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Ballistic and shift currents in the bulk photovoltaic effect theory

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Contents

Abstract. The bulk photovoltaic effect (BPVE) — the generation of electric currents by light in noncentrosymmetric materials in the absence of electric fields and gradients — was intensively investigated at the end of the last century. The outcomes, including all main aspects of this phenomenon, were summarized in reviews and books. A new upsurge of interest in the BPVE occurred recently, resulting in a flood of misleading theoretical and experimental publications centered around the so-called shift current. Numerous top-rated recent publications ignore the basic principles of charge-transport phenomena and the previous results of joint experimental-theoretical studies. Specifically, leading (or substantial) contributions to currents caused by asymmetry of the momentum distributions of electrons and holes are missed. The wide-spread basic relation for the shift current ignores the kinetic processes of relaxation and recombination of photo-excited electrons and leads to nonvanishing shift currents in thermal equilibrium. The goals of this methodological note is to specify and substantiate the benchmarks of the BPVE theory and return studies to the right track in the interest of developing photovoltaic devices.

Keywords: media without central symmetry, bulk photovoltaic effect, polarization properties, ballistic currents, shift currents, kinetic processes, photoexcitation asymmetry

1. Introduction

The bulk photovoltaic effect (BPVE) — spatially uniform generation of electric currents by light in noncentrosymmetric materials — was massively investigated in the 1970s and 1980s. Hundreds of experimental and theoretical papers were published and dozens of different materials (ferroelectrics and piezoelectrics) were considered. The results of these studies are summarized in books [1, 2]. They cover many aspects of the BPVE: the general definition of the effect, its mechanisms for different types of light-induced transitions, applications to particular materials, the influence of magnetic fields, a comparison between theory and experiment, and the fallacies that have arisen. Numerous further applications to semiconductor nanostructures are summarized in book [3].

A new upsurge of interest in the BPVE occurred several years ago. It is caused by the progress in materials science, increased computational capabilities, and the prospects of employing the BPVE in efficient light batteries. Unfortunately, the ongoing progress is aggravated by oversights in the basics of the BPVE theory and by misinterpretations of the experimental and theoretical results. These drawbacks are centered around the notion of so-called *shift* current. They are relevant to numerous recent publications [4–13], including review [10]. Our goal is to outline what and why is not correct in the latest developments to return the studies to the right track. When necessary, we refer to the original papers cited in [1–3].

The BPVE is conventionally defined by the tensorial relation for the DC current density **j**:

$$j_i = (\beta^{\mathrm{L}}_{inm} e_n e^*_m + \beta^{\mathrm{C}}_{in}\, \kappa_n) I\,. \qquad (1)$$

Here, I is the light intensity, **e** is the unit polarization vector, $\boldsymbol{\kappa} = \mathrm{i}(\mathbf{e} \times \mathbf{e}^*)$, while $\beta^{\mathrm{L}}_{inm} = \beta^{\mathrm{L}}_{imn}$ and β^{C}_{in} are two photovoltaic tensors with the respective symmetries of piezo- and gyration tensors. This definition uses nothing but symmetry considerations. The first contribution to **j** is nonzero for the linear polarization ($\mathbf{e} = \mathbf{e}^*$); it corresponds to the so-called linear BPVE. The second contribution is zero for the linear polarization and maximal for the circular polarization ($|\boldsymbol{\kappa}| = 1$); it corresponds to the circular BPVE. Using Eqn (1), numerous experimental data on $\mathbf{j}(I, \mathbf{e})$ have been identified with the BPVE, and nonzero components of the tensors $\hat{\beta}^{\mathrm{L}}$ and $\hat{\beta}^{\mathrm{C}}$ were measured for dozens noncentrosymmetric materials, including the ferroelectrics $BaTiO_3$, $LiNbO_3$ and cubic piezoelectric crystals GaAs, GaP.

The microscopic theory includes general relations, simplified models, and applications to particular materials. Most of the results have been obtained within the paradigm of quasi-

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free band electrons, implying that the electron (hole) momentum k exceeds the inverse mean free path ℓ. The opposite case of hopping transport is also considered. The crystal asymmetry is presumed to be small. This means that the asymmetry parameter ξ_0 defined as the ratio of noncentral ionic displacement in a unit cell to the cell size a is small, $\xi_0 \ll 1$.

2. Ballistic and shift currents

A cornerstone of the microscopic BPVE theory is that the total current density $\mathbf{j}$ is generally the sum of two physically different ballistic and shift currents, $\mathbf{j} = \mathbf{j}_\mathrm{b} + \mathbf{j}_\mathrm{sh}$. The ballistic current is

$$\mathbf{j}_\mathrm{b} = -e \sum_{s,\mathbf{k}} f_{s,\mathbf{k}}\, \mathbf{v}_{s,\mathbf{k}}\,, \tag{2}$$

where e is the elementary charge, $\mathbf{v}_{s,\mathbf{k}} = \nabla_\mathbf{k}\, \varepsilon_{s,\mathbf{k}}/\hbar$ is the electron velocity, and $f_{s,\mathbf{k}}$ is the momentum distribution in band s. This contribution is due to the asymmetry of the momentum distributions, $f_{s,\mathbf{k}} \neq f_{s,-\mathbf{k}}$. It can be regarded as classical because of the relevance to an abundance of charge-transport phenomena. The shift current $\mathbf{j}_\mathrm{sh}$ is caused by shifts of electrons during light-induced transitions [1–3, 14]. It originates from nondiagonal (in s). elements of the electron-density matrix.

In noncentral media, any electronic process, including photo-excitation, recombination, and elastic and inelastic scattering, is asymmetric. Correspondingly, kinetic equations for $f_{s,\mathbf{k}}$ are not inversion invariant. In the absence of thermal equilibrium, each process contributes to $\mathbf{j}_\mathrm{b}$. However, in thermal equilibrium, where the detailed balance between transitions $s,\mathbf{k} \leftrightarrow s',\mathbf{k}'$ takes place, the kinetic equations give $\mathbf{k}$-symmetric Fermi distributions for electrons and holes and $\mathbf{j}_\mathrm{b} = 0$. The principles of calculation of $\mathbf{j}_\mathrm{b}$ are documented for all main types of light-induced transitions, including trap–band and band–band transitions [1, 2, 15–18]. They are illustrated with simple models. The existence of $\mathbf{j}_\mathrm{b}$ is undeniable for both the linear and circular BPVEs.

Difficulties in calculating $\mathbf{j}_\mathrm{b}$ for particular materials are rooted not only in insufficient knowledge of the band structure. They stem greatly from bad knowledge of the kinetic characteristics, such as the momentum relaxation times, the energy relaxation times, and the recombination times, which involve numerous electron and phonon bands and interaction channels. This situation is not special for the BPVE: it is relevant to other light-induced charge transport phenomena, such as, e.g., the photon drag effect. Nevertheless, there are cases where $\mathbf{j}_\mathrm{b}$ can be calculated and compared with experiment.

Regardless of details, the value of $\mathbf{j}_\mathrm{b}$ for trap–band and band–band transitions can be evaluated as

$$j_\mathrm{b} = e\, g\, \xi_\mathrm{ex}\, \ell_0\,, \tag{3}$$

where $g = \alpha I/(\hbar\omega)$ is the generation rate, α is the light absorption coefficient, $\hbar\omega$ is the light quantum energy, $\ell_0 = v_0\tau_0$ is the mean free path of photo-excited hot electrons (holes), τ_0 is their momentum relaxation time, and ξ_ex is the excitation asymmetry parameter. The last is the only BPVE-specific parameter in Eqn (3). According to model estimates, ξ_ex ranges from 10^{-1} to 10^{-3}.

Properties of the electron wave function $\Psi_{s,\mathbf{k}}(\mathbf{r})$ have to be commented on to avoid confusion. One might suggest that it is a Bloch function $\Psi^\mathrm{B}_{s,\mathbf{k}}(\mathbf{r})$ obeying the micro-reversibility relation $\Psi^\mathrm{B}_{s,\mathbf{k}} = \Psi^{\mathrm{B}*}_{s,-\mathbf{k}}$. With this choice, the excitation and recombination rates for electrons are symmetric in $\mathbf{k}$ for the linear light polarization and $\mathbf{j}^\mathrm{L}_\mathrm{b} = 0$. However, identification of $\Psi_{s,\mathbf{k}}$ with $\Psi^\mathrm{B}_{s,\mathbf{k}}$ is generally incorrect. For trap–band transitions, the effect of trap potential is important. Here, the functions $\Psi^-_\mathbf{k}(\mathbf{r})$ and $\Psi^+_\mathbf{k}(\mathbf{r})$ comprising converging $(-)$ and diverging $(+)$ waves (see Fig. 1a) must be used to describe the excitation and recombination probabilities [19]. None of the $\Psi^\pm_\mathbf{k}$ functions satisfies the micro-reversibility relation; this gives the asymmetry of the excitation and recombination rates. At the same time, the micro-reversibility relation $\Psi^{+*}_{-\mathbf{k}} = \Psi^-_\mathbf{k}$ links the differential probabilities of excitation and recombination: $w^\mathrm{ex}_\mathbf{k}(\mathbf{e}) = w^\mathrm{rec}_{-\mathbf{k}}(\mathbf{e}^*)$ [1, 2]. An analogous situation occurs for VB $\rightarrow$ CB transitions. The Coulomb interaction of light-induced electrons and holes, which is typically strong, causes not only localized exciton states, but also the inequality $\Psi_{s,\mathbf{k}} \neq \Psi^*_{s,-\mathbf{k}}$ [1, 2, 18]. The excitation asymmetry parameter can be estimated as $\xi_\mathrm{ex} \approx \xi_0$. For transitions between electron (or hole) bands, the electron–phonon interaction plays the role of a perturbing potential [1, 2, 16, 17]. Here, the excitation asymmetry parameter can be estimated as $\xi_\mathrm{ex} \approx \xi_0 a/\ell_0 \ll \xi_0$.

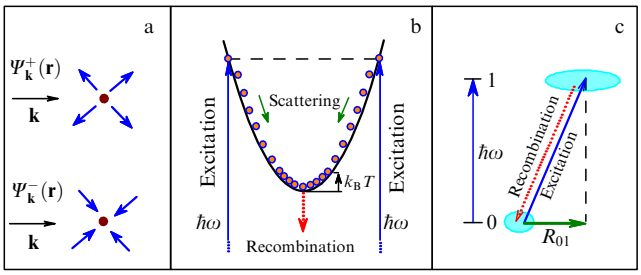

Figure 1. (Color online.) (a) The functions $\Psi^+_\mathbf{k}(\mathbf{r})$ and $\Psi^-_\mathbf{k}(\mathbf{r})$ comprising diverging and converging waves and relevant to the recombination and excitation processes, respectively. (b) A cycle of excitation, energy relaxation, thermalization, and recombination processes typical of trap–band and band–band transitions. (c) Zero steady-state shift current for transitions between two localized states 0 and 1.

The terms *shift* BPVE and $\mathbf{j}_\mathrm{sh}$ were introduced in 1982 after a breakthrough in the understanding of the physics of the nondiagonal contribution to $\mathbf{j}$ [14]. It was realized that an electron transition from the Bloch state $|n\rangle = |s,\mathbf{k}\rangle$ to the Bloch state $|n'\rangle = |s',\mathbf{k}'\rangle$ is accompanied by the shift $\mathbf{R}_{n'n}$ within a unit crystal cell:

$$\mathbf{R}_{n'n} = -\mathbf{R}_{nn'} = -(\nabla_\mathbf{k} + \nabla_{\mathbf{k}'})\, \Phi_{n'n} + \boldsymbol{\Omega}_n - \boldsymbol{\Omega}_{n'}\,, \tag{4}$$

where $\Phi_{n'n}$ is the phase of the transition matrix element and $\boldsymbol{\Omega}_n$ is the Berry connection as defined in [20]. The shift is even in $\mathbf{k}$ and $\mathbf{k}'$ and nonzero only in the absence of inversion symmetry. It does not depend on the choice of the phase of $\Psi^\mathrm{B}_{s,\mathbf{k}}$ (gauge invariance). The shift current is expressed generally by $\mathbf{R}_{n'n}$ as [1–3, 14]

$$\mathbf{j}_\mathrm{sh} = e \sum_{n,n'} W_{n'n}\, \mathbf{R}_{n'n}, \tag{5}$$

where $W_{n'n}(f_n, f_{n'})$ is the transition rate from n to n'. In thermal equilibrium, where the detailed balance takes place, $\mathbf{j}_\mathrm{sh} = 0$. Since $\mathbf{R}_{n'n}$ already accounts for the crystal asymmetry, $\mathbf{j}_\mathrm{sh}$ has to be calculated on symmetric distributions,

$f_{s,\mathbf{k}} = f_{s,-\mathbf{k}}$. Small differences between $\Psi^{\mathrm{B}}_{s,\mathbf{k}}$ and $\Psi_{s,\mathbf{k}}$ are not important for the shift BPVE.

Application of Eqns (4) and (5) to light-induced band-band transitions gives an explicit expression for $\mathbf{j}_{\mathrm{sh}}$ [1, 2, 14]. It consists of partially compensating contributions $\mathbf{j}^{\mathrm{ex}}_{\mathrm{sh}}$ and $\mathbf{j}^{\mathrm{rec}}_{\mathrm{sh}}$ relevant to electron shifts during the excitation and recombination processes. The excitation contribution $\mathbf{j}^{\mathrm{ex}}_{\mathrm{sh}}$ is proportional to the light intensity I and includes no kinetic characteristics. The recombination contribution $\mathbf{j}^{\mathrm{rec}}_{\mathrm{sh}}$ does incorporate such characteristics: hot electrons (holes) experience the energy relaxation and recombine, being predominantly (or partially) thermalized; see Fig. 1b. Because the rates of excitation and recombination are the same in the steady state, the value of $\mathbf{j}_{\mathrm{sh}}$ depends on particular values of the shift for hot and thermalized electrons. In the absence of relaxation, as in the case of Fig. 1c, the total shift current would vanish because of an exact compensation of $\mathbf{j}^{\mathrm{ex}}_{\mathrm{sh}}$ and $\mathbf{j}^{\mathrm{rec}}_{sh}$. Simple models show that the contribution $\mathbf{j}^{\mathrm{rec}}_{\mathrm{sh}}$ can be dominating in ferroelectrics [1, 2, 21]. The value of the shift current can be estimated as

$$j_{\mathrm{sh}} = eg\bar{R}\,, \tag{6}$$

where $\bar{R} \approx \xi_0 a$ is an effective shift.

The condition of dominating ballistic current is thus $\xi_{\mathrm{ex}}\ell_0 \gg \bar{R}$. It is expected to be satisfied for VB $\rightarrow$ CB transitions where the strong electron–hole interaction provides the excitation asymmetry parameter $\xi_{\mathrm{ex}} \approx \xi_0$. In the case of transition between electron (or hole) bands, we have $\xi_{\mathrm{ex}} \approx a/\ell_0$ and $j_{\mathrm{b}} \approx j_{\mathrm{sh}}$. More accurate calculations support these simple estimates (see Section 4).

3. Alternative BPVE theory

Studies [4, 5, 10] put forward an alternative version of the linear BPVE theory, which strongly contradicts [1–3]. This version is centered around the notion of shift current and deals with band–band transitions. It treats the linear BPVE as a dynamic nonlinear-optical phenomenon, free of the influence of kinetic parameters. The classical ballistic contribution $\mathbf{j}_{\mathrm{b}}$, caused by asymmetry of the momentum distributions for electrons and holes, is absent within this approach. The basic relation for $\mathbf{j}^{\mathrm{L}}_{\mathrm{sh}}$ is not different from the expression of [1, 2, 14] for $\mathbf{j}^{\mathrm{ex}}_{\mathrm{sh}}$. In other words, the shift currents considered do not include the recombination contribution $\mathbf{j}^{\mathrm{rec}}_{\mathrm{sh}}$. Since the expression for $\mathbf{j}^{\mathrm{L}}_{\mathrm{sh}}$ includes only band (but not kinetic) characteristics, it can be used for calculations from 'first principles'. Such calculations have been performed for a number of ferroelectric materials [4–9, 13]. Broad frequency ranges, which are not restricted to the excitation of charge carriers near band edges, are a remarkable feature of these calculations. Neither discussion nor criticism of [1] can be found within the alternative BPVE theory.

Remarkably, the formulae for $\mathbf{j}$ from [22, 23] served as the basis for new developments. The model employed in these papers includes only the interaction of Bloch electrons with a classical electromagnetic field. The electron–phonon and electron–hole interactions leading to the ballistic current $\mathbf{j}_{\mathrm{b}}$, as well as the common processes of energy relaxation, thermalization, and recombination, are beyond this over-simplified model. The authors of [23] and of the computational papers [4–9, 13] refer to [2] as a general source, but pay no attention either to the specific results on $\mathbf{j}_{\mathrm{b}}$ and $\mathbf{j}_{\mathrm{sh}}$ or to the general argumentation. In essence, the model expression for $\mathbf{j}^{\mathrm{L}}$ from [22, 23] pretends to be general for the linear BPVE. Referring to [4, 5, 22, 23], numerous experimental papers [24–30] erroneously declare observation and employment of shift currents.

Surprisingly, no attention was paid to copious evidences (qualitative, quantitative, experimental) of the presence of ballistic contributions to $\mathbf{j}^{\mathrm{L}}$ or to the pathology of the model where the energy relaxation and recombination processes are ignored. Ignoring the recombination leads evidently to a wrong conclusion about the presence of a steady-state shift current for an ensemble of localized two-level centers subjected to resonant excitation; see Fig. 1c. For crystals of the pyroelectric symmetry, this leads to nonzero currents in thermal equilibrium owing to the thermal-photon excitation processes, i.e., to a perpetual motion machine of the second kind.

4. Applications to GaAs crystals

The BPVE theory has been applied to a number of noncentrosymmetric semiconductors with well-known band properties and explored kinetic characteristics (GaAs, GaP, Te). The results of the calculations, performed for near-band-edge absorption, have shown good agreement with experimental data [1, 2]. Taken together, they prove that the ballistic current $\mathbf{j}_{\mathrm{b}}$ is either dominating over or comparable to $\mathbf{j}_{\mathrm{sh}}$. This applies to both the linear and circular BPVEs.

Here, we exhibit some results obtained for GaAs. This cubic piezoelectric has only the linear BPVE characterized by the component $\beta = \beta^{\mathrm{L}}_{123}$ of the photovoltaic tensor $\hat{\beta}^{\mathrm{L}}$. The band structure of GaAs for $ka \ll 1$ is shown in Fig. 2a. It is characterized by a single CB and a compound VB comprising light (h_{l}), heavy (h_{h}), and split-off (h_{Δ}) hole sub-bands. The band gap E_{g} and spin–orbit splitting Δ are $\simeq 1.53$ and 0.34 eV, respectively. The band structure is described by the Kane Hamiltonian, which is a $\mathbf{k}$-dependent 8×8 matrix [31]. Calculations of $\mathbf{j}_{\mathrm{b}}(\omega)$ for CB $\rightarrow$ VB transitions were performed in [32–34] near the fundamental absorption edge, $E_{\mathrm{g}} < \hbar\omega < E_{\mathrm{g}} + \Delta$ for He temperatures. The Coulomb interaction between photo-excited electrons and holes was found to be the dominating mechanism of the excitation asymmetry. The complexity of the quantitative calculations is rooted not only in the simultaneous excitation of three bands but also in the involvement of different mechanisms of momentum relaxation. The strongest of them is scattering on optical phonons (Ω frequency in Fig 2a). This mechanism is allowed for sufficiently large distances $\hbar\omega - E_{\mathrm{g}}$ and gives

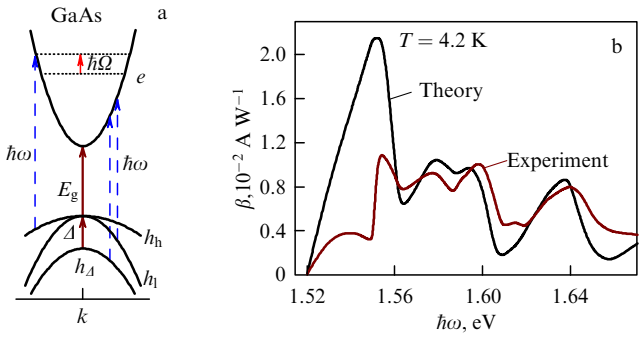

Figure 2. (Color online.) (a) Band structure of GaAs and the main light-excitation channels (blue arrows). (b) Spectral dependence of the BPVE-tensor element $\beta = \beta^{\mathrm{L}}_{123}$, theory and experiment [2, 34].

only partial momentum relaxation. This is why weaker kinetic processes — scattering on acoustic phonons and remnant neutral and charged point defects — contribute to the relaxation. As a result, the dependence $\beta(\hbar\omega)$ acquires a characteristic jagged structure (see Fig. 2b), which is the fingerprint of the ballistic nature of $\mathbf{j}$. The shift current $j_{\rm sh}$ was found to be smaller than $j_{\rm b}$ by more than one order of magnitude, $j_{\rm sh}/j_{\rm b} < 0.1$.

BPVE experiments were performed with epitaxial films of GaAs at $T = 4.2$ K [34]; they also included Hall measurements. The main features of the experimental spectrum in Fig. 2b nicely correspond to the theory (to the spectral dependence of the free-pass length l_0). The maximal values of the Hall mobility and mean free pass occur at $\simeq 1.56$ eV; they are about 5×10^5 cm^2 (V s)$^{-1}$ and 8 μm. The corresponding excitation asymmetry parameter is $\xi_{\rm ex}^{\rm max} \approx 2 \times 10^{-3}$.

Importantly, theoretical and experimental studies of two allied kinetic photovoltaic phenomena — the photon-drag effect and the surface photovoltaic effect — were performed independently for the same interband transitions in GaAs at Helium temperatures [35–37]. Good agreement between sophisticated theoretical and experimental spectral dependences was obtained. A great body of results thus gives comprehensive knowledge of the interband photovoltaic effects in GaAs.

The relation between $j_{\rm b}$ and $j_{\rm sh}$ changes dramatically for transitions between the $h_{\rm l}$ and $h_{\rm h}$ hole subbands when the Coulomb mechanism of the ballistic current is absent. In particular, it was shown theoretically and experimentally for $\hbar\omega = 117$ meV that a strong compensation of $\mathbf{j}_{\rm b}$ and $\mathbf{j}_{\rm sh}$ takes place in the temperature range 130 – 570 K [1, 2, 38, 39]. The total current $\mathbf{j} = \mathbf{j}_{\rm b} + \mathbf{j}_{\rm sh}$ is relatively small and sign-changing.

5. Influence of magnetic field

Investigation of the influence of magnetic DC fields on the photovoltaic current sheds light on the nature of the shift currents and on close links between $\mathbf{j}_{\rm b}$ and $\mathbf{j}_{\rm sh}$. Since the electronic shifts occur instantaneously during light-induced transitions, one might suggest that the effect of magnetic DC field $\mathbf{H}$ on $\mathbf{j}_{\rm sh}$ is negligible compared to the effect on $\mathbf{j}_{\rm b}$. The latter can be viewed for small fields as the generation of the Hall current $\delta\mathbf{j}_{\rm b} \approx \pm(\mu_0/c)(\mathbf{H} \times \mathbf{j}_{\rm b})$, where μ_0 is the mobility of the dominating photo-excited charge carriers, c is the speed of light, and the signs + and − correspond to dominating electrons and holes. This effect is due to the action of the Lorentz force during the free electron path. Applying strong magnetic fields, $\mu_0 H/c \gg 1$, leading to suppression of the ballistic current transverse to $\mathbf{H}$, one can hope to get the transverse shift current experimentally.

Unfortunately, the above suggestion about the negligible influence of the magnetic field on $\mathbf{j}_{\rm sh}$ is not fully correct. The point is that this field breaks the time-reversal invariance leading to inequality $\Psi_{\mathbf{k}}^{\rm B} \neq \Psi_{-\mathbf{k}}^{\rm B*}$ for Bloch electrons. This causes magneto-induced asymmetry of photo-excitation (the inequality $w_{\mathbf{k}}^{\rm ex} \neq w_{-\mathbf{k}}^{\rm ex}$) without any perturbing effect of the electron–hole and electron–phonon interactions. Correspondingly, an additional magneto-induced contribution $\delta\mathbf{j}_{\rm b}^{\rm M}$ to the ballistic current joins the game. Surprisingly, this ballistic contribution is expressed by the shift current [1, 2, 40]: $\delta\mathbf{j}_{\rm b}^{\rm M} = \pm(C\mu_0/c)(\mathbf{H} \times \mathbf{j}_{\rm sh})$, where C is a model-dependent dimensionless constant whose value can be smaller or modestly larger than 1. This formula shows that the shift and ballistic currents become mutually related in the presence of a magnetic field. For large magnetic fields, the current $\delta\mathbf{j}_{\rm b}^{\rm M}$ compensates the transverse component of the shift current and the total transverse current therefore vanishes. Thus, a decisive phenomenological separation of $\mathbf{j}_{\rm b}$ and $\mathbf{j}_{\rm sh}$ is not possible in Hall experiments. With simplifying assumptions, one can demonstrate merely that $\mathbf{j}_{\rm sh}$ is present.

The use of the Hall model for determination of the mobility and sign of photo-excited electrons is justified only when $j_{\rm b} \gg j_{\rm sh}$, including the VB → CB and trap–band transitions. Large values of the mobility obtained in such experiments [1, 2, 34, 41–43], $\mu_0 \gtrsim 10^2$ cm^2 (V s)$^{-1}$, once again support the conclusion about the smallness of the shift current and give evidence in favor of the ballistic models of the BPVE.

6. Conclusions

There are no reasons to identify the measurable total BPVE current $\mathbf{j}$ or the linear BPVE current $\mathbf{j}^{\rm L}$ with the shift current $\mathbf{j}_{sh}$. Numerous theoretical and experimental arguments indicate that the classical ballistic contribution $\mathbf{j}_{\rm b}$ caused by asymmetry of the momentum distributions for electrons and/or holes is either dominating or substantial. The ballistic current is missing in the alternative BPVE theory. The recombination contribution $\mathbf{j}_{\rm sh}^{\rm rec}$ to the shift current, which is nonzero in ferroelectric crystals, is also missing within the alternative theory. This leads to a perpetual motion machine of the second kind.

Both missing contributions, $\mathbf{j}_{\rm b}$ and $\mathbf{j}_{\rm sh}^{\rm rec}$, involve kinetic characteristics, such as momentum and energy relaxation times. Correspondingly, it is necessary to treat the BPVE as a kinetic phenomenon, substantially different from and more complicated than the quadratic response effects caused solely by the band structure. The difference stems from the fact that the generation of a DC current is always a dissipative process, in contrast to the generation of nonlinear polarization. This difference disappears in the frequency domain where the frequency difference between two light waves substantially exceeds the reciprocal of the momentum relaxation time τ_0. The shift and ballistic contributions to the BPVE current have the same symmetry properties; they cannot be decisively separated in light-polarization experiments. The same is greatly valid with respect to Hall measurements. Deep knowledge of the electron band structure and kinetic processes is necessary to judge about the relation between $\mathbf{j}_{\rm b}$ and $\mathbf{j}_{\rm sh}$.

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