Photogalvanic effect in monolayer transition metal dichalcogenides under double illumination

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Abstract
We study the photogalvanic effect caused by a simultaneous action of two light sources: circular-polarized interband and linearly-polarized intraband. It is found that, in such conditions, the steady photocurrent appears. The effect originates from the valley-selective pumping by the circular-polarized light, the trigonal symmetry of the valleys and the linear polarization of intraband electromagnetic field, that produces a polar in-plane asymmetry of the electron and hole distribution functions, leading to the photocurrent. The approach is based on the solution of the classical kinetic equation for carriers with accounting for the quantum interband excitation.

Keywords: photogalvanic effect, transport, transtion metal dichalcogenides

Introduction
The transition metal dichalcogenides (TMDs), such as MoSe₂, MoS₂ etc attracted much attention as real 2D materials consisting of single molecular layers [1]. These materials demonstrate unique optical and transport properties. Having the indirect-band structure in a 3D phase they become the direct band materials in a 2D phase. The band structure of these materials consists of two independent valleys related by the time-reversal symmetry [2]. The large distance between valleys in the reciprocal space suppresses the intervalley scattering processes resulting in the conservation of valley quantum number. This property opens the way to use the valley quantum number as an additional to the spin degree of freedom in modern applications for electronic devices based upon quantum laws. The new research direction, valleytronics, attracts much attention in modern condensed matter physics [3, 4].

Lately, the main attention has been paid to studying the transport phenomena in these materials [6–10]. One of the intriguing transport phenomena is the so-called valley Hall effect [5–7]. If the TMD monolayer is placed in the in-plane static electric field, the Hall current appears in each valley directed across the field. This current depends on the valley quantum number and has its opposite direction in valleys having the opposite value of valley quantum number. The time-reversal symmetry relates different valleys and results in the vanishing of the net Hall current in equilibrium. To destroy this symmetry, the circularly polarized external electromagnetic (EM) field, having the frequency exceeding the TMD layer bandgap, should be applied to the sample. Due to the valley selectivity of optical transitions, such EM field creates the imbalance of electron populations in different valleys resulting in the nonzero valley Hall current in the system. Usually, the circularly polarized EM field is assumed to be weak enough and it is studied by means of the perturbation theory. The valley Hall effect under the resonant interband excitation due to the strong interband EM field was analyzed in detail [11].

Recently [12] we have developed the quantum field theory of the coherent photogalvanic valley Hall effect in TMD.
materials. Similarly with the valley Hall effect in [11], the external EM field pumping the valleys was considered in the nonperturbative manner. It was shown that if a sample is illuminated by two light sources having circular (with basic frequency) and linear polarizations (with double frequency), the stationary valley Hall current arises. It is important to emphasize that this effect needs the intercoherence between the light sources, in particular, two synchronized monochromatic sources with frequencies $\omega$ and $2\omega$.

The other mechanism of photocurrent which does not need the coherence of light sources is considered in the present paper. The main idea is as follows. Due to the time-reversal symmetry, the total electron spectrum has also its inversion symmetry. At the same time, the $p \leftrightarrow -p$ symmetry of electron dispersion $\varepsilon_p$, where momentum $p$ is counted from the valley extremum $K$, exists only approximately, for $p \ll K$. If the valleys are selectively populated (figure 1), the lack of $p \leftrightarrow -p$ symmetry yields the photogalvanic effect (PGE), see figure 2.

Here we will assume that the TMD layer is illuminated by two light sources. The first source with frequency $\Omega$, corresponding to the interband transitions, is circularly polarized. It predominately populates valley $K$. The second source with frequency $\omega$ in the domain of free-electron absorption is linearly polarized. This field creates the stationary current in the system due to intraband electron processes. Both fields are supposed to be weak, and the current arises as a second order response to the linear-polarized radiation. The frequency of linear-polarized light $\omega$ is assumed to be less than the characteristic energy of photoexcited carriers.

The stationary current density under the microwave probe electric field $E(t) = E_0 \cos(\omega t)$ is described by a phenomenological expression

$$j_\beta = \beta_\beta E_{\alpha 0} E_{\alpha k}. \quad (1)$$

Depending on the initial state of the dichalcogenide monolayer, one should distinguish two cases. The first one occurs if the monolayer is in the $n - or p - doped regime, whereas the second case occur in the dielectric regime when both conduction and valence bands are empty. In the first case the interband pump field creates the carriers, whereas in the latter case the circularly-polarized EM field creates the nonequilibrium electron and hole densities additional to the equilibrium ones.

If there is only one linearly polarized light source, the photocurrent contribution from individual valleys (valley photocurrents [13, 14]) cancel each others. In the total photocurrent under linearly-polarized light the valley contributions cancel each other. The selective population of valleys by circular-polarized light violates the valley balance restoring the total PGE current.

The photogalvanic tensor $\beta_\beta$ in this case is proportional to $\eta \alpha J/\hbar \Omega$, where the light, causing the interband pumping, is characterized by frequency $\Omega$, intensity $J$, absorption coefficient $\alpha$, and the degree of circular polarization $\eta = \eta_+ - \eta_-$. ($\eta_\pm$ are the photon fractions with right or left polarizations).

The symmetry of the dichalcogenide electron dispersion in point $K$ is $C_{3v}$. Taking into account the fact that linear tensor $\beta_\beta$ originates from the spectrum warping, we find the non-zero components of $\beta_\beta$: $\beta_{xy} = \beta_{yx} = \beta_{xy} = -\beta_{xx} = -\beta$. Thus, it is enough to calculate the component $\beta$ only. For simplicity, we neglect a relatively small spin splitting; its influence will be discussed below.

Initially, we discuss the valley selective pumping and then present the PGE theory based on the Boltzmann equation accounting for the intraband impurity scattering. The scattering by neutral and charged impurities will be considered. This approach is justified by the assumption that the intravalley relaxation is much quicker than the recombination and intervalley ones, allowing for the separation of the process into two stages. The low symmetry of point $K$ is reflected in the electron spectrum $\varepsilon_p = \epsilon_p + w_p$, where $\epsilon_p = p^2/2m$ is the electron energy, $w_p = C_\beta (p_k^2 - 3p^2) = 4p^3 \cos(3\phi_p)$ is the
trigonal warping correction, \( p = p(\cos \phi_p, \sin \phi_p) \) (this choice corresponds to the reflection symmetry relative to axis \( x \)). Note that the anisotropy of the particle dispersion leads also to the unusual character of electron–electron scattering [13], second harmonic generation [15], and optical alignment [16, 17] of photoexcited carriers in gapless materials (graphene). In the present paper, just quantity \( w_p \) is responsible for PGE.

**Valley pumping**

The possibility of PGE is determined by the disbalance between the populations in the valleys \( \mathbf{K} \) and \(-\mathbf{K}\). The selective photoexcitation is controlled by the circular polarized interband radiation, see figure 1. The selectivity of photoexcitation \( \gamma \) is determined by the interband matrix element dependence on momentum \( p \). In the two-band Dirac Hamiltonian [2, 5, 11] near the fundamental absorption edge, \( \gamma = 2\Delta \Omega/(\Delta^2 + \Omega^2) \), where \( \Omega \) is the pumping light frequency, \( \Delta \) is the bandgap. Just at the absorption threshold \( \Omega = \Delta, \gamma = 1 \), and at \( \Omega \gg \Delta, \gamma \to 0 \).

Valley populations are equal in the equilibrium state. The same is true for the case of linearly polarized interband excitation. The population stationary values of \( \tilde{n} \) are determined by the balance between the generation and recombination or intervalley scattering processes. We will assume that the probability of these processes is much less than the intravalley scattering. In this case, the intravalley population is established, while the disbalance between valleys remains. The balance is described by the equation

\[
\frac{\delta n_{-\mathbf{K}} - \delta n_{\mathbf{K}}}{\tau_p} - \frac{\delta n_{\mathbf{K}}}{\tau_r} + g_{\mathbf{K}} = 0, \tag{2}
\]

where \( \delta n_{\mathbf{K}} \) is the concentration of photoexcited carriers, \( \tau_r, \tau_p \) are intervalley and recombination times, \( g_{\mathbf{K}} \) is the photogeneration rate, accordingly. Quantity \( g_{\mathbf{K}} \) is determined by

\[
g_{\pm\mathbf{K}} = \alpha J \eta_{\pm\mathbf{K}} \hbar/\Omega. \tag{3}
\]

From equation (2) we find

\[
\delta n_{\mathbf{K}} - \delta n_{-\mathbf{K}} = \tau_0 \alpha J \eta_{\mathbf{K}} \gamma / \hbar \Omega, \tag{4}
\]

where \( 1/\tau_0 = 1/\tau_r + 2/\tau_p \). If there are finite valley populations at equilibrium (\( n_p \)-doped regime), the relaxation times do not depend on the intensity of external illumination, whereas, in the absence of carriers at equilibrium, the relaxation time depends on \( \delta n_{\pm\mathbf{K}} \) and, as a result, on pumping field intensity \( J \). Note, that the values of \( \tau_0 \) for electrons and holes (and, consequently, their concentrations) can differ. Note that above we used \( \alpha \) and \( \gamma \) for the transitions from the upper spin-split valence band. Other transitions appear for higher frequencies, and that slightly (\( \propto \) a spin splitting ratio to the energy gap) modifies the expressions for \( \alpha \) and \( \gamma \) coefficients.

Below we will use the stationary quasiequilibrium distribution function of photogenerated carriers \( f(p) \) corresponding to the valley population \( n_{\mathbf{K}} \),

\[
\delta n_{\mathbf{K}} \equiv n = \int \frac{d^2p}{(2\pi)^2} f(p). \tag{5}
\]

**Calculation of PGE coefficient**

Our analysis of PGE coefficient \( \beta \) is based on the classical kinetic equation approximation. For simplicity, we consider one type of carriers, namely electrons, keeping in mind that the total current is determined by the summation of contributions from different types of carriers and valleys. Let us have valley \( \mathbf{K} \) to be populated, while \(-\mathbf{K}\) is empty. Note here that the case when the pumping field has its arbitrary polarization is described by the same final equations with the additional factor \( \eta \) reflecting the circular polarization degree. In specific cases of positive or negative circular polarization—\( \eta = \pm 1 \).

The classical kinetic equation for distribution function \( F(p, t) \) and its formal solution in the expansion on electric field powers are

\[
(\hat{I} - \partial_t) F = eE\nabla_p F, \tag{6}
\]

\[
F = \sum_n \left[ (\hat{I} - \partial_t)^{-1} eE\nabla_p \right]^n f(p). \tag{7}
\]

Quantity \( \hat{I} \) represents the collision operator with impurities. This operator in the Born approximation is

\[
\hat{I} F(p) = 2\pi n_i \int \frac{d^2p'}{4\pi^2} |V(p - p')|^2 \delta(\varepsilon_p - \varepsilon_p') (F(p) - F(p')). \tag{8}
\]

Here \( V(q) \) is the Fourier transform of the impurity potential, \( n_i \) is the impurity concentration. Independently from the spectrum asymmetry, the collision operator vanishes if \( F(p) \) depends only on the electron energy (in particular, if it is the equilibrium distribution function). The collision operator bears the valley asymmetry via the electron spectrum and can be separated into two parts, \( I = I_+ + I_- \). The first one, \( I_+ \), contains the isotropic part of electron spectrum, \( \varepsilon_p \), whereas \( I_- \) is determined by the spectrum asymmetry. Expanding equation (8) with respect to small \( w_p \), we find

\[
\hat{I}_- F(p) = 2\pi n_i \int \frac{d^2p'}{4\pi^2} |V(p - p')|^2 \delta(\varepsilon_p - \varepsilon_p')(w_p - w_p')(F(p) - F(p')). \tag{9}
\]

The stationary electron current density is expressed via the time-average \( \overline{F}(p) \) as

\[
\hat{I} = e \int (\nabla_p \varepsilon_p) \overline{F}(p) \frac{d^2p}{4\pi^2}. \tag{10}
\]

In the second-order with respect to the electric field,

\[
\overline{F} = \frac{e^2}{2} \text{Re}\left( I^{-1} E_0 \nabla_p \left[ (i\omega + I)^{-1} E_0 \nabla_p f(p) \right] \right). \tag{11}
\]

The function \( f(p) \) is produced by pumping field. It is assumed that, due to long intervalley and recombination times, \( f(p) \) is a quasiequilibrium function within the pumped valley. At the same time, this function is anisotropic in the momentum space due to the spectrum warping.

The photogalvanic current equation (10) arises due to the asymmetry of the spectrum directly (figure 2) and via the
collision operator. Assuming the smallness of $w_p$ we expand the current with respect to $C_i$. The expansion affects velocity operator $\nabla_p w_p$, stationary distribution function $f(p)$, and collision operator $I$. Thus, we have

$$\nabla_p z_p = \frac{p}{m} + \nabla_p w_p, \quad f(p) \approx f_0(p) + w_p \frac{\partial f_0(p)}{\partial p},$$

(12)

where $f_0(p)$ is the stationary particle distribution function taken at $w_p = 0$. The operator $(I - \partial_l)^{-1}$ can be also expanded with respect to the asymmetric part

$$(I - \partial_l)^{-1} = (I_+ - \partial_l)^{-1} - (I_+ - \partial_l)^{-1} I_+ (I_+ - \partial_l)^{-1} + \ldots$$

(13)

Thus, we have three contributions to the current which comes from the velocity operator, stationary distribution function and the collision operator, respectively.

At $C_i = 0$ the system is isotropic in the $(x, y)$ plane. In this case, the action of $I_+$ onto the $M$th angular harmonics of distribution function $F(M) \propto e^{iM\theta}r$ reduces to the multiplication by the corresponding relaxation rate:

$$I_+ F(M) = -F(M)/\tau_M,$$

(14)

where

$$\frac{1}{\tau_M} = 2\pi m n_0 \int |V(p - p')|^2 (1 - \cos(\cos(M\theta)))d\theta.$$

(15)

Here $p = p'$, $\theta$ is an angle between $p$ and $p'$. For the further calculation we use the identity

$$\frac{1}{\xi + I_+ [g(p) \cos(M\varphi_p)]} = \frac{g(p) \cos(M\varphi_p)}{\xi - 1/\tau_M}$$

(16)

valid for any function $g(p)$ and any number $\xi$.

In the following section we calculate these contributions assuming the simplified $\tau$-constant approximation of the isotropic collision integral $I_+ = 1/\tau$ which corresponds to the electron scattering by short-range impurities. This approximation is also valid for Coulomb scattering when the screening length becomes less than the electron wavelength. Although this condition can be hardly fulfilled if impurities are screened by the same carriers, it is valid if there is an additional screening mechanism, for example due to the presence of gate electrode. The generalization to the case of unscreened Coulomb impurities will be given in a further section.

### Short-range impurities

The contribution to the current which corresponds to correction $\nabla_p w_p$ is given by

$$j_l = -\frac{e^2 r^2}{2(1 + \omega^2 r^2)} \int \frac{(\nabla_p w_p)^2 dp}{(2\pi)^2} (E_0 \cdot \nabla_p)^2 f_0(p).$$

(17)

It can be readily shown that the other contributions to the PGE current vanish.

For the scattering on short-range impurities $V(q) = V_0 = \text{const}$, and $1/\tau = mn_0 V_0^2$ does not depend on the electron energy. Substituting $w_p$ in equation (17), we find

$$j_{1x} = \frac{e^2 r^2 E_0}{2(1 + \omega^2 r^2)} \int \frac{(p_x^2 - p_y^2) dp}{(2\pi)^2} \frac{\partial^2 f_0(p)}{\partial p_x^2}.$$  

(18)

The last integral can be directly expressed via $n_K$. Finally, the total PGE coefficient including the summation over carrier kinds is

$$\beta = 3e^3 \eta r \gamma \left[ \frac{n_e r^2 C_{x_e}}{1 + \omega^2 r^2} - \frac{n_h r^2 C_{x_h}}{1 + \omega^2 r^2} \right], \quad \tau = \frac{m_e}{m_h},$$

(19)

where subscripts $e$ and $h$ indicate carrier types.

It is interesting to note that this result is analogous to the photon drag effect [18] with the change of $3C_{x_e}r \gamma \rightarrow 2\eta/\omega m^2$, where $\eta, \omega$ are the in-plane component of photon wavevector and its frequency.

### Coulomb impurities

Here the scattering caused by the non-screened charge-impurities with concentration $n_i$ is studied. The Fourier transform of the impurity potential is $V(q) = 2\pi e^2 / (\kappa q)$ ($\kappa$ is the dielectric constant). Quantity $\tau_M$ is

$$\frac{1}{\tau_M} = \frac{\pi m e^2 n_i}{\kappa^2 p^2} \int d\phi \frac{1 - \cos(M\phi)}{1 - \cos \phi} = \frac{\pi^2 e^2 n_i |M|}{\kappa^2 \epsilon_p}.$$  

(20)

The dependence of the Coulomb scattering times on the electron energy (see equation (15)) brings additional contributions to the current. Equation (9) is converted into

$$I_+ F(p) = \frac{m^2 n_i e^4 C_3}{2\kappa^2 p} \int_0^{2\pi} d\phi \frac{d}{dp'} \left[ (F(p) - F(p')) \right] \times \frac{p^3 \cos(3\phi) - p'^3 \cos(3\phi')} {p'^2 + p^2 - 2pp' \cos(\phi - \phi')}.$$  

(21)

Further calculations are carried out with the use of angular harmonics and equations (16), (15) and (21). We found the current for the Boltzmann distribution function of photoexcited carriers. The resulting PGE coefficient reads

$$\beta = 16e^3 \eta r \gamma r^2 (n_h C_{x_h} - n_e C_{x_e}) F(\omega \gamma),$$

$$F(\gamma) = \frac{1}{32} \int_0^{2\pi} \frac{x^2 e^{-4x} dx}{(4 + x^2)^2} \left[ 4x^2 + 2x + 10 - 20\gamma^2 x^2 + x^4 \gamma^2 ight],$$

(22)

where

$$\tau = \int_0^{\infty} e^{-\tau / \gamma} d\tau = \frac{\pi n_i}{2\pi^2 e \gamma n_i}.$$  

(23)

Function $F(\gamma)$ has asymptotic behaviour $F(\gamma) \approx 1 - 135y^2/8$ at $y \ll 1$, and $F(\gamma) \approx 7/(32y^2)$ at $y \gg 1$.

For unscreened Coulomb impurities the relaxation times of electrons and holes are identical, equation (20). Then, the total PGE of electrons and holes is determined by the same function $F(\gamma)$ in equation (22).
In a simple situation $n_e = n_h$ for interband transitions. In a two-band model $C_{3h} = C_{3h}$. The Coulomb scattering also does not depend on the charge sign, and $\tau_e = \tau_h$. In such case the PGE current should vanish. Nevertheless, $C_{3h} \neq C_{3h}$ due to the influence of other bands on the electron spectrum (see, e.g. [2]). Besides, $n_e \neq n_h$ if these quantities are controlled by different mechanisms of carrier capture.

Figure 3 demonstrates the frequency dependence of the coefficient $\beta$ in MoS$_2$ for neutral impurities calculated by means of equation (19), and for Coulomb impurities (equation (22)) with the use of values $C_{3h} = -5.71 \text{eV} \cdot \AA$, $C_{3h} = -3.49 \text{eV} \cdot \AA^3$ [2], $m_0 = 0.61 m_0$, $m_e = 0.44 m_0$, ($m_0$ is electron mass in vacuum). We set $\eta = \gamma = 1$, $\tau = \tau_e = 10^{-10} \text{s}$, $n_e = n_h = 10^{10} \text{cm}^{-2}$. As seen from figure 2, in the Coulomb case the current has its constant sign. The alternating sign in the neutral impurity case and the difference of the effect orders of magnitude result from the concurrence of electron and hole contributions. The sharp dependence of $\beta(\omega)$ is explained by the essential difference between $\tau_1$ and $\tau_2$ in the Coulomb case.

Conclusions and discussions

The effect studied here differs from the known photogalvanic effect (see [19] and references therein) by its origin from the spectrum asymmetry rather than the asymmetry of interaction potential or the crystal-induced Bloch wave function asymmetry. The circularly polarized light causes the selective excitation of a separate valley to the photocurrent. The valley population lives during a relatively long intervalley time, as compared to the momentum relaxation time (responsible for usual PGE). This circumstance amplifies the effect.

The photocurrent is determined by both electrons and holes. As seen in equation (19), the $e$--$h$ asymmetry (in particular, difference between $\tau_1$ and $\tau_2$), together with a different direction of partial currents, results in the complex frequency dependence of the photocurrent, up to its alternating sign.

The obtained results are related to the interband phototransitions when $\Omega$ is near the fundamental threshold. The transitions from the spin-split bands affect the valley population, in particular, lead to the appearance of additional kink in the dependence $\alpha(\Omega)$ and the slight modification of coefficient $\gamma$, and does not affect the intraband current at a given valley population.

It is desirable to compare the effect predicted here to other PGEs. The usual PGE appears in the second order in the external alternating electric field. It requires the medium asymmetry. The coherent PGE [12] appears, at least, in the third order of electric field, does not require the asymmetry of the media, but needs the intercoherence of two light sources with the first and second harmonics.

As compared to the coherent PGE, the effect considered here has the forth order in the external field, which can be produced by two independent light sources. Hence, the intercoherence of two light sources is not assumed.

The considered effect depends on different parameters describing the system, namely, the asymmetry of valley spectrum, intervalley scattering time, momentum relaxation time and valley pumping selectivity. All these factors contribute to the effect and, hence, can be studied by the effect measurements.

Note, that an idea of pure valley currents (PVCs) in dichalcogenides, discussed in [14], has some similarity with the PGE studied here. Unlike PGE, PVC vanishes after the summation over the valleys. The PGE considered in our paper can be treated as PVCs under a selective excitation of a separate valley. It gives a more realistic way to study PVC under microwave illumination.

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