustrated by Fig. 2, which shows the processes of photoionization of a particle from a noncentral potential well and of recombination.

Asymmetry of the elementary processes substantially affects the kinetics of electrons in media lacking a center of symmetry. As we see already from Fig. 1, fluxes of particles with opposing momenta cease to cancel each other out after scattering. Under these conditions, as we shall show in Sec. 5, we can treat thermodynamic equilibrium as an exceptional situation in which complete elimination is attained of the contributions to the current from different groups of processes and different regions in k-space. The character of this compensation is determined by the concrete mechanisms of the asymmetry of the electronic processes. The distinctive role of thermodynamic equilibrium has the result that practically any nonequilibrium situation in media lacking a center of symmetry breaks down the fine mechanism of compensation, i.e., it gives rise to a current.

We should note that the following equality holds in the absence of asymmetric scattering under the condition of T-invariance:

$$W_{\mathbf{k}\mathbf{k}'} = W_{\mathbf{k}'\mathbf{k}}. \tag{1.5}$$

This is often called the principle of detailed balancing.[23,24] This principle does not stem from any general symmetry relationships, and it breaks down when even any one of the above-cited conditions is not satisfied. In particular, breakdown of detailed balancing can arise from a magnetic field. The failure of detailed balancing in collision of noncentrosymmetric molecules was already noted by Boltzmann[25] (Ref. 26 is devoted to elucidating this situation in the quantum domain). It was subsequently shown that failure of detailed balancing substantially affects the kinetic description of a gas.[27] Thus the distribution function of the particles necessarily becomes dependent not only on the velocities but also on the angular momenta. Failure of Eq. (1.5) is also required for the appearance of the anomalous Hall effect.[27,28] It is useful to note that the breakdown of detailed balancing begins to be manifested only starting with the second Born approximation,[22] whereas the overwhelming majority of studies restrict the treatment in terms of kinetics to first-order perturbation theory. Apparently this involves the misunderstanding in which a considerable fraction of the literature on problems of kinetics (e.g., Refs. 29–31) has viewed Eq. (1.5) as universal.

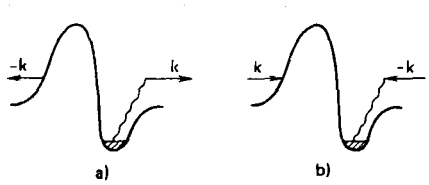

FIG. 2. Asymmetry of photoexcitation from a noncentral potential well (a) and recombination (b).

Remarkably, the fact of existence of the PGE, its relationship to the failure of detailed balancing (asymmetry of the elementary processes), the nonequilibrium character of the medium, and the nontrivial character of the vanishing of the current under conditions of thermodynamic equilibrium—all these general regularities can be understood in terms of simple models. We shall treat these models in Sec. 2.

As we shall show below, the PGE can occur in all media without exception that lack spatial-inversion symmetry. In addition to crystals lacking a center of symmetry, they include also isotropic media—liquids and gases containing right-handed or left-handed molecules, i.e., possessing natural optical activity. The source of nonequilibrium can be not only light but also sound, or opposing or isotropic particle fluxes, etc. *Fluxes of particles, charges, heat, and other physical quantities are an inalienable feature of nonequilibrium states lacking a center of symmetry.* To no small degree, this statement pertains also to nonstationary phenomena not sustained by external sources. Any process of relaxation toward thermodynamic equilibrium in media possessing polar directions should also be accompanied by a current.

Interestingly, an effect has actually been known for more than 20 years that is akin to the photogalvanic effect in nature. In 1956 Lee and Yang proposed in their famous study[32] that parity is not conserved in weak interactions. That is, our space, although isotropic, nevertheless does not possess a center of symmetry. As Lee and Yang showed, electrons produced in the β-decay of a neutron: $n \to p + e + \nu$, should show an asymmetric distribution in the presence of a magnetic field H. That is, a current should arise in the direction ηH, where η is a pseudoscalar, that characterizes the noncentrosymmetry of our space. Precisely this effect was observed in the experiments of Wu with ^{60}Co nuclei at $T \approx 10^{-2}$ K.[33]

In this review we wish to acquaint the reader with the general properties of the new effect and its fundamental mechanisms, and also to point out the relationship of the PGE to other physical phenomena. We shall pay major attention to crystalline media. We shall analyze the experiments on the PGE and compare them with the theoretical concepts.

2. ELEMENTARY MODELS OF THE PGE

a) The wedge model

We consider a gas of noninteracting particles that are being scattered by randomly located, but identically oriented wedges (Fig. 3). Evidently this medium does not possess a center of symmetry. In the absence

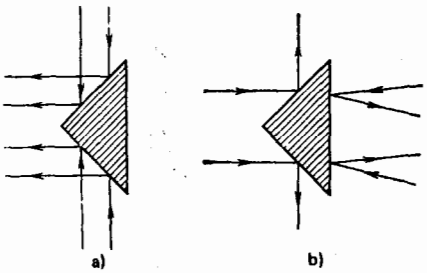

FIG. 3. Current originating in scattering by a wedge: a) the field oscillates the particles vertically—current to the left; b) field directed horizontally—current flows to the right.

of external agents, collisions will establish an isotropic velocity distribution of the particles, since a spherically symmetric distribution of particles remains spherically symmetric upon elastic scattering by any convex body. Here the mutually compensated fluxes are not those travelling in opposite directions, but the direct and time-reversed fluxes.

Let the source of nonequilibrium be the alternating field $e\tilde{E}\cos\omega t$. This agent maintains an anisotropy of the distribution of particles. That is, it increases the fraction of particles moving with and against $\tilde{E}$. As we see from Fig. 3(a), the scattering of vertically moving particles yields an overall flux directed to the left. If the direction of the field changes to the horizontal [see Fig. 3(b)], the flux changes sign, i.e., it will be directed to the right. Thus we have established a relation of the fluxes to the nonequilibrium of the medium lacking a center of symmetry.

We can also estimate the magnitude of the flux within the framework of this model. In the first stage we must determine the fraction of the particles moving anisotropically under the action of the high-frequency field. As we can easily understand, we have

$$\frac{\delta n_a}{n_0} \sim \left(\frac{v_E}{v_T}\right)^2 \ll 1.$$

Here n_0 is the total concentration, $v_T = \sqrt{T/m}$ is the thermal velocity, and $v_E = e\tilde{E}/m\omega$ is the oscillatory velocity of the particles. Although the presented example is not entirely perspicuous, it does not involve the properties of the scattering. Asymmetry of scattering is manifested when anisotropically moving particles collide with the wedges. Evidently, the magnitude of the flux must be proportional to the frequency Γ of these collisions and to the time $\Gamma_{\rm iso}^{-1}$ for which the particles constituting the flux keep their directed momentum. This time can be governed not only by the collisions with the wedges, but also those with other scatterers (not necessarily asymmetric). Thus we have the following expression for the flux:

$$j_{\rm ph} \sim e n_0 v_T \left(\frac{v_E}{v_T}\right)^2 \frac{\Gamma}{\Gamma_{\rm iso}} \xi. \tag{2.1}$$

The quantity $\xi \leq 1$ is determined by the geometry of the wedge and characterizes its degree of asymmetry.

b) The model of asymmetric wells

Asymmetry of a potential well, which serves as a model of an impurity (Fig. 4), causes a particle lying

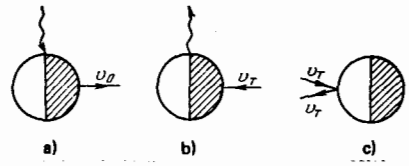

FIG. 4. Current originating in the processes of ionization, recombination, and scattering, for a noncentral potential well. The absorbing part of the center is hatched.

in it to emerge mainly to the right when acted on by light. This model contains three independent contributions to the total flux. Let us examine them in detail.

Each event of absorption of a light quantum gives rise to a particle with the velocity v_0, as determined by the excitation conditions, e.g., the frequency ω of the light. If κ is the absorption coefficient for the light, and J is its intensity, then the number of particles emerging per unit time is $\kappa J/\hbar\omega$. Taking into account the fact that the particles emerging toward the right participate in creating a flux only for the time $\Gamma_{\rm iso}^{-1}$ (the time for isotropization owing to collisions), we have the following expression for the contribution to the flux arising from excitation: $j_e \approx e v_0 \kappa J/\hbar\omega\Gamma_{\rm iso}$.

The second contribution to the flux involves recombination. Owing to invariance under time inversion, the only particles that can recombine are those arriving at the well from the right [see Fig. 4(b)]. Evidently the removal of the particles moving from right to left leads to a flux in the opposite direction. Thus the fluxes caused by recombination and excitation run in the same direction and cannot compensate one another in equilibrium with blackbody radiation. Of course, this situation stems directly from (1.3) and (1.4). To estimate this magnitude of the flux j_r, we must account for the fact that the rates of excitation and recombination are equal ($\kappa J/\hbar\omega$) under steady-state conditions, while the asymmetry of velocities of the particles that arises after recombination again relaxes within the isotropization time $\Gamma_{\rm iso}^{-1}$. Let us also take into account the fact that the particles that participate in recombination are mainly those that have been able to become thermalized by interaction with the thermostat. That is, they have the characteristic velocity v_t. Taking the abovesaid into account we have $j_r \approx (v_t/v_0) j_e$.

Finally, the third contribution to the flux comes from the scattering process. Evidently, only particles moving from left to right can be scattered [see Fig. 4(c)]. The corresponding contribution to the flux is opposite in direction to the contributions from excitation and recombination. Since the number of events of recombination and collision is the same, while the mean velocity of the particles is v_t, then $j_{\rm col} = -2j_r$. Thus the total flux is

$$j_{\rm ph} \approx e \frac{\kappa J}{\hbar\omega\Gamma_{\rm iso}} (v_0 - v_t)\xi. \tag{2.2}$$

The parameter ξ characterizes the degree of asymmetry of the potential and must be determined by quantum-mechanical calculations. If the potential barrier in Fig. 4 is large, then $\xi \approx 1$, but if the potential well is almost symmetric, then $\xi \ll 1$.

The sign of the flux depends on the relationship between v_0 and v_t. If the medium is in equilibrium with the radiation, then the excitation of the particles by the thermal photons occurs at the rate v_t, and the total flux is $j_{ph}=0$.

3. PHENOMENOLOGICAL TREATMENT OF THE PGE

The constant component of the electric current in a homogeneous medium can be expanded in a power series in the electric field:

$$j_i=\sigma^0_{ij}E_j+\beta^0_{inl}E_lE_n+\sigma^0_{ilnm}E_lE_nE_m+\gamma_{ilnm}E_l\tilde{E}_n\tilde{E}^*_m+\beta_{iln}(\omega)\tilde{E}_l\tilde{E}^*_n. \tag{3.1}$$

Here E is the constant electric field, and $\tilde{E}(\omega)=\tilde{E}^*(-\omega)$ is the intensity of the field of frequency ω. The first three terms describe the static conductivity taking the nonlinear corrections into account, and the fourth term describes the photoconductivity. The last term describes the photogalvanic effect, or photocurrent in the medium in the absence of a constant field. For partially polarized light, the combination $\tilde{E}_l(\omega)\tilde{E}^*_n(\omega)$ must be replaced by the polarization density matrix.

All the information on the PGE is included in the photogalvanic tensor $\beta_{iln}(\omega)$. Let us examine the general restrictions on its components that stem from the transformation properties of the photocurrent:

$$j_i^{ph}=\beta_{iln}\tilde{E}_l\tilde{E}^*_n. \tag{3.2}$$

The current $\mathbf{j}_{ph}$ changes sign upon spatial inversion, while the quantity $\tilde{E}_l\tilde{E}^*_n$ does not do so. Hence the tensor β_{iln} can differ from zero only in media lacking a center of symmetry.[18]

Since $\mathbf{j}_{ph}$ is real, the right-hand side of (3.2) cannot be altered when we take the complex conjugate. Hence we have

$$\beta_{iln}=\beta^*_{inl}. \tag{3.3}$$

Thus the real component of β_{inl} is symmetric with respect to the last two indices, while the imaginary component is antisymmetric:

$$j_i^{ph}=\beta^s_{inl}\tilde{E}_n\tilde{E}^*_l+i\beta^{as}_{il}[\tilde{E}\tilde{E}^*]_l,\quad \beta^s_{iln}=\beta^s_{inl}. \tag{3.4}$$

The second term in (3.4) differs from zero only for elliptically polarized light. Hence we shall call the associated photocurrents circular. We shall call the photocurrents described by the tensor β^s_{inl} linear.

The time-inversion operation changes the sign of $\mathbf{j}_{ph}$, while $\tilde{E}_n(\omega)\tilde{E}^*_l(\omega)$ transforms into $\tilde{E}^*_n(\omega)\tilde{E}_l(\omega)$. Therefore the tensor β^s_{inl} changes sign under this operation, while β^{as}_{il} does not do so. This circumstance has far-reaching consequences. Thus, the tensor β^s_{inl} must equal zero in the absence of dissipation of light, whereas the condition of T-invariance does not imply the vanishing of β^{as}_{il}. This very fact indicates an essential difference in the mechanisms that lead to circular and linear photocurrents.

In crystals the tensor $\beta^s_{inl}=\beta^s_{iln}$ is analogous in its transformational properties to the piezotensor, while β^{as}_{il} is analogous to the gyration tensor. The classes of crystals for which β^s_{inl} and β^{as}_{il} differ from zero can be conveniently divided into four groups (Fig. 5)[34]: I–C_1, C_2, C_s, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, C_{6v}. II–C_{3h}, D_{3h}, T_d. III–D_2, D_4, D_{2d}, D_3, D_6, S_4, T. IV–O.[3)] This classification exhausts the crystals lacking a center of symmetry.

The number of independent components of β_{inl} is determined by the symmetry of the crystal. In ferroelectrics, β^s_{inl} has at least three independent components, while β^{as}_{il} has one:

$$\begin{aligned}\beta^s_{inl}&=\tilde{\alpha}c_i\delta_{nl}+\tilde{\beta}c_ic_nc_l+\tilde{\gamma}(c_l\delta_{in}+c_n\delta_{il}),\\ \beta^{as}_{il}&=\beta\varepsilon_{lnm}c_{in}.\end{aligned} \tag{3.5}$$

Here c_i is a unit polar vector lying along the spontaneous polarization of the crystal, while ε_{lmn} is a unit antisymmetric tensor. The representation (3.5) is realized in ferroelectric crystals of classes C_{4v} and C_{6v}. Moreover, it holds also for noncrystalline media having a polar direction. For the tensor β^{as}_{il}, Eq. (3.5) continues to hold also in ferroelectrics of class C_{3v}. We note that the current $\mathbf{j}_{ph}$ averaged over the polarization of the light can differ from zero only in ferroelectric crystals.

In crystals of classes T and T_d, β^s_{inl} has only one independent component: $\beta^s_{inl}=\gamma|\varepsilon_{inl}|$.

A circular PGE can also occur in completely isotropic media: liquids and gases possessing natural optical activity. In gases and liquids (and also in crystals of classes T and O), we have

$$\beta^{as}_{nl}=\eta\delta_{ln}. \tag{3.6}$$

Here η is a pseudoscalar characterizing the degree of gyrotropy of the medium.

4. ASYMMETRY OF THE ELEMENTARY ELECTRONIC PROCESSES

a) Asymmetry of scattering

As is well known, one of the simplest forms of scattering is elastic scattering of an electron by a static potential produced, e.g., by an isolated impurity. The probability $W_{\mathbf{kk}'}$ of transition of the electron from the state of momentum $\mathbf{k}'$ to the state $\mathbf{k}$ is expressed in terms of the scattering amplitude $f_{\mathbf{kk}'}$. It differs from zero on the isoenergy surface $\varepsilon_{\mathbf{k}}=\varepsilon_{\mathbf{k}'}$. Upon neglecting the spin of the electron, we have

$$W_{\mathbf{kk}'}=\frac{2\pi}{\hbar}|f_{\mathbf{kk}'}|^2\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'}). \tag{4.1}$$

The quantity $|f_{\mathbf{kk}'}|^2$ is unambiguously related to the differential cross-section for scattering of a particle into

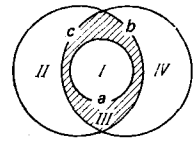

FIG. 5. Types of crystals that allow a PGE. The regions bounded by the curves a–c are respectively the ferroelectrics, piezoelectrics, and gyrotropic crystals. The intersections of these regions give the crystal groups I, II, III, and IV.

[3)]Henceforth, for brevity we shall term nonferroelectric piezoelectrics (crystals of groups II and III) piezoelectrics.

a solid angle near k.[22] Just like the probability $W_{\mathbf{kk}'}$, the scattering amplitude satisfies the reciprocity theorem $f_{\mathbf{kk}'} = f_{-\mathbf{k}',-\mathbf{k}}$. The scattering probability $W_{\mathbf{kk}'}$ can always be separated into components symmetric and antisymmetric with respect to permutation of the momenta k and k′:

$$W_{\mathbf{kk}'} = W^{s}_{\mathbf{kk}'} + W^{as}_{\mathbf{kk}'},$$
$$W^{s}_{\mathbf{kk}'} = W^{s}_{\mathbf{k}'\mathbf{k}} = W^{s}_{-\mathbf{k},-\mathbf{k}'}, \quad W^{as}_{\mathbf{kk}'} = -W^{as}_{\mathbf{k}'\mathbf{k}} = -W^{as}_{-\mathbf{k},-\mathbf{k}'}. \tag{4.2}$$

For centrosymmetric potentials, $W^{as}_{\mathbf{kk}'}$ is exactly zero.

In order to determine $W^{as}_{\mathbf{kk}'}$ by perturbation theory, we must go outside the framework of the first Born approximation and calculate the amplitude $f_{\mathbf{kk}'}$ up to second-order perturbation theory with respect to the potential.[22] The contribution to $W^{as}_{\mathbf{kk}'}$ arises from the product of the amplitude in first-order perturbation theory times the pole contribution to $f_{\mathbf{kk}'}$ in the second order[21]:

$$W^{as}_{\mathbf{kk}'} = \frac{1}{(2\pi)^6 \hbar} \operatorname{Im} \int V_{\mathbf{kk}''} V_{\mathbf{k}''\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}''}) \, d\mathbf{k}''. \tag{4.3}$$

Here $V_{\mathbf{kk}'} = V^{*}_{-\mathbf{k}',-\mathbf{k}}$ is the matrix element of the potential of the impurity taken between Bloch functions. The fact that Eq. (4.3) contains the product of two δ-functions with respect to the energy is far from fortuitous. Upon employing the reciprocity theorem, one can show that each term of the perturbation-theory series for $W^{as}_{\mathbf{kk}'}$ always contains an even number of δ-functions with respect to the energy. An expression analogous to (4.3) is employed also in the theory of the anomalous Hall effect.[27,28] In this case the need of going outside the framework of first-order perturbation theory is dictated by the invariance of $W_{\mathbf{kk}'}$ with respect to spatial invertion and T-invariance.

Let us examine a concrete model of an impurity in a ferroelectric. Let the scattering center have a short-range potential with the scattering length r_0 and the asymmetric dipole potential

$$V^{as}(\mathbf{r}) = e(\mathbf{d}\cdot\mathbf{r})/\varepsilon_0 r^3. \tag{4.4}$$

Here ε_0 is the dielectric permittivity. The quantity d in (4.4) can be considered to be equal in order of magnitude to the dipole moment of the unit cell. One can most simply calculate $W^{as}_{\mathbf{kk}'}$ for small momenta, $ka \ll 1$, where a is the dimension of the unit cell. The result has the form[21]

$$W^{as}_{\mathbf{kk}'} = \frac{4e\hbar r_0^2}{\varepsilon_0 m k} \frac{(\mathbf{k}\cdot\mathbf{k}')}{q^2} (\mathbf{d}\cdot\mathbf{q}) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}), \quad \mathbf{q} \equiv \mathbf{k} - \mathbf{k}'. \tag{4.5}$$

The existence of a short-range symmetric potential is an essential detail of the model of an impurity. In its absence, asymmetry would arise only in the third order in the dipole potential. As applied to piezoelectrics, one can naturally choose the octupole potential as $V^{as}(\mathbf{r})$. The probability $W^{as}_{\mathbf{kk}'}$ is calculated by analogy to (4.5) and is expressed in terms of the octupole moments of the impurity Q_{nlm}.[35]

In addition to elastic collisions with impurities, a possible mechanism of asymmetry is scattering of electrons (or holes) by phonons, excitons, and other defects of the periodicity of the lattice (see also Sec. 6).

b) Asymmetry of photoexcitation and recombination. Impurity-band transitions

Let the energy spectrum of the crystal be characterized by a narrow impurity level separated from the edge of the conduction band by a gap of width Δ. The probability $W^{i,r}_{\mathbf{k}}$ of excitation of an electron from the impurity into the conduction band in a state of momentum k under the action of a light wave of polarization $\mathbf{e}_\alpha$ and intensity J, and that of radiative recombination with the impurity have the form

$$W^{i}_{\mathbf{k},\alpha} = n_\alpha w^{i}_{\mathbf{k}\alpha}, \quad W^{r}_{\mathbf{k}} = \langle w^{r}_{\mathbf{k}\alpha} \rangle. \tag{4.6}$$

Here n_α is the number of photons having the polarization $\mathbf{e}_\alpha$ associated with the light intensity $J_\alpha = n_\alpha \hbar\omega c$. The averaging in (4.6) is performed over the polarizations and directions of the emitted photons. In all the microscopic calculations we are neglecting the wave vector of the light wave as compared with the quasimomentum of the electron. The differential probabilities $w^{i,r}_{\mathbf{k}}$ are interrelated owing to the invariance under time inversion,[36]

$$w^{i}_{\mathbf{k},\mathbf{e}_\alpha} = w^{r}_{-\mathbf{k},\mathbf{e}^*_\alpha} \tag{4.7}$$

[cf. (1.4)]. They are given by the standard formula of perturbation theory

$$w^{i}_{\mathbf{k},\alpha} = \frac{\omega}{2\pi} |\mathbf{e}_\alpha \mathbf{D}_{\mathbf{k}}|^2 \delta(\hbar\omega - \Delta - \varepsilon_{\mathbf{k}}). \tag{4.8}$$

Here $\mathbf{D}_{\mathbf{k}} = \langle \psi_{\mathbf{k}} | \hat{\mathbf{D}} | \psi_0 \rangle$ is the matrix element of the dipole-moment operator taken between states of the discrete and the continuous spectrum. Without loss of generality, we can consider the exact wave function ψ_0 of the bound state to be real. Hence the transformation properties of $w^{i,r}_{\mathbf{k}}$ are determined by the symmetry of the wave functions of the continuous spectrum.

We proceed to determine the asymmetric transition probabilities

$$W_{\mathbf{k}} = W^{s}_{\mathbf{k}} + W^{as}_{\mathbf{k}},$$
$$W^{s}_{\mathbf{k}} = W^{s}_{-\mathbf{k}}, \quad W^{as}_{\mathbf{k}} = -W^{as}_{-\mathbf{k}}. \tag{4.9}$$

The procedures of calculating $W^{as}_{\mathbf{k}}$ for circular and linear polarization of the light prove to differ substantially. In the former case it suffices to employ Bloch functions as the wave functions of the continuous spectrum and the exact wave function of the bound state as ψ_0. The matrix element of the dipole moment taken between these states has the symmetry property $\mathbf{D}^0_{\mathbf{k}} = \mathbf{D}^{0*}_{-\mathbf{k}}$. This stems from the relationship $\psi_{\mathbf{k}} = \psi^*_{-\mathbf{k}}$ for the Bloch functions, which in turn reflects the invariance of the Schrödinger equation under time inversion. For simplicity, we have treated the states of the electron in the conduction band and at the impurity as nondegenerate. Upon turning to (4.8), we see that $w^{i}_{\mathbf{k}}$ has an asymmetric component when the polarization vector e is complex, i.e., for circularly polarized light.[37] When e is real, the $w^{i}_{\mathbf{k}}$ are fully symmetric.

For small momenta, $\mathbf{D}^0_{\mathbf{k}}$ can be expanded as[38]

$$D^0_i(\mathbf{k}) = f_i + i g_{il} k_l + h_{iln} k_l k_n + \ldots. \tag{4.10}$$

Here f_i, g_{il}, and h_{iln} are real quantities. We can assume for the sake of definiteness that the transitions occur between the s- and the p-states of the impurity

and an s-band.[4)] If the impurity exists in an s state, then the asymmetry of the crystal is accounted for in (4.10) by the terms even in k. Here the first term of the expansion, $f_i = fc_i$, can exist only in ferroelectric crystals. Yet if the state of the electron in the impurity level is a p state, then the asymmetry is characterized by the terms odd in k in the expansion.

For ferroelectric crystals, we obtain the following from (4.8) and (4.10)[37]:

$$W_k^{as} = i \frac{f_g}{(2\pi)^3 \hbar} (\mathbf{k}[\mathbf{c} \times (\mathbf{E} \cdot \mathbf{E}^*)]) \, \delta(\varepsilon_k - \varepsilon_{k_0}). \tag{4.11}$$

We have neglected the anisotropy of the crystal, by assuming that $g_{il} = g\delta_{il}$. The momentum k_0 with which the electrons are photoexcited is determined by the obvious condition $\varepsilon_{k_0} = \hbar\omega - \Delta$. W_k^{as} changes sign upon change of direction of rotation of the polarization. The recombination probability, which involves averaging over the polarization of the emitted photons, as implied by (4.6) and (4.11), is a symmetric quantity.

In piezoelectrics W_k^{as} is determined by the tensor $h_{ij} = h_{nmi}\varepsilon_{nmj}$, i.e., by the component of the tensor h_{nlm} antisymmetric in the first two indices.[37] As one can show, the degree of smallness of h_{ij} is relativistic. For linear polarization of the light ($\mathbf{e} = \mathbf{e}^*$), according to (4.11), the probability W_k^{as} is zero. In this situation we must take into account the distortion of the electronic wave functions by the potential of the impurity. From the formal standpoint, this potential causes the coefficients of the expansion (4.10) for $\mathbf{D}_k$ to be complex, and it breaks down the relationship $\mathbf{D}_k = \mathbf{D}_{-k}^*$. The magnitude of the probability W_k^{as} depends on the concrete properties of the impurity. There are two independent contributions to W_k^{as}. The first one stems from the distortion of the wave functions of the band electrons by the asymmetric potential of the impurity.[20,21] The second contribution arises from simultaneously taking into account the action of the symmetric component of the potential on the wave functions of the continuous spectrum and the oddness of the matrix element, $\mathbf{D}_k^0 \neq \pm \mathbf{D}_{-k}^0$. Let us examine the first contribution in greater detail. When we take into account the potential of the impurity, the wave functions of the band electrons begin to differ from Bloch functions. As we know, there are two complete sets of wave functions $\psi_k^{\pm}(\mathbf{r})$ of the continuous spectrum, which contain divergent and convergent waves. In calculating the photoionization, we must take the function ψ_k^- as the wave function of the final state.[22] The matrix element of the dipole moment taken between the wave function of the electron at the impurity and $\psi_k^-(\mathbf{r})$ satisfies the relationship

$$\mathbf{D}_k = \mathbf{D}_k^0 + \int \frac{\mathbf{D}_{k'} V_{k'k}}{\varepsilon_k - \varepsilon_{k'} + i\delta} \frac{d\mathbf{k}'}{(2\pi)^3}. \tag{4.12}$$

This directly stems from the Schrödinger equation. An analogous equation holds for the scattering amplitude.[22]

Let us represent $\mathbf{D}_k$ as the sum of the matrix element $\mathbf{D}_k^s = \pm \mathbf{D}_{-k}^s$, without taking the asymmetry of the crystal into account, and the correction $\mathbf{D}_k^{as}$ to it, which is associated with $V^{as}(\mathbf{r})$. As is implied by (4.8), the existence of W_k^{as} requires that the quantities $\mathbf{D}_k^s$ and $\mathbf{D}_k^{as}$ should have different parities. Upon using the well-known identity $(x + i\delta)^{-1} = P/x - i\pi\delta(x)$, where P is the symbol for the principal value, we obtain the following expression from (4.12):

$$\mathbf{D}_k^{as} = -i\pi \int V_{k'k}^{as} \mathbf{D}_{k'}^s \delta(\varepsilon_k - \varepsilon_{k'}) \frac{d\mathbf{k}'}{(2\pi)^3}. \tag{4.13}$$

The asymmetry of the photoexcitation arises solely from the pole contribution to (4.12). This situation is not fortuitous, and it involves the fact that time inversion transforms in different way the contributions to $\mathbf{D}_k$ from the pole and from the principal value of the integral. Generally we cannot consider the matrix element $\mathbf{D}_k^s$ to be close to $\mathbf{D}_k^0$, since the potential $V^s(\mathbf{r})$ possesses bound states, and therefore is not small.

As we see from (4.13), for small excitation momenta $\mathbf{k}$, the momentum $\mathbf{k}'$ is also small. This means that for ferroelectrics we can employ the dipole potential as $V^{as}(\mathbf{r})$. Again we shall consider the symmetric potential to be short-range. Upon employing (4.13) and assuming the impurities to exist in a p-state, we can represent the asymmetric component of the photoexcitation probability in the form[21]

$$W_k^{as} = 2 \frac{(\mathbf{d} \cdot \mathbf{k})}{e a_B k} W_k^s. \tag{4.14}$$

Here $a_B = \hbar^2 \varepsilon_0 / me^2$ is the Bohr radius.

In many cases the probability W_k^s can be easily expressed in terms of the cross-section for light absorption.

In piezoelectrics, W_k^{as} is determined by the octupole moment of the impurity.[39]

Finally we consider the second contribution to W_k^{as}, which arises from the existence of terms of differing parity in the expansion (4.10) for $\mathbf{D}_k^0$. This contribution has been treated in Refs. 40 and 41, where the photoionization of a shallow neutral impurity was studied. It was assumed that the wave function of the bound state does not possess a definite parity when the asymmetric potential is taken into account; $\psi_0(\mathbf{r})$ was chosen in the form of a superposition of hydrogenlike s and p wave functions. The states of the electrons in the continuous spectrum were described by the exact Coulomb wave functions, which made possible a calculation of W_k^{as}.

A possible source of asymmetry in crystals in impurity-band transitions (as a rule of lesser importance) can be scattering by phonons.

5. ELEMENTS OF THE KINETIC THEORY OF THE PGE

a) General relationships

Asymmetric transition probabilities constitute the basis of the kinetic description of the PGE. The electric current is expressed in the standard way in terms of the distribution function f_k of the electrons:

$$\mathbf{j} = \frac{e}{\hbar} \int \frac{\partial \varepsilon_k}{\partial \mathbf{k}} f_k \, d\mathbf{k}. \tag{5.1}$$

Owing to the invariance under time inversion and to ne-

[4)]The states are classified neglecting the asymmetry and anisotropy of the crystal.

glect of spin, we have $\varepsilon_{\mathbf{k}} = \varepsilon_{-\mathbf{k}}$. Hence, in order to find the current, we must determine the asymmetric component of the distribution function, $f_{\mathbf{k}}^{as} = -f_{\mathbf{k}}^{as}$.

We shall write the kinetic equation for $f_{\mathbf{k}}$ in the following form[5)]:

$$\frac{\partial f_{\mathbf{k}}}{\partial t} = \mathrm{St}(f_{\mathbf{k}}), \quad \mathrm{St}(f_{\mathbf{k}}) = I_{\mathbf{k}}^{i} - I + I_{\mathbf{k}}^{im} + I_{\mathbf{k}}^{ph}. \tag{5.2}$$

Here the $I_{\mathbf{k}}^{i,r}(f_{\mathbf{k}})$ are the rates of excitation and recombination, and the $I_{\mathbf{k}}^{im,ph}(f_{\mathbf{k}})$ are the collision integrals for impurities and phonons. We shall treat the latter as being in thermodynamic equilibrium.

Let the total collision integral be resolvable into symmetric and asymmetric components:

$$\begin{gathered}\mathrm{St}(f_{\mathbf{k}}) = I_{\mathbf{k}}^{s}(f_{\mathbf{k}}) + I_{\mathbf{k}}^{as}(f_{\mathbf{k}}), \\ I_{\mathbf{k}}^{s}(f_{\mathbf{k}}^{s}) = I_{-\mathbf{k}}^{s}(f_{\mathbf{k}}^{s}), \quad I_{\mathbf{k}}^{as}(f_{\mathbf{k}}^{s}) = -I_{-\mathbf{k}}^{as}(f_{\mathbf{k}}^{s}), \quad f_{\mathbf{k}}^{s} = f_{-\mathbf{k}}^{s}.\end{gathered} \tag{5.3}$$

In this case the stationary solution of (5.2) cannot be purely symmetric. It must contain an asymmetric component. That is, a constant current arises, in agreement with (5.1). We shall see below that the resolution into symmetric and asymmetric collision integrals can be performed for each of the elementary processes treated above. Therefore each of these processes yields a photocurrent. We stress that this pertains to the nonequilibrium situation. In the thermodynamic-equilibrium distribution functions of the electrons and phonons, the asymmetric collision integral $I_{\mathbf{k}}^{as}$ and the current $\mathbf{j}_{ph}$ must always vanish. Henceforth we shall restrict the treatment to the first approximation in the asymmetry parameter. Consequently we get the following from (5.2) and (5.3):

$$I_{\mathbf{k}}^{s}(f_{\mathbf{k}}^{as}) + I_{\mathbf{k}}^{as}(f_{\mathbf{k}}^{s}) = 0; \quad I_{\mathbf{k}}^{s}(f_{\mathbf{k}}^{s}) = 0. \tag{5.4}$$

To progress further, we must concretize the structure of $I_{\mathbf{k}}^{s}$. Generally this collision integral contains four characteristic times: γ^{-1}—the recombination time for the electrons at the impurities, Γ_{im}^{-1}—the reciprocal of the rate of collisions with the impurities, and Γ_{iso}^{-1} and Γ_{c}^{-1}—the relaxation times for the momentum and the energy. As a rule, we shall assume that $\Gamma_{iso} \gg \Gamma_{c}$, and $\Gamma_{im} \gg \gamma$. This hierarchy of times is the most typical.[1] Thus we assume that the electrons ejected by light into the conduction band are first "smeared out" over the isoenergy surface by collisions with impurities and phonons. Then the small inelasticity of electron-phonon scattering gives rise to slow energy relaxation toward the quasi-Fermi distribution function $f_{\mathbf{k}}^{0}$. And only after this do the electrons recombine with the impurities. Taking the abovesaid into account we shall take $I_{\mathbf{k}}^{s}$ in the form

$$I_{\mathbf{k}}^{s} = I_{\mathbf{k}} - \gamma_{\mathbf{k}} f_{\mathbf{k}} - \Gamma_{iso}(f_{\mathbf{k}} - \overline{f}_{\mathbf{k}}) + I_{\mathbf{k}}^{t}(f_{\mathbf{k}}). \tag{5.5}$$

Here we have $I_{\mathbf{k}} \equiv (I_{\mathbf{k}}^{i})^{s}$, $I_{\mathbf{k}}^{t}(f_{\mathbf{k}})$ describes the thermalization, and $I_{\mathbf{k}}^{t}(f_{\mathbf{k}}^{0}) = 0$ (the structure of this term is not essential below). The bar denotes averaging over the isoenergy surface. As Eqs. (5.4) and (5.5) imply, we have

$$f_{\mathbf{k}}^{as} = \Gamma_{iso}^{-1} I_{\mathbf{k}}^{as}(f_{\mathbf{k}}^{s}). \tag{5.6}$$

The symmetric component $f_{\mathbf{k}}^{s}$ must be determined from (5.4) and (5.5). In the general case it has the form $f_{\mathbf{k}}^{s} = f_{\mathbf{k}}^{0} + \delta f_{\mathbf{k}}^{s}$. We can consider the function $f_{\mathbf{k}}^{0}$ for dielectrics to be a Boltzmann distribution normalized to the total concentration of electrons n_0 in the conduction band. The latter is determined from the condition $\gamma n_0 = \int I_{\mathbf{k}} d\mathbf{k}$.

Employing Eqs. (5.1) and (5.6) allows us to calculate easily the PGE within the framework of a concrete model for $I_{\mathbf{k}}^{as}$.

We should pay special attention to the meaning of the quantity Γ_{iso} that enters into the fundamental formula (5.6). As defined, the isotropization rate $\Gamma_{iso}(\mathbf{k})$ is the reciprocal of the relaxation time of the direction of the momentum $\mathbf{k}$ for the nonequilibrium electrons, which essentially are the source of the photocurrents. Hence the applicability of the results obtained below is generally not restricted to the region $\Gamma_{iso} < T$, outside of which one cannot describe the quasiequilibrium electrons (with energies $\varepsilon_{\mathbf{k}} \sim T$) by the kinetic equation.[42] The region of applicability of the kinetic description of the PGE is broader: $\Gamma_{iso}(\mathbf{k}_0) < \varepsilon_{\mathbf{k}_0}$. In particular, this region can include also crystals having polaron conduction.[43] In this case we must take $\varepsilon_{\mathbf{k}}$ to be the nonrenormalized energy of the electron, since the optical transition occurs with stationary ions, owing to the adiabatic principle. The electron does not succeed in putting on a coat of phonons before the first isotropizing collision. The abovesaid also implies that estimates of Γ_{iso} from the mobility of thermal electrons can yield a false result. As a rule, isotropization is brought about by collisions with phonons. One can find the appropriate expressions for $\Gamma_{iso}(\mathbf{k})$ in Refs. 44 and 45.

b) Scattering by impurities

This process corresponds to the ordinary collision integral

$$I_{\mathbf{k}}^{im} = \int (W_{\mathbf{k}\mathbf{k}'} f_{\mathbf{k}'} - W_{\mathbf{k}'\mathbf{k}} f_{\mathbf{k}})\, d\mathbf{k}'. \tag{5.7}$$

The total transition probability $W_{\mathbf{k}\mathbf{k}'}$ is the probability of the elementary process of (4.1) multiplied by the concentration N of the scattering centers. (The use of one symbol for both probabilities should not lead to misunderstanding.) We shall consider the scattering centers to be distributed randomly, but with identical orientations. This is precisely how the lack of a center of symmetry in the medium is manifested.

The collision integral of (5.7) conserves the total number of particles: $\int I_{\mathbf{k}}^{im} d\mathbf{k} = 0$. Taking (4.2) into account we resolve it into symmetric and asymmetric components:

$$I_{\mathbf{k}}^{s} = \int W_{\mathbf{k}\mathbf{k}'}^{s}(f_{\mathbf{k}'} - f_{\mathbf{k}})\, d\mathbf{k}', \quad I_{\mathbf{k}}^{as} = \int W_{\mathbf{k}\mathbf{k}'}^{ac}(f_{\mathbf{k}} + f_{\mathbf{k}'})\, d\mathbf{k}'. \tag{5.8}$$

We see from (5.8) that $I_{\mathbf{k}}^{as}$ actually exhibits the property (5.3). The structure of the integrals $I_{\mathbf{k}}^{s}$ and $I_{\mathbf{k}}^{as}$ differs substantially. The features of the kinetics in the absence of detailed balancing can be seen already from the fact that the balance of input and output is realized not by the scheme $\mathbf{k} \rightleftarrows \mathbf{k}'$, but via the cycles $\mathbf{k} \to \mathbf{k}' \to \mathbf{k}'' \to \cdots \to \mathbf{k}$.

A very interesting problem is that of the form of $I_{\mathbf{k}}^{im}$

5)Eq. (5.2) is written for impurity-band transitions.

in the limit of small-angle scattering: $|k'-k| \ll k$. That is, the integral equation (5.2) is replaced by the simpler Fokker-Planck differential equation (FPE). The FPE for elastic scattering constitutes the continuity equation in momentum space:

$$\frac{\partial f_{\mathbf{k}}}{\partial t} = -\operatorname{div} \mathbf{P}_{\mathbf{k}}. \tag{5.9}$$

Here $\mathbf{P}_{\mathbf{k}}(f_{\mathbf{k}})$ is the flux of particles in this space. Usually one treats the FPE in the absence of asymmetry (assuming the principle of detailed balancing to hold). In this case the flux $P_{\mathbf{k}}$ is determined by the first derivatives of $f_{\mathbf{k}}$ with respect to the momentum, while (5.9) describes the diffusion in k-space. The FPE proves to be substantially modified in the absence of detailed balancing.[46] The asymmetry of scattering leads to appearance of the second derivatives with respect to the momentum in the expression for the particle flux $\mathbf{P}_{\mathbf{k}}$. That is, it increases the order of the Fokker-Planck equation. The additional terms describe the drift of the perturbations $f_{\mathbf{k}}$ in k-space. The parity of the terms on the right-hand side of (5.9) begins to differ (for more details see Ref. 46).

Now let us examine the problem of the vanishing of $I_{\mathbf{k}}^{\text{im}}$ at thermodynamic equilibrium. Since $W_{\mathbf{kk}'} \propto \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})$, the vanishing of $I_{\mathbf{k}}^{s}$ for any function of the energy is obvious. The vanishing of $I_{\mathbf{k}}^{\text{as}}[f(\varepsilon_{\mathbf{k}})]$ is not so obvious. It arises only when the extra condition is fulfilled that:

$$\int W_{\mathbf{kk}'}^{\text{as}}\, d\mathbf{k}' = 0. \tag{5.10}$$

We shall show that it is always fulfilled. To do this, we take into account the fact that the optical theorem holds for elastic scattering:

$$\int W_{\mathbf{k}'\mathbf{k}}\, d\mathbf{k}' = 4\pi \operatorname{Im} f_{\mathbf{kk}}.$$

Here $f_{\mathbf{kk}}$ is the amplitude of forward scattering. According to the reciprocity theorem we have $f_{\mathbf{kk}} = f_{-\mathbf{k},-\mathbf{k}}$, and hence

$$\int W_{\mathbf{k}'\mathbf{k}}\, d\mathbf{k}' = \int W_{\mathbf{k}',-\mathbf{k}}\, d\mathbf{k}'.$$

This directly implies the relationship (5.10).[6)] Thus we have $I_{\mathbf{k}}^{\text{as}} = 0$ for any function of the energy.[21,47] In particular, we can easily show that the relationship (5.10) is actually fulfilled for the $W_{\mathbf{kk}'}^{\text{as}}$ given by (4.5). But if we create an increment $\delta f_{\mathbf{k}}$ arising from external sources that is not a function of $\varepsilon_{\mathbf{k}}$, this increment must have an asymmetric component. That is, a current arises. Let us calculate the current using the impurity model treated in subsection A of Sec. 4. As (5.6) implies, a nonzero result arises only in the second order in Γ_{iso}^{-1}, since in the first approximation for $f_{\mathbf{k}}^{s}$ the function $f^0(\varepsilon_{\mathbf{k}})$ causes $I_{\mathbf{k}}^{\text{as}}$ to vanish. A departure of $f_{\mathbf{k}}^{s}$ from being a function of the energy arises when we account for anisotropy of excitation and recombination. We obtain the following expression from (5.5) for the correction $\delta f_{\mathbf{k}}^{s}$ to the Boltzmann distribution:

$$\delta f_{\mathbf{k}}^{s} = \Gamma_{\text{iso}}^{-1}(I_{\mathbf{k}} - \gamma_{\mathbf{k}} f_{\mathbf{k}}^{0}).$$

For the sake of simplicity, let the electrons be excited from symmetric s-centers. Then the second term in the expansion (4.10) is essential, and electrons are excited into the conduction band at the rate

$$I_{\mathbf{k}} = \frac{3\varkappa J}{4\pi k^2 \hbar\omega} \frac{|\mathbf{k}\cdot\mathbf{e}|^2}{k^2}\, \delta(\mathbf{k}-\mathbf{k}_0). \tag{5.11}$$

Thus anisotropy of excitation is associated with the polarization of the light. The recombination term $\gamma_{\mathbf{k}} f_{\mathbf{k}}$, which contains an averaging over the polarization and momenta of the emitted photons, is isotropic, and does not contribute to $f_{\mathbf{k}}^{\text{as}}$. Employing (5.11), we can easily derive the following expression for ferroelectrics[21]:

$$\mathbf{j}_{\text{ph}} = \frac{4\pi e J}{15\hbar\Gamma_{\text{iso}}} k_0 a \frac{e d N a}{\varepsilon_0 \hbar\omega} \frac{\hbar k_0 \varkappa}{m \Gamma_{\text{iso}}} \{\mathbf{c} - 3\mathbf{e}(\mathbf{c}\cdot\mathbf{e})\}. \tag{5.12}$$

The direction of the current essentially depends on the polarization of the light. The currents differ in sign in the cases $\mathbf{e} \perp \mathbf{c}$ and $\mathbf{e} \parallel \mathbf{c}$. The quantity $\mathbf{j}_{\text{ph}}$ vanishes on averaging over the direction of propagation and the polarization of the light. In piezoelectrics, the current is expressed in terms of the octupole moment of the scattering center.[39] Anisotropy of excitation (or recombination) can involve not only the polarization of the light, but also the anisotropy of the crystal. In this case the current averaged over the polarization of the light does not vanish for ferroelectrics.

The mechanisms of the PGE based on asymmetry of scattering are apparently the simplest. Yet, as a rule, for impurity-band and band-band transitions, they yield values of the photocurrents smaller than those obtained in the models based on asymmetric ionization and recombination processes. We now proceed to treat these models.

c) Ionization and recombination

Let us study an impurity-band transition. Then we have the following expressions for $(I_{\mathbf{k}}^{\text{i},r})^{\text{as}}$:

$$I_{\mathbf{k}}^{\text{i},\,\text{as}} = N_0 W_{\mathbf{k}}^{\text{i},\,\text{as}}, \quad I_{\mathbf{k}}^{\text{r},\,\text{as}} = (N - N_0) f_{\mathbf{k}} W_{\mathbf{k}}^{\text{r},\,\text{as}}. \tag{5.13}$$

Here N_0 is the number of electrons on the impurities, and N is the total number of impurities. Employing Eq. (5.6), we can easily see that $f_{\mathbf{k}}^{\text{as}}$ differs from zero in the first order in the parameter Γ_{iso}^{-1}. However, before we proceed to calculate the current within the framework of concrete models of the impurity, we must make a remark. As (4.7) and (5.13) imply, and as we have already seen from the elementary model in Sec. 2, the $(I_{\mathbf{k}}^{\text{i},r})^{\text{as}}$ do not vanish at thermodynamic equilibrium, and they give contributions of the same sign to the collision integral $St(f_{\mathbf{k}})$. The kinetic equation contains additional terms of the same order as $(I_{\mathbf{k}}^{\text{i},r})^{\text{as}}$ caused by scattering processes. In order to establish this extra contribution, we again employ the optical theorem. Taking the asymmetric recombination channel into account we have

$$\int W_{\mathbf{k}'\mathbf{k}}\, d\mathbf{k}' + W_{\mathbf{k}}^{\text{r}} = 4\pi \operatorname{Im} f_{\mathbf{kk}}. \tag{5.14}$$

Upon employing the reciprocity theorem, $f_{\mathbf{kk}} = f_{-\mathbf{k},-\mathbf{k}}$, we see that $W_{\mathbf{kk}'}^{\text{as}}$ satisfies the following condition instead of (5.10) in the presence of asymmetric absorbing centers[7)]:

$$\int W_{\mathbf{k}'\mathbf{k}}^{\text{as}}\, d\mathbf{k}' + W_{\mathbf{k}}^{\text{r},\,\text{as}} = 0. \tag{5.15}$$

[6)]It has been shown[48] that unitarity of the S-matrix suffices for the condition (5.10) to be satisfied.

[7)]If the scattering potential possesses no bound state, then $W_{\mathbf{k}}^{\text{r},\,\text{as}} = 0$. Then we return from Eq. (5.15) to (5.10).

Equation (5.15) directly implies that:

$$I_{\mathbf{k}}^{\mathrm{im,\,as}} = \int (f_{\mathbf{k}} + f_{\mathbf{k}'})\, W_{\mathbf{k}\mathbf{k}'}^{\mathrm{as}}\, \mathrm{d}\mathbf{k}' = 2I_{\mathbf{k}}^{\mathrm{r,\,as}}, \qquad f_{\mathbf{k}} = f(\varepsilon_{\mathbf{k}}). \tag{5.16}$$

We can easily convince ourselves that the complete asymmetric collision integral $(I_{\mathbf{k}}^{\mathrm{i}} - I_{\mathbf{k}}^{\mathrm{r}} + I_{\mathbf{k}}^{\mathrm{im}})^{\mathrm{as}}$ vanishes at thermodynamic equilibrium.[21] But if the photon distribution is not in equilibrium with respect to the frequency, the compensation of the three contributions breaks down and a current arises. In contrast to the scattering mechanism, it does not equal zero even in the first approximation in the parameter $\Gamma_{\mathrm{iso}}^{-1}$. Taking (5.6) and (5.16) into account we have

$$f_{\mathbf{k}}^{\mathrm{as}} = \Gamma_{\mathrm{iso}}^{-1}\, [I_{\mathbf{k}}^{\mathrm{i}}(f_{\mathbf{k}}^{0}) + I_{\mathbf{k}}^{\mathrm{r}}(f_{\mathbf{k}}^{0})]^{\mathrm{as}}. \tag{5.17}$$

Thus the effect of collisions on the processes of ionization and recombination is reduced to a change of sign of $I_{\mathbf{k}}^{\mathrm{r,as}}$. Adopting a concrete model for $(W_{\mathbf{k}}^{\mathrm{i,r}})^{\mathrm{as}}$ we can easily calculate the current. First let us study its circular component. Utilizing Eq. (5.6), we obtain the following relationship for ferroelectrics[37]:

$$\mathbf{j}_{\mathrm{ph}} = \frac{eJ}{\hbar\Gamma_{\mathrm{iso}}}\, \frac{\hbar\varkappa f}{m\omega g}\, i\, [\mathbf{c}\times(\mathbf{e}\times\mathbf{e}^{*})], \quad k_0 \gg \frac{f}{g}. \tag{5.18}$$

This current corresponds to the last term in the phenomenological expression (3.4). Only the ionization process contributes to the current. Upon averaging over the polarization $\mathbf{j}_{\mathrm{ph}}$ vanishes.

In piezoelectrics the circular current is determined by the tensor h_{ll} (see subsection B of Sec. 4). In gyrotropic crystals, the circular current is determined to a considerable extent by spin effects (Sec. 8).

To calculate the linear photocurrent in crystals, we must take into account the distortion of the Bloch functions by the potential of the impurity. Employing (4.14), (5.1), and (5.17), we obtain the following expression for dipole impurities[21]:

$$\mathbf{j}_{\mathrm{ph}} = \frac{2eJ}{3\hbar\Gamma_{\mathrm{iso}}}\, \frac{e\, dk_0\varkappa}{\hbar\omega} \left(1 - \sqrt{\frac{8}{\pi}}\, \frac{k_{\mathrm{t}}}{k_0}\right) \mathbf{c}, \qquad \varkappa \propto |\mathbf{c}\cdot\mathbf{e}|^{2}. \tag{5.19}$$

The current contains two contributions of opposite sign due to ionization and recombination. At small values of k_0 (low frequency of the light), recombination predominates. In the latter the main participation is by electrons that have been thermalized by interaction with the phonon thermostat. That is, on the average they possess the thermal momentum k_{t}. Ionization dominates at higher light frequencies, $k_0 \gg k_{\mathrm{t}}$, and the current changes sign. We shall show that the polarization properties of the photocurrent essentially depend on the state of the impurity. In principle, any dependence on the polarization of the light is possible that agrees with the phenomenology of the PGE.

In piezoelectrics the linear current is expressed in terms of the octupole moment of the impurity.[39] Then only the contribution to the current from photoexcitation exists. Upon averaging over the polarization of the incident light, $\mathbf{j}_{\mathrm{ph}}$ vanishes in agreement with the phenomenology of the PGE (Sec. 3).

We note that a so-called fluctuational model of the PGE has been proposed[49,50] for impurity-band transitions in a ferroelectric. It consists of the idea that the dipole moment of an impurity can be altered when it is ionized, and the electron moves in the field of the polarization fluctuation that is created. Upon recombination (perhaps at another impurity), the corresponding fluctuation disappears. Unfortunately there are no calculations nor concrete arguments favoring the possibility of realizing this model or showing that it does not contradict the second law of thermodynamics. Possibly the appearance of a fluctuation can yield a correction to the mechanism of asymmetric photoionization and recombination discussed above. An attempt is also known of explaining the PGE by Frank-Condon relaxation of the ionic subsystem during ionization and recombination.[51] As was shown in Ref. 52, such a model yields a zero constant current.

6. THE PGE IN INTERBAND TRANSITIONS

Intrinsic absorption of light in crystals usually leads to creation of electron-hole pairs or to transitions of electrons (or holes) between two bands. The production of electron-hole pairs is described by a two-particle function $W_{\mathbf{k}\mathbf{k}'}$. This is defined as the probability of creation of an electron with momentum $\mathbf{k}$ and a hole with momentum $\mathbf{k}'$.

In crystals lacking a center of symmetry, $W_{\mathbf{k}\mathbf{k}'}$ is asymmetric $W_{\mathbf{k}\mathbf{k}'} \neq W_{-\mathbf{k},-\mathbf{k}'}$. The asymmetry of $W_{\mathbf{k}\mathbf{k}'}$ implies that the probability of creation of an electron and a hole with momenta $\mathbf{k}$ and $\mathbf{k}'$ differs from that of creation of a pair with the opposite momenta. Hence charge transport arises upon photoexcitation.

In this section we shall present the formulas for the electronic contribution to the current. The contribution of the holes has the same sign, and as a rule, the same order of magnitude.

a) Circular photocurrent

In calculating the circular photocurrent, we can neglect the effect of electron-hole, electron-phonon, and electron-impurity interactions. In this case the transitions are vertical. That is, they conserve momentum, $W_{\mathbf{k}\mathbf{k}'} = W_{\mathbf{k}}\delta(\mathbf{k}+\mathbf{k}')$. Figure 6(a) shows the Feynman diagram for the amplitude of this process. The probability $W_{\mathbf{k}}$ is determined by Eq. (4.8) if we take $\mathbf{D}_{\mathbf{k}} = \mathbf{D}_{\mathbf{k}}^{0}$ to be the matrix element of the dipole-moment operator taken between the Bloch wave functions $\psi_{\mathbf{k}}^{c,v}$. As before, the matrix element $\mathbf{D}_{\mathbf{k}}^{0}$ has the property $\mathbf{D}_{\mathbf{k}}^{0} = \mathbf{D}_{-\mathbf{k}}^{0*}$ that arises from T-invariance. In transitions between s bands, it fits the expansion (4.10) with real interband constants f, g, h. These constants are now characteristics of the crystal, rather than of the impurity, as in Secs. 4 and 5. The previously derived formulas (4.11) and (5.18) for the probability $W_{\mathbf{k}}^{\mathrm{as}}$ and the circular current can be

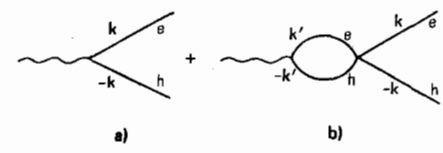

FIG. 6. Creation of an electron-hole pair: without (a) and with (b) taking the Coulomb interaction into account. The wavy lines denote photons.

fully transferred to the case treated here. Recombination processes do not contribute to j_{ph}. In the studied approximation the linear current is zero.

b) Coulomb interaction between electrons and holes

A linear photocurrent in the case of interband transitions arises when we take into account the difference of the wave functions of electrons and holes from the Bloch functions. One can obtain this difference by taking into account the Coulomb electron-hole interaction.[53] Thus there is a direct analogy with the mechanism of the PGE in the case of impurity absorption (Secs. 4, 5), where the potential of the impurity exerts the perturbing action on the electron. Figure 6(b) shows the process of creation of an electron and a hole taking their Coulomb interaction into account. Momentum is also conserved in this process. The asymmetric component of W_k is proportional to the product of the amplitudes shown in Fig. 6, i.e., to the value of the electron-hole interaction. For comparison, Fig. 7 shows the Feynman diagrams for the impurity-band transitions. In the absence of distortions [see Fig. 7(a)] we have only a circular current. With linear polarization of the light, W_k^{as} is proportional to the product of the amplitudes of the processes shown in Fig. 7.

The asymmetric collision integrals describing the photoexcitation and radiative recombination of electron-hole pairs can be written by analogy with (5.13):

$$I_{k'}^{i,\,as}=n_\alpha W_k^{as},\qquad I_{k'}^{r,\,as}=\langle W_k^{as}\rangle f_k^e f_{-k}^h,$$
$$W_k^{as}=\int \tilde{W}_{kk'}^{as}\,dk',\quad \tilde{W}_{kk'}^{as}=-\tilde{W}_{-k,\,-k'}^{as}. \tag{6.1}$$

In addition to excitation and recombination processes, it turns out to be necessary to ferroelectric crystals to take scattering processes into account (just as in the case of impurity-band transitions). Again their role reduces to a change of sign of $(I_k^r)^{as}$. Correspondingly, the asymmetric correction to the distribution function is described by Eq. (5.17). In the case of piezoelectrics, as above in Sec. 5, only the process of photoexcitation is asymmetric.

The expression for $\tilde{W}_{kk'}^{as}$ in first-order perturbation theory in terms of the electron-hole interaction has the form

$$\tilde{W}_{kk'}^{as}=\operatorname{Im}[(D_k^{*0}e_\alpha^*)(D_{k'}^0 e_\alpha)]\frac{e^2\omega}{2\pi^2\varepsilon_{ij}^0 q_i q_j}\times\delta(\varepsilon_k^e+\varepsilon_k^h-\varepsilon)\,\delta(\varepsilon_{k'}^e+\varepsilon_{k'}^h-\varepsilon). \tag{6.2}$$

Here $\varepsilon_{ji}^0(q)=\varepsilon_{ij}^0(-q)$ is the static dielectric permittivity, we have $\varepsilon\equiv\hbar\omega-E_g$, E_g is the width of the forbidden band, and $\varepsilon_k^{e,h}$ are the energies of the electron and hole referred to the edges of the corresponding bands. In

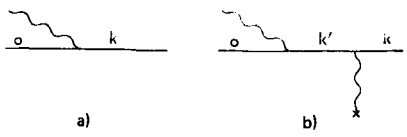

FIG. 7. Impurity-band transition without taking into account the effect of the impurity potential on the free electrons (a) and taking this effect into account (b).

the studied mechanism the asymmetry of W_k exclusively involves the asymmetry of the matrix element D_k^0, just as in the second mechanism of the linear current in the region of impurity absorption (Sec. 4).

For many piezoelectrics, the quantities D_k^0, ε_{ij}^0, and $\varepsilon_k^{e,h}$ are known from experiments or are amenable to calculation.[54] If we assume that $\varepsilon_{ij}^0=\varepsilon_0\delta_{ij}$, while taking the dispersion laws to be isotropic and quadratic and employing the expansion (4.10), we can easily derive a simple expression for the photogalvanic tensor β_{iln}^s. For piezoelectrics it has the form

$$\beta_{iln}^s=-\frac{ce}{5\pi\hbar\Gamma_{iso}}\frac{\varkappa e^2}{\varepsilon_0\hbar\omega}\frac{\mu}{m_e}\frac{k_0 h_{nli}}{g}. \tag{6.3}$$

Here μ is the reduced mass of the electron and hole.

Equation (6.2) holds under the condition that the Coulomb interaction is small:

$$\frac{a}{a_B}\ll k_0 a\ll 1. \tag{6.4}$$

That is, it holds for crystals having a large enough dielectric permittivity and small effective mass. In particular, they include the well studied crystals of the $A^{III}B^{V}$ group. In concrete calculations we must allow for the fact that the hold bands in these crystals are degenerate at $k=0$ and are not spherical.

In the region of small k, the applicability of perturbation theory breaks down[8)] (exciton effect). However, there is a simple model within whose framework the calculations can be performed for any strength of Coulomb interaction.[53] This is the model of nondegenerate spherical bands. The transition probability is determined by Eq. (4.8) with $\varepsilon_k=k^2\hbar^2/2\mu$, and we have

$$D_k=e\int\psi_k^-(r)\,r\,dr. \tag{6.5}$$

Here the $\psi_k^-(r)$ are the Coulomb wave functions of the continuous spectrum for a particle of mass μ and charge $e\varepsilon_0^{-1/2}$. We can rewrite Eq. (6.5) by making use of the fact that the system of Bloch functions forms a complete set:

$$D_k=\int D_{k'}^0\psi_k^-(k')\frac{dk'}{(2\pi)^3}. \tag{6.6}$$

For small k, employing the expansion (4.10) for D_k^0 and transforming in Eq. (6.6) to the coordinate representation, we get

$$D_k^i=\left(f_i+g\frac{\partial}{\partial x_i}-h_{iln}\frac{\partial^2}{\partial x_l\,\partial x_n}\right)\psi_k^-(r)\Big|_{r=0}. \tag{6.7}$$

The limit in (6.7) is taken in the following order: first one averages over the angles, and then lets $|r|\to 0$. By using (6.7), one can easily derive explicit expressions for the linear and circular currents, both in ferro- and in piezoelectrics. We should point out that a linear current arises in this model only from the complex nature of the function $\psi_k^-(r)$ and of its derivatives for $r=0$.

We can also employ Eq. (6.7) to calculate W_k^{as} in the case of ionization of an electron from a deep neutral impurity. Its region of applicability is $k_0 a\ll 1$. In the

8)An analogous situation arises in calculating the probability of ionization of a neutral impurity center.

ionization of a shallow neutral impurity, the region of applicability narrows: $k_0 a_B \ll 1$.

c) Electron-phonon interaction

Electron-phonon interaction also distorts the Bloch wave functions, and hence gives rise to a linear photocurrent. This "phonon" mechanism of the PGE competes with the "Coulomb mechanism" treated above. The processes of photoexcitation are shown by Feynman diagrams in Fig. 8.

The diagrams of Figs. 8(a, b) describe the processes of real emission of phonons by an electron and a hole (indirect interband transitions), while the diagram of Fig. 8(c) shows the process without real emission of phonons (renormalization of the electron-photon interaction vertex).

There are two such contributions to $W^{as}_{kk'}$, and correspondingly two contributions to the linear current. The first one arises from the product of the probability amplitudes shown in Fig. 6(a) and 8(c). This contribution is diagonal in the momenta k and k′. The second contribution comes from the product of the amplitudes in Fig. 8(a, b). It is nondiagonal in k and k′, since the momentum of the electron (or hole) is not conserved upon emission of real phonons.

The Hamiltonian of the electron-phonon interaction is chosen in the standard way.

For optical phonons, we can write the matrix element of the Hamiltonian in the form

$$H^{e,h}_q = \left(\frac{4\pi i e Q_{ij} q_j}{\varepsilon^{\infty}_{\alpha\beta} q_\alpha q_\beta a^2} + D^{e,h} c_i\right) u^i_q. \tag{6.8}$$

Here the u^i_q are the phonon amplitudes, Q is the effective charge of the optical mode, and D is the deformation potential constant.

The methods of calculating the currents arising from electron-phonon and electron-hole interactions are quite analogous. In the case under discussion, the current is proportional to the product of the electron-phonon and hole-phonon interaction constants.

As we see from (6.8), the electron-phonon interaction is *per se* asymmetric, with $H_q \neq H_{-q}$. Thus it differs from the fully symmetric Coulomb interaction. Hence there are two independent contributions to the current involving the asymmetries of D^0_k and of $H^{e,h}_q$. The electronic contribution to the photogalvanic tensor has the form[55]

$$\beta^s_{iln} \approx \frac{ec}{\hbar\Gamma_{iso}}\left(\frac{T}{\hbar\omega}\right)\left(\frac{e^2}{a\hbar\Omega\varepsilon_\infty}\right)^2 \frac{\mu}{M}\frac{Q^2}{e^2}\frac{\varkappa}{ag}\left[h_{iln}e_l e_n + tga\,(c_i - 3e_i\,(\mathbf{c}\cdot\mathbf{e}))\right],$$
$$t = (D^e - D^h)\,\varepsilon_\infty a^2 \frac{1}{8\pi e Q}. \tag{6.9}$$

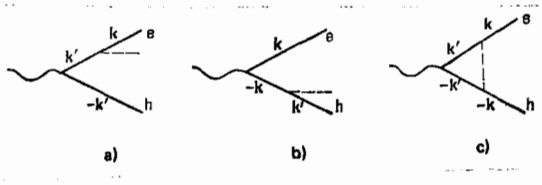

FIG. 8. Indirect interband transitions with emission of a phonon by an electron (a) and by a hole (b); renormalization of the electron-phonon interaction vertex (c). Dotted lines: phonons.

Here Ω is the frequency of an optical phonon, and M is the mass of the unit cell. The second contribution to β^s_{iln}, which characterizes the asymmetry of the electron-hole interaction, can differ from zero not only in ferroelectrics but also in piezoelectrics (e.g., for holes in $A^{III}B^{V}$ compounds).

In treating the interaction with acoustic phonons, we must take into account both the deformation and the piezoelectric potentials. We can estimate β^s_{ijl} by replacing the quantity $4\pi eQ/\varepsilon_\infty k_0^2 a^3$ by the deformation potential constant D_{ak}. Naturally, the concrete tensor structure is altered.

Generally the effect of electron-phonon interaction does not reduce merely to the asymmetry of the ionization-recombination processes. As has been shown,[55] the scattering by phonons is also asymmetric. However, such asymmetry arises in a higher order of perturbation theory with respect to the electron-phonon interaction. In its interpretation it is analogous to the asymmetry of the electron-impurity scattering (Sec. 4). We note that the existence of a photocurrent owing to asymmetric electron-phonon scattering does not require anisotropy of the nonequilibrium increment to the distribution function. Owing to the inelasticity of electron-phonon scattering, a current arises in ferroelectrics if the nonequilibrium correction to the distribution function is a function of the energy.

In closing this section, we shall make two general remarks on the method of calculating the PGE. Taking into account all the contributions to the current that exist in a certain order of perturbation theory is important not only from the standpoint of quantitative calculations. In the absence of detailed balancing, a neglect of even one of the processes shown in Fig. 8 unavoidably leads to a current at thermodynamic equilibrium, i.e., to an internal contradiction of the theory. A general prescription for distinguishing the groups of processes that yield a zero current at thermodynamic equilibrium (valid in any order of perturbation theory) is given in Ref. 55.

As one can show by employing invariance under time inversion, the contributions to I^{as}_k that lead to β^s_{ijl} must contain an even number of pole terms (no less than two). The contributions to I^{as}_k that lead to β^{as}_{ij} must contain an odd number. Correspondingly, the tensor β^s_{ijl} must contain an odd number of dissipative constants (of the type of Γ_{iso} and γ), while the tensor β^s_{ij} must contain an even number. The proof of this rule rests on the fact that the dissipative constants (when calculated by perturbation theory) contain and odd number of pole contributions, since invariance under time inversion is broken in the kinetics by the definite rules of passing around the poles of the energy denominators.

d) The role of anisotropy and nonparabolicity

Above we have neglected anisotropy and nonparabolicity of the dispersion law for the electrons. In a number of cases it may be essential to take them into account. For example, let us study indirect optical transitions in a crystal having the band structure shown in

Fig. 9. On the basis of the studied models, one might assume that in this situation the PGE is especially large, since the phononless process is energy-forbidden. However, generally this is not so. In the given situation, the contribution to β^{s}_{iln} caused by emission of phonons in the process of photoionization is zero. Actually, by virtue of arguments involving invariance under time inversion, a contribution to β^{s}_{iln} arises only from the pole terms. That is, the tensor β^{s}_{iln} is proportional to the product of two δ-functions of the energy. If we neglect the energy of the phonon, these products have the form

$$\delta(\hbar\omega - \varepsilon^{c}_{k} - \varepsilon^{h}_{k'})\,\delta(\varepsilon^{c}_{k} - \varepsilon^{c}_{k'})$$

or

$$\delta(\hbar\omega - \varepsilon^{h}_{k'} - \varepsilon^{c}_{k})\,\delta(\varepsilon^{h}_{k} - \varepsilon^{h}_{k'}).$$

We can easily see from Fig. 9 that the product of the δ-functions near the absorption edge is zero, since their arguments do not vanish simultaneously. However, anisotropy should not strongly affect the order of magnitude of the PGE whenever the phononless process is energy-allowed. Actually, the renormalization of the matrix element of the dipole moment contains a product of δ-functions of the form $\delta(\hbar\omega - \varepsilon^{e}_{k} - \varepsilon^{h}_{k})\delta(\hbar\omega - \varepsilon^{e}_{k'} - \varepsilon^{h}_{k'})$, which do not vanish, even in the case of substantial anisotropy.

Reference 56 has treated the case of practical importance of optical transitions between two subbands of a complex band. In many cases, this situation is convenient both for calculating the PGE and for experiment. Calculations have been performed for the piezoelectric n-GaP of the photoexcitation of electrons from the minimum of the conduction band X^{1}_{c} (lying on the $\langle 100\rangle$ axis) to the higher band X^{c}_{3}. Taking the asymmetry of the crystal into account the degeneracy of this band is removed; the splitting amounts to 0.3 eV. The band structure of GaP is substantially nonparabolic, however all the parameters of the crystal are well known. Taking the interaction with optical phonons into account in photoexcitation (subsection C, Sec. 6) made it possible to obtain quantitative agreement between the results of the calculations and the experimental data.[57]

7. INTRABAND TRANSITIONS

The mechanisms of the PGE treated in the previous sections involved impurity-band and band-band resonance transitions. A PGE can also arise when the energy of the photon does not suffice for such transitions, and one can speak only of intraband movements of charge carriers. An important feature of the studied

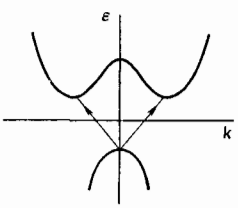

FIG. 9. Diagram of indirect band structure. The phononless process is energy-forbidden.

situation is the need for taking into account correctly the contributions to the photocurrent that are nondiagonal in the band numbers.[9)] The physical meaning of the nondiagonal contributions consists of the renormalization of the law of dispersion of an electron by light owing to crossing of different bands. As was noted in Ref. 17, the renormalized energy $\tilde{\varepsilon}_{k}$ of the electron has the asymmetry $\tilde{\varepsilon}_{k} \neq \tilde{\varepsilon}_{-k}$. However, asymmetry of the dispersion law alone does not suffice for appearance of a PGE. It was shown[58] that the nondiagonal contributions to the current always cancel a part of the diagonal contributions. The contributions to the current from the asymmetry of the group velocity $\nabla_{k}\tilde{\varepsilon}_{k}$ cancel those from the asymmetry of the distribution function, since

$$\int \nabla_{k}\tilde{\varepsilon}_{k} f(\tilde{\varepsilon}_{k})\,\mathrm{d}\mathbf{k} \equiv 0. \tag{7.1}$$

Thus the photocurrent without taking the electron-phonon, electron-impurity, or other interactions into account is exactly equal to zero. In other words, the PGE involves the real absorption of light, and is impossible without taking dissipative processes into account. We note that an underestimate of the cancellation described above led the authors of Refs. 5, 17, 59, and 60 to the erroneous conclusion of a possible PGE in the absence of collisions. The absence of a current when we neglect collisions naturally agrees also with the simple views of the impossibility of maintaining an ordered state of the system in the total absence of dissipative processes.

A photocurrent based on free carriers caused by asymmetric scattering by impurities and phonons has been treated in Ref. 58. The mechanism of the PGE corresponds to the elementary wedge model of Sec. 2.1. The electrons perform ordered oscillatory motions in the field of the wave and are scattered from time to time by impurities or phonons. In principle, both the diagonal matrix elements of the impurity potential or of the Hamiltonian of the electron-phonon interaction and those nondiagonal in the band numbers can be substantial. If the frequency of the light is much smaller than the interband spacings, the contribution of the nondiagonal elements is small.

In treating intraband processes, we can distinguish three characteristic frequency regions: $\omega \ll \Gamma$; $\hbar\Gamma \ll \hbar\omega \ll T$; $T \ll \hbar\omega$. At low frequencies the current ceases to depend on ω and actually coincides with the quadratic correction to Ohm's lwa [the second term in the phenomenological relationship (3.1)], which has been discussed in Ref. 47.

In the intermediate frequency region, $\hbar\Gamma \ll \hbar\omega \ll T$, the electromagnetic field $\mathbf{E}(t) = \tilde{\mathbf{E}}e^{-i\omega t}$ + complex conjugate can be treated classically. That is, it can be taken into account via the drift term $e\mathbf{E}(t)\partial f_{k}/\partial \mathbf{k}$ in the kinetic equation (5.2). A high-frequency correction to

[9)]In calculating the PGE by Kubo's formula for the nonlinear response, one contracts the principal terms, while one can get the final result by an accurate evaluation of the indeterminacies of the type 0/0 that arise. Similar difficulties are also encountered in the theory of various dissipative effects (see, e.g., Ref. 42, p. 222).

the distribution function appears in the first order in $E(t)$. In the second order, the quantity f_k becomes anisotropic, i.e., the following correction arises:

$$\delta f_k^s = \frac{2e^2}{m^2 T^2 \omega^2} |\mathbf{k}\tilde{\mathbf{E}}|^2 f_k. \tag{7.2}$$

Just as happened in subsection B, Sec. 5, the anisotropic increment after taking into account the asymmetry of the collision integral gives rise to a current. Using the model of dipole impurities, we have

$$\mathbf{j} = \frac{4\pi e J}{\hbar \Gamma_{iso}} k_t a \frac{e\, dNa}{\varepsilon_0 T} \frac{\hbar k_t \varkappa}{m \Gamma_{iso}} (\mathbf{c} - 3\mathbf{e}(\mathbf{c}\cdot\mathbf{e})). \tag{7.3}$$

The absorption coefficient $\kappa = 8\pi n_0 e^2 \Gamma_{iso}/mc\omega^2$ in this model does not contain any extra parameters of the crystal [as compared with (4.5)].

We note that Eq. (7.3) has been derived under the assumption $d\Gamma_{iso}/d\varepsilon = 0$. Otherwise an additional contribution to the current arises that involves another order of iteration in solving the kinetic equation.

In the frequency region $\omega \gg T$, the interaction with light is of a quantum nature. We must deal with processes of quantum absorption and emission of photons by electrons with simultaneous scattering by impurities or phonons. Figure 10 shows typical Feynman diagrams for such processes as applied to scattering by impurities. A contribution to the current arises from the product of the amplitudes of the processes shown by the diagrams in Fig. 10. One can find the pertinent calculations in Ref. 58. We shall point out only the characteristic temperature-dependences of the tensors β^s and β^{as}. In scattering of electrons by octupole impurites in piezoelectrics, we have $\beta^s \propto T^{-1/2} n_0(T)$, and $\beta^{as} = 0$, where $n_0(T)$ is the concentration of free carriers. In scattering by optical phonons we have $\beta^s \propto T^{5/2} n_0(T)$, $\beta^s \propto T^3 n_0(T)$ (we assume that $T \gg \hbar\Omega_D$, where Ω_D is the Debye frequency). The value of the photocurrent normalized to the absorption coefficient is of the same order of magnitude for intraband transitions as for band-band and impurity-band transitions.

8. SPIN EFFECTS

a) Polarization of electrons by light

Spin-orbital interaction causes the electric-current operator of an electron to depend on the spin. If the electrons are polarized, an additional contribution to the photocurrent arises. In a number of cases this contribution is the principal one in spite of its relativistic smallness. Polarization of electrons arises in semiconductors in interband optical transitions caused by elliptically polarized light.[61] Here a circular photocurrent arises in the crystal, since the spin polarization of the electrons is proportional to the degree of circular polarization of the light.

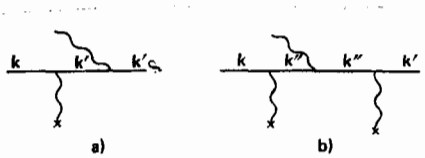

FIG. 10. Typical Feynman diagrams for intraband electron-impurity scattering.

Let us study a very simple model that produces such an effect.[62] Let the conduction band and the valence band be s- and p-bands. Figure 11 shows the band structure in the neighborhood of an extremal point. The Hamiltonian of an electron in the valence band and that in the conduction band taking intraband spin-orbital interaction into account have the following forms for small k:

$$H_v = -\frac{\hbar^2 k^2}{2m_v} + \frac{1}{3}\Delta_0 (1 - 2\sigma \mathbf{L}),$$
$$H_c = \varepsilon_0 + \gamma_{ij} k_i s_j + \frac{\hbar^2 k^2}{2m_c}. \tag{8.1}$$

Here L are the orbital angular momentum matrices, σ are the Pauli matrices, and Δ_0 is the spin-orbit splitting of the valence band. The tensor γ_{ij} is analogous in its transformational properties to the gyration tensor. Hence we have $\gamma_{ij} \neq 0$ in crystals that allow a circular PGE. The photocurrent is expressed in terms of the spin density matrix. Its electron component has the following form (the hole contribution has a similar appearance):

$$\mathbf{j}_{ph} = \mathrm{Sp}\left(\int \nabla_k H_c(\mathbf{k})\, \delta\rho_k\, d\mathbf{k}\right),$$
$$\delta\rho_k^{\alpha\beta} = (4\pi^2 \Gamma_{iso})^{-1} \sum_\nu \delta\left(-\frac{\hbar^2 k^2}{2\mu} + \hbar\omega - E_g^\nu\right) \langle\alpha|\mathbf{D}\cdot\mathbf{E}^*|\nu\rangle\langle\nu|\mathbf{D}\cdot\tilde{\mathbf{E}}|\beta\rangle. \tag{8.2}$$

Here ν are the quantum numbers pertaining to the valence band, and we have $\mathbf{D} = \mathbf{D}^0(\mathbf{k} = 0)$. The spin polarization and current are maximal when the total energy $\hbar^2 k^2/2\mu$ is much smaller than the spin-orbit splitting Δ_0. In this limit we have

$$\beta_{ij}^s = \frac{8ec}{3\pi\hbar\Gamma_{iso}} \frac{\varkappa}{\hbar\omega} \gamma_{ij}, \quad \varkappa = \frac{16\,|\mathbf{D}|^2 k_0 m\omega}{3c\hbar^2}. \tag{8.3}$$

We noted earlier in subsection B, Sec. 4 that in piezoelectrics the mechanism of the circular current not involving spin has the relativistic degree of smallness v^2/c^2. It proves to be suppressed in comparison with the spin mechanism (in terms of the parameter $k_0 a \ll 1$). The above-discussed mechanism of the origin of the circular current is also of interest in being realized in crystals of class O, which have no piezotensor, but only a gyration tensor.

The mechanism of the PGE in tellurium proposed in Ref. 63 also involves polarization of the electrons by light. The band structure of tellurium in the neighborhood of an extremum resembles that shown in Fig. 11. However, the extremal point lies at the boundary of the Brillouin zone (we have implicitly assumed above that the extremum lies in the center of the zone), so that there are several equivalent extrema. The method of calculation is analogous to that discussed above, but it explicitly takes into account the anisotropy of the crys-

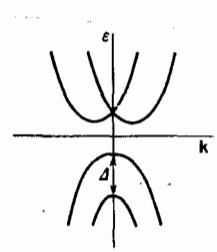

FIG. 11. Band structure in the region of an extremum of the Brillouin zone taking spin-orbit splitting into account.

tal and the difference in mass between light and heavy holes that are known from experiment.

References 63 and 64 have also treated the PGE in tellurium based on free carriers. They calculated a process of absorption of light by an electron in the conduction band consisting of two stages: absorption by the electron of a photon with virtual transition to the valence band and emission (or absorption) of a phonon in an inverse transition. These processes are depicted by the diagrams in Fig. 8; here the vertex functions for optical phonons nondiagonal in the band number are taken into account. In this mechanism of the PGE, the asymmetry of the dispersion law with spin taken into account is the decisive factor that leads to a photocurrent. The electronic contribution to the photogalvanic tensor has the form[64]

$$\beta^{a}_{zz}=\frac{ce}{4\pi\hbar\Gamma_{\rm iso}}\sqrt{\frac{\omega}{T}}\frac{\varkappa}{E_g}\gamma_{zz},\quad \varkappa=\frac{e^2}{\hbar c}\frac{8\pi c}{\hbar\omega}\frac{n_0}{\rho_0 E_g}\sum_{\nu=1,\,2}|D_\nu|^2\frac{T}{\hbar\Omega_\nu^2}. \tag{8.4}$$

Here ρ_0 is the density of the crystal, the D_ν are the interband deformation potential constants for optical phonons, and the Ω_ν are the phonon frequencies. Agreement between theory and experiment[64] is attained at room temperature for $|D_1|=|D_2|=9$ eV/Å. The hole contribution to the PGE dominates at temperatures below 230 K and is calculated analogously to the electronic contribution discussed above.

b) Effect of a magnetic field on the PGE

When a weak magnetic field is applied to a crystal, the following increment to the photocurrent arises:

$$\delta j_i=\gamma_{ilnm}\tilde{E}_l\tilde{E}^*_n H_m. \tag{8.5}$$

There are two different contributions to $\delta\mathbf{j}$. The more perspicuous contribution to the photocurrent comes from the Lorentz force acting on the current of electrons arising from the ordinary PGE. This correction is analogous to the Hall current, and it has the degree of smallness as compared with the ordinary photocurrent of $\omega_c/\Gamma_{\rm iso}$, where $\omega_c=eH/mc$. If the photocurrent is directed along the polar axis $\mathbf{c}$, then the "Hall" current flows along the vector $\mathbf{c}\times\mathbf{H}$.

In the photoionization of electrons from paramagnetic impurities, the electrons enter into the conduction band in a polarized state. The polarization of the electron spin is proportional to the magnetic field: $\bar{s}\propto\hbar\omega_c/T$. This polarization yields a second contribution to the photocurrent that can be calculated in the same way as the spin contribution caused by light.[65] This extra contribution differs from the ordinary photocurrent j_{ph} by the presence of the extra factor $(Ze^2/\hbar c)^2(ak_0)^{-1}\omega_c/T$. We can conclude that the effect of the magnetic field is determined at high temperatures by the "Hall" contribution, while spin effects are important at low temperatures. At low temperatures $\delta\mathbf{j}$ increases in proportion to T^{-1}.

In a quantizing magnetic field with a fixed frequency of light, the photocurrent must undergo the usual oscillations as a function of the variable $1/H$ involving the passage of the Landau level through the resonance energy.

The mechanisms of the photocurrent is magnetic materials lacking a center of symmetry are of especial interest in the theory of the PGE, in particular, in ferroelectric-magnetics. The dispersion law in such crystals without taking spin into account contains terms odd in the momentum:

$$\varepsilon_{\mathbf{k}}=\varepsilon_0+\tilde{\gamma}_{ij}M_i k_j+\frac{1}{2}m^{-1}_{ij}k_i k_j+\delta_{ijln}k_i k_j k_l M_n. \tag{8.6}$$

Here $\mathbf{M}$ is the magnetization of the crystal. The expression (8.6) is quite analogous to (8.1), but with the spin of the electron replaced by the magnetization. The microscopical nature of such terms involves the "spin-foreign orbit" interaction.

Evidently any nonequilibrium in a crystal having an asymmetric dispersion law like (8.6) should give rise to a current. For optical transitions between s-bands and with $\mathbf{D}^0_{\mathbf{k}}=ig\mathbf{k}$, we have

$$\beta^{s}_{ijln}=\frac{ec}{4\pi\hbar\Gamma_{\rm iso}}\frac{\varkappa\gamma_{ij}M_j}{\hbar\omega}\delta_{ln}. \tag{8.7}$$

In calculating β^s_{ijl}, there is no need to take into account the distortion of the wave function of the electron, since the magnetization $\mathbf{M}$ changes sign upon time inversion.

9. FEATURES OF THE PGE AT HIGH LIGHT INTENSITIES

Thus far we have been treating the PGE at low light intensities. As we know, the condition for J to be small consists of having the characteristic frequency of the transitions $\lambda_{\mathbf{k}}=\tilde{\mathbf{E}}\cdot\mathbf{D}_{\mathbf{k}}\ll\tau^{-1}_{\rm max}$. Here we understand $\tau_{\rm max}$ to be the longest of the relaxation times in the system. Only in this case can we treat light-induced transitions by perturbation theory. The PGE in the region of high light intensities ($\lambda_{\mathbf{k}}\tau\gg 1$) is of special interest.[10)] The photogalvanic current in the field of a circularly polarized wave proves not to depend on the relaxation parameters of the medium (γ, $\Gamma_{\rm iso}$, etc.), but remains constant as these quantities approach zero. In this sense, we can speak of realizing a nonequilibrium, nondissipative current state of the crystal.

To illustrate, let us examine the following simple model. Let the light-induced transitions occur between the nondegenerate valence band and the conduction band. We shall assume the energy $\hbar\omega$ of a light quantum to be close to the width of the forbidden band. The condition $\lambda_{\mathbf{k}}\tau\gg 1$ implies that an electron can perform a large number of interband transitions within the time between collisions with impurities, phonons, etc. Hence it seems natural in a first approximation to neglect relaxation processes completely. Owing to the smallness of the wave vector of the light wave in comparison with the momentum of the electron, the transitions between bands are vertical, so that the states of the electron in bands having momentum $\mathbf{k}$ (or states of an electron and a hole with momenta of $\mathbf{k}$ and $-\mathbf{k}$) prove to be coupled in pairs. Here the dynamics of the electrons are fully described by the formulas for a two-level system. However the existence of a current is evident without calculations. The quantity $\lambda_{\mathbf{k}}$, which determine the

[10)]Such intensities are easily attained in laser pulses.

rate of transitions between the upper and lower levels having momentum k and also the width of the resonance, is not an even function of the momentum (see Sec. 4). Hence the contributions to the current from the states k and −k do not cancel. On the other hand, the transitions of the electron between the state k in the valence band and the state k in the conduction band give rise to a current, since the velocities of the electrons in the bands $\nabla_k \varepsilon_k^{c,v}$ differ (they are simply opposite to one another if the dispersion laws for electrons and holes are the same).

Assuming all the electrons at $t=0$ to lie in the lower band, employing the known formulas for a two-level system,[22] and summing over the momenta, we can easily derive the following expression for the constant current[66]:

$$j_{ph} = e\int \frac{|\lambda_k|^2}{|\lambda_k|^2+\xi_k^2}\nabla_k\varepsilon_k \frac{dk}{(2\pi)^3}. \tag{9.1}$$

Here $\xi_k=(2\varepsilon_k-\hbar\omega-E_g)/2$ is the detuning from resonance. The integral in (9.1) is determined by the resonance energy region, $\xi_k \sim \lambda_k$. Assuming the dispersion law of ε_k to be quadratic and employing the expansion (4.10) for small k, we obtain

$$j_{ph} = \frac{e}{12\pi\hbar} k_0^3 \frac{g}{|c\cdot\tilde{E}|} i[c[\tilde{E}\cdot\tilde{E}^*]]. \tag{9.2}$$

A characteristic feature of (9.2) is the square-root dependence of the current on the light intensity. On reversing the direction of rotation of the polarization j_{ph} changes sign, in agreement with the invariance of the equations of motion under time inversion. Analogously one can construct a dynamic model of the PGE for impurity-band transitions.

It should be stated that the above-discussed dynamic description of the PGE is not completely consistent. It completely ignores the slow relaxation processes that generally remove electrons from the resonance energy region. A consistent theory of the effect must be based on rigorously taking into account the slow "mixing" processes in k-space. A technique for taking into account relaxation processes at high light intensities has been developed.[67,68] It is based on introducing new quasiparticles that are superpositions of electrons and holes in the field of the light wave. This takes the resonance interaction with the light into account exactly. In contrast to ε_k, the energy of the quasiparticles is not an even function of the momentum:

$$\tilde{\varepsilon}_k = \sqrt{|\lambda_k|^2+\xi_k^2}.$$

The distribution function of the new particles obeys the usual kinetic equations. The presence of light is reflected only in the form of the coefficients of these equations and of the energy $\tilde{\varepsilon}_k$. The stated technique enables one to obtain a consistent expansion of the characteristics of the crystal in the small parameter $(\lambda\tau)^{-1}$.

Following Refs. 67 and 68, we can derive explicit expressions for the photocurrent taking the electron-phonon interaction and radiative recombination into account. The form of the current and its magnitude turn out to depend on the relationship between the relaxation constants. If radiative recombination is the fastest of the relaxation processes ($\Gamma_{iso}/\gamma \ll 1$), then the expression for the current coincides identically with (9.1) which follows from the dynamic model. This result stems directly from the vertical nature of the transitions in radiative recombination, i.e., the lack of energy transport. In the more typical situation ($\Gamma_{iso}/\gamma \gg 1$), the expression for the current takes on the form[66]

$$j_{ph} = \frac{e}{2}\sum_k \tilde{\varepsilon}_k^{-1} \tanh\frac{\tilde{\varepsilon}_k}{2T}\nabla_k|\lambda_k|^2. \tag{9.3}$$

Just like (9.1), it does not contain any constants characterizing relaxation. The distribution of electrons and holes corresponding to the situation discussed above has the form of a step-function with the boundary momentum k_0, which is determined by the condition of resonance, $\xi_{k_0}=0$.[67] This means that the electrons are removed from the resonance region and fill the bottom of the conduction band. As compared with (9.1), the current of (9.3) is diminished by a factor of $\lambda_{k_0}/\varepsilon_{k_0}$; we assume that $\varepsilon_{k_0} \gg T$. Interestingly, the case $\Gamma_{iso}/\gamma \gg 1$ corresponds to the Fermi distribution functions of the fictitious quasiparticles $(\exp\varepsilon_k/T+1)^{-1}$. In this sense the current is calculated with equilibrium distribution functions.

Let us stress the difference between the relationships given in this subsection and the mechanisms of the PGE treated above. The photocurrents of (9.2) and (9.3) do not vanish as the parameters γ, Γ_{iso}, and $\varkappa$ characterizing the dissipative processes approach zero. Generally the conductivity σ of the crystal approaches infinity in this limit.

In the case of linear polarization of light, the currents of (9.1)–(9.3) vanish. In order to describe the PGE in this situation, we must take the asymmetry of the relaxation processes into account. Here the PGE is dissipative in character.

10. THE PGE IN GASES

Existence of the PGE in gases (and also in liquids) must be associated with the existence in them of free charge carriers. The simplest mechanism of the effect can involve photoionization of the molecules. Evidently, in order to describe the PGE one must determine $\langle W_k\rangle$ as, i.e., the asymmetric component of the probability of photoexcitation of an electron averaged over all possible orientations of an individual molecule. One can obtain a nonzero result for gyrotropic (i.e., right-handed or left-handed) molecules. Such molecules must consist of a minimum of four atoms not lying in one plane. The approximations employed in Sec. 4 prove insufficient for calculating $\langle W_k^{as}\rangle$. The simplest approach here is the following. Let us study an expansion for small k of the matrix element of D_k taken between the exact wave functions of the initial and final states [cf. (4.10)]:

$$D_i(k) = \tilde{f}c_i + i\tilde{g}_{il}k_l + \ldots, \qquad \tilde{f} = \tilde{f}^*. \tag{10.1}$$

The tensor $\tilde{g}_{il}$ and the vector c_i are rigidly bound to the orientation of the molecule. The asymmetric component of the ionization probability (4.8) does not vanish upon averaging over the angles:

$$\langle W_{\mathbf{k}}^{as}\rangle = \frac{i}{4\pi^2}\tilde{f}\eta\,(\mathbf{k}\cdot\tilde{\mathbf{E}}\times\tilde{\mathbf{E}}^*)\,\delta(\hbar\omega-\Delta-\varepsilon_{\mathbf{k}}), \tag{10.2}$$

since the tensor $\tilde{g}_{il}$ for gyrotropic molecules possesses the antisymmetric component $\mathrm{Im}\langle c_i g_{jl}\rangle = \eta\varepsilon_{ijl}$, where η is a pseudoscalar. Actually the result obtained corresponds to interference of the first and second orders of perturbation theory for D_k in terms of the asymmetric potential of the molecule. To find the current, we can directly employ the formulas (5.1) and (5.6):

$$\mathbf{j}_{\mathrm{ph}} = \frac{eJ}{2\hbar\Gamma_{\mathrm{iso}}}\frac{\hbar\varkappa}{m\omega}\frac{\eta\tilde{f}}{\tilde{g}^2}[\mathbf{e}\times\mathbf{e}^*], \quad \tilde{g}^2 = \frac{1}{3}g_{ij}^2. \tag{10.3}$$

The isotropization rate Γ_{iso} in gases can be considerably smaller than in solids.

Thus far the PGE has not been studied in either liquids or gases. Hence it is expedient to give an estimate, however crude, of the current. Let us assume that the dimensionless parameter $\eta/\tilde{g}$, which characterizes the degree of asymmetry of the molecule, is of the order of 10^{-3}, and that the velocity of the photoexcited electrons $\hbar k_0/m$ is $\sim 10^7$ cm/s, with $\Gamma_{\mathrm{iso}} \sim 10^{10}\,\mathrm{s}^{-1}$ and $\varkappa \sim 1\ \mathrm{cm}^{-1}$. Then we get the following value for the photocurrent:

$$j_{\mathrm{ph}}(\mathrm{A/cm^2}) \sim 10^{-7} J(\mathrm{W/cm^2}).$$

Interestingly, the literature has described an effect essentially akin to the PGE in gases and liquids.[69,70] This concerns the mechanism of separation of right- and left-handed molecules in a liquid by an alternating rotating field. The fluxes of right- and left-handed helical molecules turn out to be oppositely directed and are proportional to the vector product $\mathbf{e}\times\mathbf{e}^*$. The mechanism of separation differs essentially from the mechanisms of the PGE and consists of the following. If the molecules have a dipole moment, they will rotate in the external field, following its polarization vector. Then, owing to the "propeller effect," the rotational motion of the helical molecules in the liquid is converted into translational motion. Here the directions of translational motions for the right- and left-handed molecules are, naturally, opposite.

11. COMPARISON OF DIFFERENT MECHANISMS OF THE PHOTOCURRENT

This review has treated a considerable number of mechanisms of the PGE. It is useful to carry out a preliminary comparison of them, and also to estimate the size of the competing effects: the Dember effect and the effect of light pressure, which exist in homogeneous crystals. To estimate the photocurrent, it is convenient to normalize to the light intensity and the absorption coefficient $\varkappa$:

$$j_{\mathrm{ph}} = G\varkappa J. \tag{11.1}$$

In Table I we show the results of estimates of the Glass constant G for different optical transitions and different types of crystal symmetry. Of course, these estimates cannot encompass the entire variety of possible physical situations. They serve mainly for a rough orientation of the reader as to the size of the various mechanisms of the effect.

We must discuss in greater detail the choice of values

TABLE I.

Type of current	Circular	Linear	Linear	Circular	Linear
Type of transition	Impurity-band	Impurity-band, neutral impurity	Impurity-band, charged inpurity	Band-band	Band-band, Coulomb interaction
I	$\frac{kh}{m\omega}$, $5\cdot10^{-8}$	$\frac{kh}{m\omega}$, $5\cdot10^{-8}$	$\frac{edk}{\varepsilon_0\hbar\omega}$, 10^{-9}	$\frac{kh}{m\omega}$, $5\cdot10^{-8}$	$\frac{\hbar}{a_{\mathrm{B}}m\omega}$, 10^{-8}
II	$\frac{k^3h_{ij}\hbar}{m\omega f}$, $5\cdot10^{-12}$	$\frac{k^3h_{ijl}\hbar}{m\omega f}$, $5\cdot10^{-11}$	$\frac{eQk^3}{\varepsilon_0\hbar\omega}$, 10^{-12}	$\frac{k^3h_{ij}\hbar}{m\omega f}$, $5\cdot10^{-12}$	$\frac{k^2h_{ijl}\hbar}{m\omega f a_{\mathrm{B}}}$, 10^{-10}
III	Ditto	Ditto	Ditto	Ditto	Ditto
IV	0	0	0	0	0
Type of current	Linear	Linear	Circular	Linear	Circular
Type of transition	Band-band, acoustic phonons	Band-band, optical phonons	Spin mechanism	Intraband, scattering by impurities	Intraband, scattering by phonons
I	$\frac{\sigma}{\hbar\omega}\frac{T}{Mc_s^2}\frac{m\sigma a^2}{kh^2}$, 10^{-8}	$\frac{4\pi\alpha}{\omega}\sqrt{\frac{2\Omega\hbar}{m}}\frac{k_t^2}{k^2}$, $5\cdot10^{-8}$	$\frac{\gamma_{ij}}{\omega}$, $5\cdot10^{-9}$	$\frac{edk}{\varepsilon_0\hbar\omega}$, 10^{-8}	$\sqrt{\frac{\hbar\omega}{T}}\frac{\hbar\gamma_{ij}}{E_g}$, $5\cdot10^{-8}$
II	$\frac{4\pi ed}{\varepsilon_\infty\hbar\omega}\frac{T}{Mc_s^2}\times\frac{m\sigma}{kh^2}$, 10^{-10}	$\frac{4\pi\alpha}{\omega}\times\sqrt{\frac{8\pi\hbar d^2k^2}{\varepsilon_\infty mM\Omega a^3}}\times\frac{k_t^2}{k^2}$, $5\cdot10^{-10}$	$\frac{\gamma_{ij}}{\omega}$, $5\cdot10^{-9}$	$\frac{eQk^3}{\varepsilon_0\hbar\omega}$, 10^{-11}	$\sqrt{\frac{\hbar\omega}{T}}\frac{\hbar\gamma_{ij}}{E_g}$, $5\cdot10^{-8}$
III	Ditto	Ditto	Ditto	Ditto	0
IV	0	0	$\frac{\gamma_{ij}}{\omega}$, $5\cdot10^{-9}$	0	$\sqrt{\frac{\hbar\omega}{T}}\frac{\hbar\gamma_{ij}}{E_g}$, $5\cdot10^{-8}$

Note. Row I—ferroelectrics, II—gyrotropic piezoelectrics, III—nongyrotropic piezoelectrics, IV—crystals of class O. The upper line of each row gives the symbol estimate of the quantity $G\hbar\Gamma_{\mathrm{iso}}/e$, and under it the numerical estimate of $G(A\cdot\mathrm{cm/W})$. The numerical values of the parameters contained in the table are: $\Gamma_{\mathrm{iso}} = 10^{13}\ \mathrm{s}^{-1}$—isotropization rate; $m = 10^{-27}$ g—mass of an electron; $\omega = 3\times10^{15}\ \mathrm{s}^{-1}$—frequency of the light; $\varepsilon_0 = 10$—static dielectric permittivity $\varepsilon_\infty = 2$—high-frequency dielectric permittivity; $a = 3\times10^{-8}$ cm—lattice constant; $T = 300$ K; $\Omega = 10^{14}\ \mathrm{s}^{-1}$—optical phonon frequency; $c_s = 5\times10^5$ cm/s—velocity of sound; $M = 10^{-22}$ g—mass of the unit cell of the crystal; $\sigma = 5\times10^{-12}$ erg—deformation potential; $\alpha \approx 1$—electron-phonon coupling parameter; $N = 10^{19}\ \mathrm{cm}^{-3}$—impurity concentration; $E_g \approx \hbar\omega$—width of forbidden band.

of the parameters involving the asymmetry of the crystals. The asymmetry parameter for ferroelectrics is $\xi_f = d/ea$, where d is the dipole moment of the unit cell. For piezoelectrics we have $\xi_p = Q/ea^3$, where Q is the octupole moment of the unit cell. The degree of gyrotropy of the crystal is characterized by the quantity $\xi_g = g\lambda a^{-1}$,[34] where g is the gyration vector and λ is the wavelength of the light. For ferroelectrics we find $\xi_f \approx 10^{-1}$–10^{-2},[71] and for piezoelectrics $\xi_p \approx 10^{-2}$–10^{-3},[35,72] i.e., an order of magnitude smaller. For gyrotropic crystals we find $\xi_g \approx 10^{-2}$–10^{-3}.[34] We shall assume that the parameters f, h_{iln}, h_{il}, and γ_{il} (see Sec. 4) are of an order of magnitude fixed by the atomic scale and the corresponding asymmetry parameter. Thus $f \approx d \approx \xi_{cl}ea$ is the characteristic dipole moment, and $h_{iln} \approx Q_{ln} \approx \xi_p ea^3$ is the octupole moment. The constants h_{il} and γ_{il} have a relativistic degree of smallness: $h_{il} \approx \xi_p(Ze^2/\hbar c)^2 ea^3$; $\gamma_{il} \approx \xi_g c(e^2/\hbar c)^3 Z^2 \approx 10^6$ cm/s. This is of the order of the velocity of the polarized electrons at the edge of the band, $Z = 25$. We have chosen the characteristic momentum of an ionized electron by the condition of maximizing the coefficient

$G : k_0 \approx f'$

The fundamental conclusion that arises from the table is that the coefficient G depends considerably more strongly on the type of symmetry of the crystal than on the mechanism of light absorption (the type of optical transition). In other words, the value of the photocurrent critically depends on the absorption coefficient $\varkappa$, rather than on the Glass constant G, which is to a considerable extent universal for a given type of crystals.

Let us discuss the temperature- and frequency-dependence of the parameters that govern the PGE. The collision rate Γ_{iso} and the asymmetry parameter ξ_f show a strong temperature-dependence. In the low-temperature region we find $\Gamma_{iso} \approx \Gamma_0 + (T/\theta)^5\theta$, and $\Gamma_{iso} \propto T$ in the high-temperature region. The asymmetry parameter shows a substantial temperature-dependence near the phase-transition temperature: $\xi_f \approx (T - T_c)^{1/2}$, since ξ_f is defined as being proportional to the order parameter. In the neighborhood of a ferroelectric phase transition, we must account for the temperature-dependence of the dielectric permittivity: $\varepsilon_0 \approx (T - T_c)^{-1}$. Screening effects involving the increased concentration of free carriers can be substantial at high temperatures.

Near the absorption edge, as we see from the concrete expressions for the PGE, the Glass constant G is proportional to a power of the parameter $k_0 = h^{-1}[2m \times (\hbar\omega - E_g)]^{1/2}$.

Let us estimate the magnitude of the effects competing with the PGE. The current caused by entrainment of electrons by photons can be easily estimated by taking into account the fact that the electron acquires the momentum $2\pi\hbar/\lambda$ per absorption event. Hence we have[15]

$$j_{entr} \approx \frac{eJ}{\hbar\Gamma_{iso}} \frac{\varkappa k_0 \hbar}{m\omega} \frac{2\pi}{\lambda k_0}. \tag{11.2}$$

The current arising from the Dember effect differs from zero in interband transitions and is caused by diffusion of photoelectrons and holes that have been inhomogeneously excited by light absorption. The magnitude of the current depends strongly on the relationship between the absorption length, the Debye radius, and the diffusion length. In the most typical case of bipolar diffusion, in which the concentration of photoelectrons is much larger than the dark concentration,[1,2] we have

$$j_D \approx \frac{eJ}{\hbar\omega} \varkappa \sqrt{\frac{D}{\gamma}}, \quad D \approx \frac{k_t^2 \hbar^2}{m^2 \Gamma_{iso}}. \tag{11.3}$$

The diffusion coefficients for electrons and holes are assumed to be of the same order of magnitude.

Upon comparing (11.2) and (11.3) with the estimate for the photogalvanic current of (2.2), we see that the parameters $\xi\lambda k_0/2\pi$ and $\xi(k_0/k_t)(\gamma/\Gamma_{iso})^{1/2}$ serve as a measure of the smallness of the competing effects. Since $2\pi/\lambda k_0$ is of the order of magnitude of the fine structure constant, usually the photocurrent should be smaller than j_{entr}. As a rule, for interband transitions $j_D > j_{ph}$. We note that the PGE can be distinguished against the background of other effects by its dependence on the orientation of the crystal and the polarization of the light.

12. MACROSCOPIC MANIFESTATIONS OF THE PGE

This section will treat a number of secondary effects that are directly caused by the PGE. These effects are important mainly in high-resistance ferroelectrics characterized by large values of the electrostatic fields arising from the PGE (up to 10^4–10^5 V/cm).

a) Spatially oscillating current

Most crystals lacking a center of symmetry possess a considerable birefringence. When polarized light is incident on such a crystal, two electromagnetic waves propagate in it with differing wave vectors and polarizations.[73] Here the overall polarization of the light oscillates in space with a period determined by the difference in velocity of the intrinsic modes,

$$\tilde{E}(r) \propto \exp[i(q_1 - q_2)\cdot r], \qquad cq_{1,2} = n_{1,2}\omega. \tag{12.1}$$

According to the phenomenological relationship (3.2), the photocurrent is also modulated in space along with the polarization. The degree of modulation of the current depends on the conditions of illumination and the structure of the photogalvanic tensor β_{ijl}.

Generally the linear photocurrent has both a spatially oscillating and a constant component. The oscillating component is absent under conditions of illumination such that only one of the intrinsic modes propagates in the crystal. As a rule, the circular current in anisotropic crystals has no constant component.[37] An exception occurs in the case in which a circularly polarized wave propagates along the optic axis of a uniaxial crystal, with this axis being a screw axis.[11)34] In this case the current flows along the screw axis. This situation is realized in crystals of the classes D_2, D_3, D_4, D_6, C_3, C_4, and C_6.

In crystals of classes T and O and also in isotropic media lacking a center of symmetry, the intrinsic modes correspond to circular polarization of the light. In this case the circular current can be constant in space for any direction of propagation of the light.

b) Anomalous photovoltages

Charge separation caused by the PGE can give rise to considerable electrostatic fields and photovoltages. In contrast to the previously known photovoltaic phenomena,[1,2] the photovoltages caused by the PGE are not limited by the width of the forbidden band, i.e., to values of the order of several volts. Such photovoltages $U > E_g$ are called anomalous.[74] The problem of the maximum possible values of electrostatic fields and voltages is one of the central problems for high-resistance ferroelectrics.

Let us study a standard circuit for measuring photocurrents and photovoltages (Fig. 12). Evidently the spatially oscillating component of the current does not contribute to the voltage. Under stationary conditions with $R_l \gg R_{cr}$, we can assume that the photocurrent j_{ph} is compensated by the ohmic current, so that the block-

11)A nonzero constant component of the circular current can arise also upon taking spatial dispersion into account.

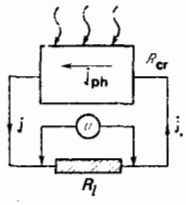

FIG. 12. Circuit for electric measurements. In measuring photovoltages one has $R_l \gg R_{cr}$; in measuring photocurrents $R_l \ll R_{cr}$. The power dissipated in the load is maximal when $R_{cr} = R_l$.

ing field E_0 and the photovoltage U_0 are equal:

$$\mathbf{E}_0 = -\hat{\sigma}^{-1}\mathbf{j}_{ph}, \quad V_0 = E_0 l_{cr}. \tag{12.2}$$

At low light intensities, when $\sigma_d \gg \sigma_{ph}$, we have $U_0 \propto J$. At high intensities, the $E_0(J)$ relationship is determined by the photoconductivity. In the converse case with $\sigma_{ph} \propto J$, the photovoltage saturates. And in the general case the $U(J)$ relationship can be more complex.

Proceeding to the problem of estimating the blocking field E_0, we immediately note that this quantity may be determined not so much by the mechanisms of the PGE as by the character of the conduction. Thus the dark conductivity σ_d can very critically depend on the temperature, the stoichiometry of composition, impurities, and the technique of preparation of the crystals. The photoconductivity is determined by the lifetime of the carriers and by their mobility. The mobility of the photoelectrons, the major part of which lie near the bottom of the conduction band with a mean energy $\varepsilon_* \approx T$ also can be determined by specific features of the crystal: modulation of the bottom of the bands owing to inhomogeneity[75] and by the polaron effect.[42] The mobility of the thermal electrons can be strongly suppressed (by several orders or magnitude) as compared with the mobility of the nonequilibrium electrons that are ejected by light with the momentum k_0 and which determine the magnitude of the PGE. For this reason one cannot draw any general conclusions concerning the value of E_0. Yet one can estimate the limiting possible value of the blocking field by very simple arguments. To do this, let us take into account a circumstance that holds however small may be the dark conductivity, mobility and lifetime of the thermal electrons in the conduction band. This is that a nonequilibrium contribution to the photoconductivity always arises from electrons ejected into the band with the momentum k_0 that have not succeeded in being thermalized or in being wrapped in a phonon coat, etc. The number of such electrons cannot be smaller than $\varkappa J/\hbar\omega\Gamma_{iso}$. Correspondingly, the conductivity is

$$\sigma \geq \frac{\varkappa J}{\hbar\omega\Gamma_{iso}} \frac{e^2}{\Gamma_{iso} m}. \tag{12.3}$$

Using the estimate for the photocurrent (2.2) and assuming that $k_0 a \approx 1$, we obtain

$$E_0^{max} \approx \xi \frac{\hbar\Gamma_{iso}}{ea}. \tag{12.4}$$

Assuming that $\xi = 10^{-1}$, $\Gamma_{iso} = 10^{13}$ sec^{-1} and $a = 3$ Å, we obtain $E_0^{max} \simeq 10^5$ V/cm. Fields of this order have been observed experimentally.[5,6,12,13,76]

c) Photoinduced change in refractive index. Recording of holograms

When a small region of a crystal is illuminated, an electrostatic field arises in its neighborhood owing to the PGE. Since crystals lacking a center of symmetry possess a linear electrooptic effect, this field gives rise to a local change in refractive index. In the literature the effect of change in refractive index under the action of light has been termed photorefraction.[52,77] In many ferroelectrics ($LiNbO_3$, $Ba_2NaNb_5O_{15}$, etc.), these changes can be very substantial, $\Delta n \approx 10^{-4}$–10^{-3}. At present a direct relationship between the PGE and photorefraction has been established for many crystals.[74,77]

If the dark conductivity of the crystal is small, $\sigma_d \ll \sigma_{ph}$, then within a time of the order of the Maxwellian time, $\tau_M = \varepsilon_0/4\pi\sigma$, a blocking field $\mathbf{E}_0 = -\sigma^{-1}\mathbf{j}_{ph}$ is established within the illuminated region. Outside the illuminated region, $\mathbf{E}(\mathbf{r})$ behaves like the field around a conductor of the same shape lying in a uniform external field $-\mathbf{E}_0$. Thus photorefraction can be described by the introduction of some effective field acting inside the crystal. Interestingly, the existence of such an internal field to explain photorefraction was postulated by Chen[5] as early as 1969, i.e., before the discovery of the PGE.

Owing to the smallness of the dark conductivity, the change in the refractive index after turning off the light can persist for a prolonged period (months or years).[52,77] This optical memory plays an important role in practical applications. We should also note, in the case $\sigma_d \approx \sigma$, that the distribution $\delta n(\mathbf{r})$ cannot at all be described by employing an effective field. The existence of the PGE in this situation leads, in particular, to the appearance of constant circular currents in the vicinity of the illuminated region.

We have not been interested above in the spatial fine structure of the electrostatic field and the Δn caused by the spatially oscillating component of the photocurrent (with a period of the order of the wavelength of the light). First we point out that the spatially oscillating component of the field, even when the unilluminated part of the crystal has a low conductivity, is not necessarily determined under stationary conditions by the condition that the total current (photogalvanic and ohmic) is zero. This already follows from the fact that $\mathbf{j}_{ph}(\mathbf{r})$ generally has not only an irrotational but also a solenoidal component (curl $\mathbf{j}_{ph} \neq 0$). Hence it is impossible to compensate $\mathbf{j}_{ph}(\mathbf{r})$ by any electrostatic field. This situation can lead to the formation of extended current domains within the illuminated region with a transverse dimension of the order of a wavelength of light.

The spatially oscillating component of the current, while of small import in recording "light spots," can play a considerable role in holographic recording and also in studying the nonlinear interaction of light waves. Let us examine a concrete example. In crystals of classes C_{3v}, C_{4v}, and C_{6v} (including the ferroelectrics $LiNbO_3$, $BaTiO_3$, $Ba_2NaNb_5O_{15}$, etc., which are characterized by anomalous photovoltages[74]), the circular current has no constant component and hence cannot be

detected by direct measurements. According to the results of Sec. 3, this contribution is determined by only one independent constant β:

$$\delta j_{ph} = i\beta[c\times(\tilde{E}\times\tilde{E}^*)]. \tag{12.5}$$

Let two waves of the same frequency with orthogonal polarizations (Fig. 13), which become correspondingly the ordinary and the extraordinary waves, be incident on the crystal. The charge separation caused by the component of the current of (12.5) perpendicular to the fringes of the interference pattern of the two waves will give rise to a space grating of dielectric permittivity $\delta\hat{\varepsilon} \propto \exp[i(q_1 - q_2)\cdot r]$. A readout wave having the wave vector and polarization of one of the recording waves can be diffracted by this holographic grating. The relative intensity of the wave diffracted by the grating is called the diffraction efficiency, and is a very important characteristic of the hologram. Measurement of the diffraction efficiency is a sensitive method of studying the nature of an optical record. An important point, under the conditions of Fig. 13, is that the previously known mechanisms of producing holographic gratings (diffusion and field[78-80]) are lacking, and the circular PGE is the only possible mechanism of recording. The diffraction efficiencies determined in Ref. 81 enable direct optical measurement of the circular component of the photocurrent in electrooptic crystals. If we assume the circular current to be of the same order of magnitude as the linear current, then, in addition to recording of holograms, the PGE must lead to an effective nonlinear interaction of waves. The length of this interaction at intensities of 1 W/cm^2 for crystals of the $LiNbO_3$ type can amount to 10^{-1}–1 cm. The distinctive feature of the cited nonlinear effects is that the amplification or attenuation of the waves under stationary conditions is not determined by the ratio of intensities, but by the sign of the photogalvanic constant β.[81] Thus the asymmetry of the crystal is manifested at the level of nonlinear-optical effects (see also Refs. 80 and 82).

d) Effect of the PGE on phase transitions in ferroelectrics

Let a ferroelectric be characterized by a single polar vector, the spontaneous polarization P. Upon assuming for simplicity the polarization of the light in the crystal to be linear, we can write an expression for the photocurrent near a phase-transition point in the form

$$j_{ph} = [\tilde{\alpha}P + \tilde{\beta}e(P\cdot e)]J + O(P^3). \tag{12.6}$$

We see that in insulated crystals the small group of nonequilibrium electrons that contribute to the PGE gives rise to a blocking field $E_0 = -\sigma^{-1}j_{ph}$, which amounts

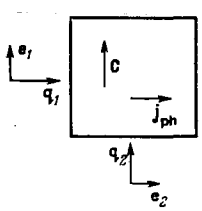

FIG. 13. Diagram of optical recording of holographic gratings via the circular PGE.

to a series in odd powers of the polarization P. This field makes an additional contribution δF to the free energy of the ferroelectric, with $d\delta F = E\cdot dP$. This has the form of a power-series expansion in P^2:[83]

$$\delta F = -\frac{J}{2\sigma}(\tilde{\alpha} + \tilde{\beta}\cos^2\theta)P^2 + O(P^4). \tag{12.7}$$

The renormalization of the coefficients of the expansion of F given by (12.7) fully determines the effect of the PGE on the phase transition.[12)] Thus, for example, in line with the ordinary theory of ferroelectric transitions,[73,84] Eq. (12.7) leads to a shift of the Curie point

$$\delta T_c = -\frac{C\delta F}{P^2} \approx \frac{CE_0}{2\pi P}. \tag{12.8}$$

Here C is the Curie-Weiss constant. According to (12.2), the value of δT_c saturates at high enough light intensities.

Estimates show[83] that the temperature shifts can be quite considerable, reaching values of the order of tens of degrees at saturation. The sign of the shift is determined by the direction of j_{ph}. As a rule, experimentally one finds that $j_{ph} \uparrow\downarrow P$. Under these conditions, illumination lowers the phase-transition temperature.

Interestingly, a photoinduced transition of a crystal from a paraelectric to a ferroelectric phase can be treated as a breakdown of the symmetry of the crystal under the action of light. Evidently the mechanism of such a transition consists in amplification of fluctuations by the field arising from the PGE. It is not ruled out that this mechanism plays a role in the recently discovered[86] effect of increased photoinduced fluctuations near a phase-transition point.

e) Efficiency of a crystal as a current source

Regardless of the concrete microscopic mechanisms, the PGE must satisfy a general requirement that stems from the law of conservation of energy. Evidently illumination of a crystal can only heat it. Hence the condition must be satisfied that $\tilde{Q} + j\cdot E \geq 0$, where $\tilde{Q}$ is the rate of absorption of light energy. The electrostatic field E arising from the PGE and the total current $j = j_{ph} + \sigma E$ are opposite in direction. The field E depends on the boundary conditions and can vary from zero (short-circuit regime) to $E_0 = -\sigma^{-1}j_{ph}$ (insulated crystal). The minimum of $j\cdot E$ is reached when $E = -j_{ph}/2\sigma$. Assuming that the light absorption does not depend substantially on the electrostatic field, we obtain $\tilde{Q} > 4j_{ph}\sigma^{-1}$.[66] At low light intensities for which we can assume that $\tilde{Q} = \varkappa J$ and $j_{ph} = G\varkappa J$, we have

$$\sigma \geqslant 4Gj_{ph}. \tag{12.9}$$

Thus phenomenological arguments already indicate a lower bound on the value of the conductivity and the photoconductivity constant. We can also rewrite the condition (12.9) in the form $\eta \equiv 4GE_0 \leqslant 1$. As one can easily show from an electric-circuit calculation (see Fig. 12), the quantity η amounts to the maximum pos-

[12)]We stress the fact that the effect of the PGE on a phase transition does not reduce to the action of an external field. As is known,[85] an external field is described by the term $P\cdot E$ in the expansion of the free energy, and it smears out the ferroelectric transition.

sible efficiency for the given crystal for conversion of light energy into energy released in the load. It is interesting to estimate this quantity for the models of the PGE discussed above. If we assume the maximum possible value for E_0 in (12.4), then we obtain

$$\eta \approx \xi^2 \frac{\omega - \Delta}{\omega} \ll 1. \tag{12.10}$$

Assuming the asymmetry parameter $\xi = 0.1$, $\omega - \Delta \approx \omega$, we obtain $\eta \approx 10^{-2}$. In experiments,[12,13] the conversion coefficient was close to this value: $\eta \approx 10^{-3}$.

Interestingly, one can construct a simple model that allows 100% conversion of energy. Let a crystal possess the relationship among the relaxation constants $\Gamma_{\text{iso}} \gg \gamma \gg \Gamma_\varepsilon$, which means that a photoexcited electron succeeds in losing its directed momentum within the lifetime of photoexcitation, but does not succeed in becoming thermalized. Here the photocurrent does not vanish, since the differential probabilities of ionization and recombination differ. Introducing into the kinetic equation (5.2) the drift term $e\mathbf{E}\partial f_k/\partial \mathbf{k}$, which takes into account the action of the electrostatic field, multiplying both sides by ε_k and integrating, we obtain

$$\tilde{Q} = \int \varepsilon_k (I_k - \gamma_k f_k)\, d\mathbf{k} = -\mathbf{j}\cdot\mathbf{E}. \tag{12.11}$$

In the absence of the field E (which arises only in the presence of a load), absorption of light energy does not take place at all. This result has a simple meaning. The shift in the frequency of the photon in spontaneous emission in the absence of thermalizing collisions is due to the change in the velocity of the electrons in the electrostatic field.

A situation similar to that under discussion can be realized at high light intensities. As we noted in Sec. 9, when $\lambda\tau \gg 1$, the circular current does not depend at all on the relaxation constants. On the other hand, as these constants approach zero, the light absorption vanishes (saturation effect[67,68]). One can show[66] that the necessary light absorption also arises under the action of the electrostatic field in a certain region of the parameters.

13. COMPARISON WITH EXPERIMENT

Up to now several tens of experimental studies on the PGE have been published. Let us examine how well the experimental data agree with the theoretical concepts. First we should say that the existence of the PGE can now be considered firmly established for all types of crystals lacking a center of symmetry: ferroelectrics, piezoelectrics, and gyrotropic crystals. The character of the studies pertaining to the different types of crystals has a definite pattern. Most of the studies carried out pertain to ferroelectric crystals, in which the PGE is especially strongly manifested.[13)] Yet the ferroelectrics have been studied considerably more poorly than many piezoelectrics and semiconductors. As a rule, no experimentally based band theory has been devised for them, often one does not know the mechanisms of mobility of the charge carriers, and the structural defects have been poorly monitored. Hence a comparison of theory with experiment in ferroelectrics unavoidably is qualitative in nature.

The fundamental experimental results that allow one to establish the existence of the PGE in ferroelectrics are: the prolonged character of the current measurements, the anomalously large values of the photovoltages, and also the linear dependence of j_{ph} on the light intensity. Figure 14 shows a typical time-dependence of the photocurrent, as taken from Ref. 5. The initial region of the curve is explained usually by the pyroeffect, and the constant-current region corresponds to the PGE. In the experiments,[12,13] the time of observation of the constant current amounted to more than 20 hours. The charge transport over this time is so large that the possibility of interpreting the currents as transition currents involving relaxation of fields in the crystals is completely ruled out.

The existence of anomalously large photovoltages, i.e., voltages considerably exceeding the width of the forbidden band, has been established in a number of high-resistance ferroelectrics: $LiNbO_3$,[12,13,87,88] $BaTiO_3$,[14,76,89] $Ba_2NaNb_5O_{15}$,[90] SbSI,[91] $KNbO_3$,[88,92] etc. In many cases it has been shown experimentally that the anomalous photovoltages are determined by the PGE and correspond to Eq. (12.2).[74] Figure 15 shows the volt-ampere characteristics for $KNbO_3$ as taken from Ref. 92. We see both the linear dependence of j_{ph} on the light intensity typical of experiments with ferroelectrics and the lack of dependence of the intensity on the blocking field E_0 ($\sigma_{ph} > \sigma_d$). The review[74] also indicates that the shift caused by light of the phase-transition point observed in certain ferroelectrics stems from the PGE. Thus it corresponds to the mechanism discussed in Sec. 12. In many cases one can establish a direct relationship between the effect of photoinduced change in the refractive index (subsec. C, Sec. 12) and the PGE.[74] The PGE has been observed in ferroelectrics both in a region of impurity absorption and in interband transitions.[14,91,93]

Some additional experimental data is available confirming the fundamental theoretical concepts. The observed values of the currents agree with the estimates made in Sec. 11.

Moreover, an analysis of the experiments[12-14,90,94-97] performed on various ferroelectrics: SbSI, $LiNbO_3$, $KNbO_3$, etc., in regions of impurity and intrinsic absorption for various concentrations and compositions of impurities has shown that while there is considerable spread (by 5–6 orders of magnitude) in values of the photovoltage, the conductivity, and the absorption coef-

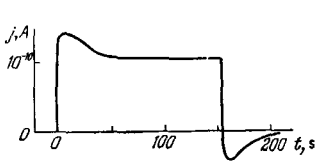

FIG. 14. Dependence of the photocurrent on the illumination time in $LiNbO_3$.

[13)]One can find a review of the experiments on the PGE in ferroelectrics that reflects the studies up to the end of 1977 in Ref. 74.

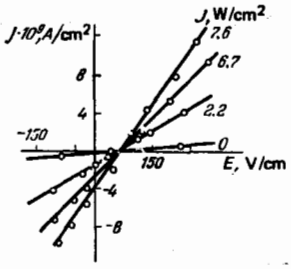

FIG. 15. Volt-ampere characteristics of $KNbO_3$.

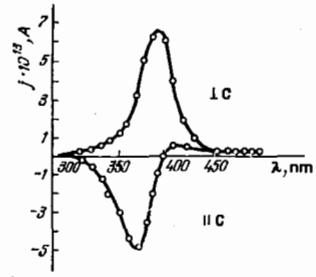

FIG. 16. Spectral and polarization properties of the PGE.

ficient, the Glass constant G varies over the relatively narrow range from 4×10^{-10} to 2×10^{-8} A·cm/W. The values of the constant G are practically independent of the technique of preparing the crystal and of its prehistory. For illustration we present a table taken from Ref. 97. The regularities noted above agree convincingly with the results of Sec. 11.

The theory indicates a possible dependence of the sign of the photocurrent and the photovoltage on the frequency and polarization of the light. Such a dependence has been observed in experiments[14,89] performed on $BaTiO_3$ crystals (Fig. 16).

References 91 and 98 have studied the temperature-dependence of the photocurrents and photoconductivity. They showed that $j_{ph}(T)$ and $\sigma_{ph}(T)$ vary in opposite directions (Fig. 17). Here the photocurrent increases with decreasing T by approximately the same law as for the mobility. These facts indicate a substantial difference in the natures of the photoconductivity and the PGE.

Reference 99 reports that constant currents were observed in the ferroelectric SbSI under the action of X-rays (of energy 8–10 keV) and α-rays. It was found that the sign of the current depended on the temperature of the crystal. Reference 100 reports observation of the PGE in a ferroelectric ceramic.

In spite of the large number of experimental studies and facts confirming the theoretical concepts, completeness of the experimental studies of the PGE in ferroelectrics is lacking even on the level of phenomenology. Actually, by starting with the symmetry of the crystal, one can establish the nonzero components of the photogalvanic tensor β_{ijl} similarly to the procedure for the electrooptic and piezo tensors. Crystal symmetry permits the existence of components of the photocurrents, not only in the direction c, but also in a direction perpendicular to the spontaneous polarization.

TABLE II. Photoelectric properties of $LiNbO_3$ doped with iron

Concentration weight %	Annealing time, min	$\varkappa$ cm^{-1}	$\sigma_d\cdot10^{15}$ $\Omega^{-1}\cdot$cm^{-1}	$\sigma_{ph}\cdot10^{14}$ $\Omega^{-1}\cdot$cm^{-1}	$E_0\cdot10^3$, V·cm^{-1}	$G\cdot10^9$, A·cm·W^{-1}
—	—	0.12	1.5	1	4.5	2.7
—	5	0.34	20	16	0.66	2.7
—	20	0.95	220	180	0.12	2.6
—	120	1.6	1000	600	0.08	2.6
0.005	—	0.6	1.5	2.8	8.6	2.6
0.005	120	10.9	8	29	4.7	0.9
0.02	—	1.2	1.3	3.6	9.0	2.6
0.03	—	2.0	2.0	4.5	11.0	2.5
0.05	—	4.4	3.0	5.5	20.0	2.5

Apparently specifically designed studies of the current components reference to which was made above have not yet been performed. A circular current in ferroelectric crystals (see subsec. C, Sec. 12) is yet to be detected. We proceed to analyze the experiments in piezoelectric and gyrotropic crystals.[8,9,57,64,101-104] The studies cited above have been performed on the four crystals Te, GaP, GaAs, and $Bi_{12}SiO_{20}$. These semiconductor crystals (except for bismuth silicate) can be considered pure compared with the ferroelectrics; their properties have been well studied. Hence the comparison of theory with experiment here can be more detailed.

The fundamental method of identifying the PGE is to measure the dependence of the photovoltage on the polarization of the light (as was stated in Sec. 3, such a dependence must be exhibited by nonferroelectric crystals). Figure 18 shows the relationship of U_{ph} to the angle θ between the linear-polarization vector of the wave and the axis *1* of the crystal for the piezoelectric Te.[102] The light was propagating along the trigonal axis *2* of the crystal. The voltages were measured between the faces of the crystal perpendicular to the axes *1* and *2*:

$$U_1 = -\chi^* \cos 2\theta + \tau^* \sin 2\theta,$$
$$U_2 = \chi^* \sin 2\theta + \tau^* \cos 2\theta.$$

The quantity χ^* characterizes the PGE, and τ^* characterizes the entrainment effect (light pressure). We see from Fig. 18 that the PGE is firmly identified, and exceeds the entrainment effect by a factor of about five. The PGE has been found in GaAs[101] and GaP[57] in an analogous way. We note that the Maxwell relaxation time in the experiments discussed above is considerably shorter than the duration of the light pulse. Hence we can definitely speak of observing a PGE rather than a transition current involving, e.g., the effect of optical rectification.

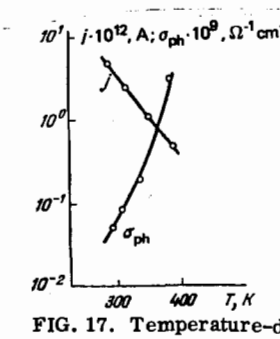

FIG. 17. Temperature-dependences of j_{ph} and σ_{ph} in $BaTiO_3$.

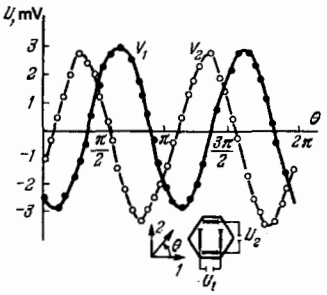

FIG. 18. Polarization properties of the PGE in Te crystals.

At present the PGE has been found in piezoelectrics both for transitions between subbands of a complex band and in intraband transitions. Most of the experiments here have been performed with a CO_2 laser, $\lambda = 10600$ Å. However, the experiments of Ref. 57 determined the dependence of the photovoltage on the wavelength of the light (Fig. 19). The peak of the curve lies near the absorption edge for transitions between the bands X_1^c and X_3^c. The energy width of the peak is of the order of the temperature of the crystal. The right-hand tail of the curve is explained by the spectral dependence of the density of states at the absorption edge. The left-hand tail involves the decline (according to the Boltzmann law) in the number of electrons that satisfy the condition of resonance with the light wave. The theoretical point taken from Ref. 56 is shown on the graph with a cross. Thus one can give a consistent quantitative interpretation of the experiments of Ref. 57.

One of the most striking experimental results on the PGE is the discovery in Te crystals (which are gyrotropic) of a circular photocurrent and of photovoltages proportional to the degree of circular polarization of the light[64,103] (Fig. 20). These experiments directly confirm the predictions of the theory. The circular photocurrent found in Te is a current based on free electrons and holes. The calculations presented in Refs. 64 and 103 explain the magnitude of the effect with reasonable values of the constants of the crystal, as well as the reversal of the photocurrent as a function of the temperature (Fig. 21). Apart from Te, a circular PGE has been recently detected in the cubic crystal of bismuth silicate $Bi_{12}SiO_{20}$.[104]

The analysis that has been carried out allows us to speak of a convincing qualitative agreement (and in a number of cases, even a quantitative agreement) between the theoretical and experimental data on the PGE.

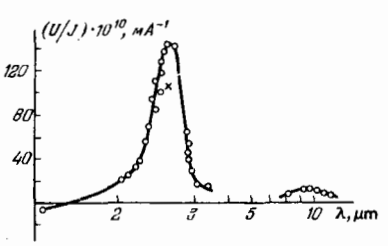

FIG. 19. Spectral properties of the PGE in GaP in transitions between the points X_1^c and X_3^c of the Brillouin zone. The points on the right correspond to the effect based on free carriers in the X_1^c band.

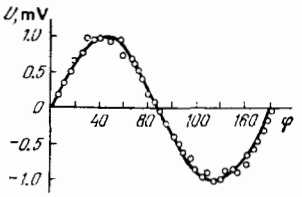

FIG. 20. Photo-emf arising on illumination of tellurium as a function of the angle φ. $p_\varphi = \sin 2\varphi$ is the degree of circular polarization. Solid line: $U = U_0 \sin 2\varphi$, $U_0 = 1$ mV.

14. CONCLUSION

To sum up what we have said, we can speak with a great deal of assurance of the completion of the first stage of study of the PGE. Its place has been established within the circle of other effects, and the general regularities and most important mechanisms of producing it have been elucidated. From the general physical standpoint the most important feature of the PGE is its direct connection with the absence of detailed balancing in media lacking a center of symmetry.

In order to perform quantitative calculations of the PGE and detailed comparison with experiment, one must take into account the specific features of the crystals: crystal symmetry, band structure, form of electron-phonon interaction, structure of the impurity centers, and the presence of many channels of recombination. The first step in this direction has been taken in Refs. 56, 64, and 103, where an attempt was undertaken for the semiconductor crystals Te and GaP to calculate the PGE quantitatively and to compare it with experiment. Investigation of the PGE in well-studied semiconductors such as Te, GaAs, and GaP is undoubtedly the most promising way to refine our concepts of its mechanisms. On the other hand, an understanding of the mechanisms of the PGE will allow us to gain from the experimental data additional information on structural features of the crystals.

We must also bear in mind that the PGE is only one of the representatives of a new type of transport phenomena in media lacking a center of symmetry. The allied effects: currents under nonequilibrium conditions that do not involve illumination and fluxes of other physical quantities (besides charge) are yet to be discovered. A possible example of this type of effect in crystals and amorphous materials characterized by a marked direction might be currents caused by slow

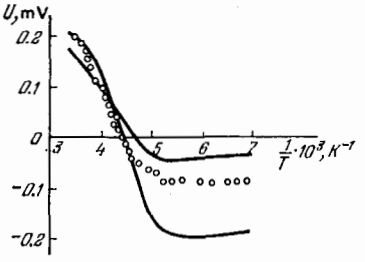

FIG. 21. Temperature properties of the circular PGE in Te. Circles: experimental data; solid curves: results of calculations for two possible mechanisms of isotropization of the momentum of the charge carriers.

relaxation of an initial nonequilibrium of an ionic subsystem, and not involving a change in polarization (the electret effect).

Because of its large magnitude, the PGE can initiate secondary effects, such as optical recording, influence of light on phase transitions, and nonlinear interaction of waves. In concrete situations, the influence on the PGE of electric and magnetic fields, spatial inhomogeneities, etc., can prove to be substantial.

Considerable prospects exist also for practical applications of the new effect. At present, anomalous photovoltages are already being used for designing photoswitches and shutters.[105] The problem of producing solar cells based on the PGE merits attention.

Undoubtedly, studies of the PGE are of considerable interest both for solid state physics and its applications, and in understanding the features of the kinetics of media lacking a center of symmetry. In the forthcoming years these studies will expand and deepen.

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