Photogalvanic effect induced by intervalley relaxation in a strained two-dimensional Dirac monolayer

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We theoretically study the photogalvanic effect in a strained two-dimensional transition-metal dichalcogenide monolayer due to deformation-induced lowering of the monolayer symmetry and electron-density difference in opposite valleys. This effect arises as a system response to a scalar nonequilibrium perturbation (electron-density difference in the valleys), which is in contrast with the conventional photogalvanic effect, represents the second-order response to an external electromagnetic radiation. Using the description of linear and nonlinear interband recombination, we develop a theory for a *p*-type and an intrinsic monolayer semiconductor. We show that at low temperatures, the photogalvanic current is caused by the impurity relaxation processes controlling the valley population imbalance.

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I. INTRODUCTION

The photogalvanic effect (PGE) is the transport phenomenon consisting in the appearance of a stationary current in the sample exposed to an external alternating electromagnetic (EM) field [1–4]. This effect is different from the light pressure or the photon drag effect [5], nonuniformity of a sample or light intensity, like the photo-induced Dember effect (currents arising in $p-n$ junctions under external illumination). Phenomenologically, conventional PGE can be described by the relation between the current density and an external electromagnetic field $j_\alpha = \chi_{\alpha\beta\gamma} E_\beta E^*_\gamma$. Depending on the polarization of the external EM field and the symmetry of the crystal lattice, one can distinguish between the linear and circular PGE. Such a PGE has been broadly studied in conventional semiconductors [1–11] and superconductors [12,13].

From the general perspective, any factor which drives the system out of the equilibrium state can produce the PGE current [14]. Such a factor, or generalized force as it is called in statistical physics, can be a scalar, vector, or even a tensor. Electric field is an example of a generalized force; other known examples include a temperature gradient and particle-density gradient. Besides, the current can be caused by scalar generalized forces such as the temperature difference [15] or particle concentration difference between different subsystems (or their time derivatives). An example of a tensor-generalized force can be constructed from second spatial derivatives of the scalar quantities, etc. An electric current can be excited in the system by the effects described by the higher orders of the vector fields together with their cross products. A general expression for a current density caused by the scalar F, vector F_j, and tensor F_{ij} fields reads

$$j_i = \gamma_i^{(0)} F + \gamma_{ij}^{(1)} \partial_j F + \gamma_{ij}^{(2)} F_j + \gamma_{ijk}^{(3)} F_j F_k + \gamma_{ijk}^{(4)} F_{jk} + \ldots. \tag{1}$$

The symmetry of the system determines the coefficients $\gamma_i^{(0)}$, $\gamma_{ij}^{(1)}$, $\gamma_{ijk}^{(3)}$, and $\gamma_{ijk}^{(4)}$. The quantity $\gamma_i^{(0)}$ may exist in materials with built-in polar axis (like pyroelectrics or ferroelectrics), whereas the tensors $\gamma_{ijk}^{(3)} \neq 0$ or $\gamma_{ijk}^{(4)} \neq 0$ demand the absence of reflection symmetry.

In this paper, we focus on the PGE effect stemming from the first term in Eq. (1) in nonpyroelectric crystals. This term describes the PGE response to the scalar perturbation, such as the temperature difference or particle concentration difference between different subsystems. Recently it was shown [15] that the PGE current can arise due to the energy relaxation of hot electrons to the equilibrium state in noncentrosymmetric quantum wells. The current originates from the real-space shift of the wavepackets of Bloch electrons due to the electron scattering by phonons, which tends to restore the thermal equilibrium between the electron and phonon subsystems. Thus, the current is determined by the temperature difference ΔT between electron gas and the crystal lattice temperatures.

We aim to develop a theory of PGE current response due to the uniform electron concentration difference ΔN in the sample. As a test-bed system we consider a transition metal dichalcogenide (TMD) monolayer MoS_2. The band structure of this material consists of two valleys coupled by time-reversal symmetry. Another important property of MoS_2 is the valley-dependent optical selection rules: a given valley is populated by the external EM field with certain circular polarization. Changing the circular polarization changes the valley, which is pumped by electrons due to interband optical transitions. Thus, the electrons in two valleys can be considered as two subsystems with different electron densities. In the simplest case when one of the valleys is empty, whereas the other one is pumped, a PGE current arises in the system. It is proportional to the difference of electron populations $j \propto \Delta N$, and depends on the intervalley relaxation processes.

The expected slowness of intervalley relaxation may enhance this effect.

It should be noted that the conventional PGE is determined by the fourth term in Eq. (1). The microscopic mechanisms of this PGE transport phenomenon is based on specific electron-impurity or electron-phonon scattering mechanisms, known as skew scattering, shift scattering, and anomalous velocity contribution related to the electron Berry phase [1–11]. All these mechanisms are well known and theoretically studied in TMDs, particularly in MoS_2 monolayers [16–18].

Besides the conventional mechanisms, PGE may arise due to the trigonal warping of the electron valleys. This mechanism is valley selective: the PGE current flows in the opposite directions in different valleys. Destroying the time-reversal symmetry produces a nonzero net PGE current in the sample [19–22].

However, in all these PGE transport effects, the driving generalized force is the external electric field. It is stationary in the monolayer plane or it is alternating in time (if external EM wave is considered).

In the present paper we suggest a PGE transport based on another microscopic mechanism. Formally, it is determined by the first term in Eq. (1) and it is related to anisotropic intervalley electron-impurity scattering. We show that the built-in vector $\gamma_\alpha^{(0)}$ is induced in a TMD monolayer by uniform strain.

In the next section we present a phenomenological analysis showing the relation between $\gamma_\alpha^{(0)}$ and the deformation tensor, and derive the general PGE current expression permitted by the MoS_2 point group. Further, we develop the microscopic theory of the effect. The final sections deal with discussions and conclusions.

II. PHENOMENOLOGICAL ANALYSIS

The PGE consists in the emergence of electric current as the response to the scalar force determined by the electron-density difference ΔN, according to Eq. (1), $j_\alpha = \gamma_\alpha^{(0)} \Delta N$. The TMDs, in particular MoS_2, do not have built-in polar axes, and thus $\gamma_\alpha^{(0)} = 0$. The situation is dramatically different in the presence of a uniform strain. Indeed, the deformation tensor reads

$$u_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right), \tag{2}$$

where $\mathbf{u}$ is the vector describing the displacement. Thus, in the presence of strain, $\gamma_\alpha^{(0)} = \lambda_{\alpha\beta\gamma} u_{\beta\gamma}$, and it is nonzero if the media supports the nonzero elements of the third-rank tensor $\lambda_{\alpha\beta\gamma}$, which takes place in noncentrosymmetric media. MoS_2 belongs to the D_{3h} symmetry group, which does not contain an inversion center. Thus, the PGE current in the presence of a weak uniform deformation and intervalley electron-density imbalance can be written in the phenomenological form

$$j_\alpha = \lambda_{\alpha\beta\gamma} u_{\beta\gamma} \Delta N. \tag{3}$$

The quantity ΔN is a pseudoscalar, whereas j_α is a polar vector, hence, $\lambda_{\alpha\beta\gamma}$ is a third-rank pseudotensor with nonzero elements [23]

$$\lambda_{xxx} = -\lambda_{xyy} = -\lambda_{yxy} = -\lambda_{yyx} = \lambda. \tag{4}$$

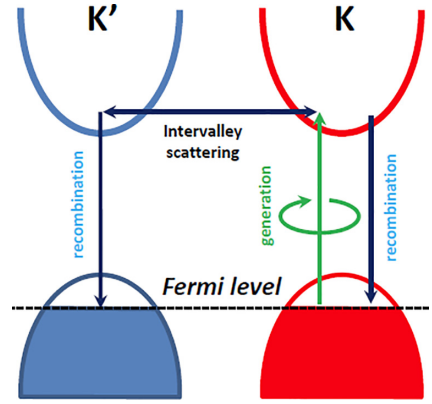

FIG. 1. The two-valley band structure of MoS_2 monolayer and the scheme of electron transitions describing the valleys-selective interband pumping, the interband recombination, and intervalley relaxation processes.

Thus,

$$j_x = \lambda(u_{xx} - u_{yy})\Delta N, \quad j_y = -\lambda(u_{xy} + u_{yx})\Delta N, \tag{5}$$

where $u_{xy} = u_{yx}$. The PGE is determined by the parameter λ. Below, we find its value from a microscopic theory.

III. MICROSCOPIC THEORY

To develop a theoretical description of the PGE effect, let us first consider a p-type doped MoS_2 monolayer at zero temperature (Fig. 1). We assume that in the equilibrium, both the K and K' valleys are occupied by (equilibrium) holes with no electrons in the conduction band. Furthermore, an external uniform circularly polarized EM field pumps only one valley with electrons. We will call this valley the active valley. In nonequilibrium but stationary regime, the relaxation processes such as interband recombination and intervalley relaxation stabilize the system, producing stationary nonequilibrium distribution function of electrons. Thus, the interband pumping provides an isotropic distribution of electrons in the active valley. Due to the symmetry of active and passive valleys (Fig. 2), the intervalley electron transitions to the passive valleys do not produce a PGE current. However, the presence of strain destroys the triangle symmetry, and a net PGE current emerges. As a microscopic mechanism of relaxation, we will consider the intervalley electron scattering off the Coulomb impurities. Then, the PGE current is determined by the balance equations for the distribution function of K and K' electrons.

A. Equations of balance and the current density

The steady-state equations of balance accounting for the intravalley-interband pumping, the interband recombination processes in both the valleys, and the intervalley relaxation read

$$\frac{f_{\mathbf{k}}^+}{\tau_R} = g_{\mathbf{k}} + \sum_{\mathbf{K}} (W_{\mathbf{kK}}^{+-} f_{\mathbf{K}}^- - W_{\mathbf{Kk}}^{-+} f_{\mathbf{k}}^+),$$

$$\frac{f_{\mathbf{K}}^-}{\tau_R} = \sum_{\mathbf{k}} (W_{\mathbf{Kk}}^{-+} f_{\mathbf{k}}^+ - W_{\mathbf{kK}}^{+-} f_{\mathbf{K}}^-), \tag{6}$$

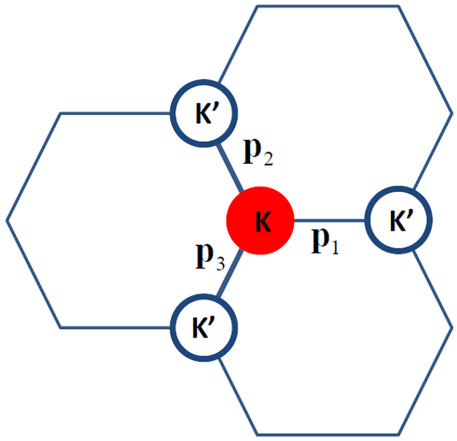

FIG. 2. Relative positions of active (pumped) valley K (filled red circle) and nearest three equivalent passive K' valleys (empty circles). In the absence of strain, the intervalley electron transitions in directions $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ give the zero net current due to the symmetry. The uniform strain being applied, say, in $\mathbf{p}_1$ direction, destroys the triangle symmetry and the net current becomes nonzero.

where $f_{\mathbf{k}}^{+}$ is the distribution function of electrons with the momentum $\mathbf{k}$ in the active "+" (K) valley, $f_{\mathbf{K}}^{-}$ is the electron-distribution function in the passive "−" (K') valleys, numerated by the index $i = 1, 2, 3$. $\mathbf{K} = \mathbf{p}_i + \mathbf{k}'$ and $\mathbf{k}'$ is counted from the center of the given "−'s" valley. The vectors $\mathbf{p}_i$ determine the positions of passive valleys K', see Fig. 2. The term $g_{\mathbf{k}}$ corresponds to the interband generation rate, and the terms $\propto W$ describe the intervalley relaxation due to the electron scattering by impurities.

We will assume that the intervalley relaxation is weak in comparison with the interband recombination $\tau_R^{-1} \gg W_{\mathbf{kK}}$. It allows us to solve Eq. (6) by successive approximations. The distribution functions can be presented in the form $f_{\mathbf{k}}^{+} = f_{\mathbf{k}}^{0} + \delta f_{\mathbf{k}}^{+}$ and $f_{\mathbf{K}}^{-} = 0 + \delta f_{\mathbf{K}}^{-}$, where the corrections $\delta f_{\mathbf{k}}^{+}, \delta f_{\mathbf{K}}^{-}$ are due to the intervalley relaxation processes. A simple calculation yields $f_{\mathbf{k}}^{0} = \tau_R g_{\mathbf{k}}$ and

$$\delta f_{\mathbf{k}}^{+} = -\tau_R^2 g_{\mathbf{k}} \sum_{\mathbf{K}} W_{\mathbf{Kk}}^{-+}, \quad \delta f_{\mathbf{K}}^{-} = \tau_R^2 \sum_{\mathbf{k}} W_{\mathbf{Kk}}^{-+} g_{\mathbf{k}}. \tag{7}$$

The current density in the active valley reads $\mathbf{j}^{+} = e\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}^{+} \delta f_{\mathbf{k}}^{+}$, whereas the current density in the passive valley is $\mathbf{j}^{\pm} = e\sum_{\mathbf{K}} \mathbf{v}_{\mathbf{K}}^{\pm} \delta f_{\mathbf{K}}^{\pm}$. Here, the electron momentum is $\mathbf{K} = \mathbf{p}_i + \mathbf{k}'$, where $\mathbf{k}'$ is counted from the center of the $\mathbf{p}_i$th valley; $\mathbf{v}_{\mathbf{k}}^{+} = \mathbf{k}/m$ and $\mathbf{v}_{\mathbf{K}}^{-} = (\mathbf{K} - \mathbf{p}_i)/m$. Thus, the total current density can be presented in the form

$$\mathbf{j} = -\frac{e\tau_R^2}{3} \sum_{\mathbf{k},\mathbf{K}} (\mathbf{v}_{\mathbf{k}}^{+} - \mathbf{v}_{\mathbf{K}}^{-}) g_{\mathbf{k}} W_{\mathbf{Kk}}^{-+}. \tag{8}$$

Here, it is assumed that the summation over $\mathbf{K}$ includes the sum over three valleys with reciprocal vectors $\mathbf{p}_{i=1,2,3}$. The integration over electron momenta $\mathbf{k}'$ inside the passive valleys must be over the valley region within the first Brillouin zone. However, it is technically simpler to extend the integration over the total values of $\mathbf{k}'$ in the valley. As a result, we acquire a factor of 3, which explains the factor $1/3$ in Eq. (8).

This simple analysis shows that in the absence of strain, Eq. (8) gives a zero current due to symmetric intervalley scattering of electrons from the active valley K (red) into the passive valleys K' (blue), see Fig. 2.

B. Coulomb impurities-induced intervalley scattering

Let us start with the case without strain. The bare two-band Hamiltonian of electrons in the MoS_2 monolayer in a given valley reads

$$H = \begin{pmatrix} \Delta/2 & vk_- \\ vk_+ & -\Delta/2 \end{pmatrix}, \tag{9}$$

where Δ is the material band gap, and $k_\pm = \eta k_x \pm i k_y$ are electron momenta counted from the valley center, $\eta = \pm 1$ is a valley index. The energy eigenvalues of the Hamiltonian Eq. (9) are $E_{c,v}(\mathbf{k}) = \pm E_{\mathbf{k}}$, $E_{\mathbf{k}} = \sqrt{\Delta^2/4 + (vk)^2}$. They correspond to the conduction and valence bands in a given valley. All energies here are counted from the center of the band gap. An electron wavefunction in the active valley K in Fig. 2 reads

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \begin{pmatrix} u_{\mathbf{k}} \\ v_k \end{pmatrix} \frac{e^{i\mathbf{kr}}}{\sqrt{S}}, \tag{10}$$

where $u_{\mathbf{k}} = \cos(\theta_{\mathbf{k}}/2)$, $v_{\mathbf{k}} = \sin(\theta_{\mathbf{k}}/2)\exp(-i\eta\varphi_{\mathbf{k}})$, $\varphi_{\mathbf{k}}$ is an angle of between vector $\mathbf{k}$ and $\mathbf{p}_1$ in Fig. 2, and $\cos\theta_{\mathbf{k}} = \Delta/2E_{\mathbf{k}}$. In the other passive valleys K' characterized by the position via $\mathbf{p}_i$, the wavefunctions have the form ($\mathbf{k}' + \mathbf{p}_i = \mathbf{K}$)

$$\Phi_{\mathbf{k}'}(\mathbf{r}) = \begin{pmatrix} u_{\mathbf{k}'} \\ v_{\mathbf{k}'} \end{pmatrix} \frac{e^{i(\mathbf{k}'+\mathbf{p}_i)\mathbf{r}}}{\sqrt{S}}. \tag{11}$$

Thus, the intervalley matrix element describing the intervalley electron scattering off the impurity potential $V(\mathbf{r})$ reads

$$M_{\mathbf{Kk}}^{-+} \equiv M_{\mathbf{k'k}}^{-+} = V(\mathbf{k}' + \mathbf{p}_i - \mathbf{k})(u_{\mathbf{k}} u_{\mathbf{k}'}^{*} + v_{\mathbf{k}} v_{\mathbf{k}'}^{*}), \tag{12}$$

where $V(\mathbf{q})$ is a Fourier transform of the impurity potential $V(\mathbf{r})$.

In the presence of strain, the TMD monolayer Hamiltonian reads

$$H = \begin{pmatrix} \Delta/2 & v(\mathbf{k} - \mathbf{a})_- \\ v(\mathbf{k} - \mathbf{a})_+ & -\Delta/2 \end{pmatrix}, \tag{13}$$

where quasivector potential $\mathbf{a}$ describes the strain field as $\mathbf{a} = \eta\Xi(u_{yy} - u_{xx}; 2u_{xy})$ and $(\mathbf{k} - \mathbf{a})_\pm = \eta(k_x - a_x) \pm i(k_y - a_y)$, with Ξ being the deformation-potential constant describing the strength of electron-strain field interaction. For definiteness, we assume that $\eta = 1$ corresponds to the active valley K, and $\eta = -1$ for passive valleys K' located at points $\mathbf{p}_i$ in Fig. 2. One can see from Eq. (13) that the strain shifts the valleys' centers on $\mathbf{a}$ vector, and this shift is proportional to the valley index η. Thus, the active valley K and passive valley K' are shifted in the opposite directions in the reciprocal space.

The intervalley matrix element describing the electron scattering by the impurity potential $V(\mathbf{r})$ in the presence of the strain changes as $V(\mathbf{K} - \mathbf{k}) \equiv V(\mathbf{k}' + \mathbf{p}_i - \mathbf{k}) \to V(\mathbf{k}' + \mathbf{p}_i - \mathbf{k} + 2\mathbf{a})$. A factor of 2 appears because the valleys K and K' being shifted on $\mathbf{a}$ in opposite directions effectively increase the value of $\mathbf{K}$: $\mathbf{K} \to \mathbf{K} + 2\mathbf{a}$. The symmetry properties of the matrix elements in the presence of strain dictate $(M_{\mathbf{Kk}}^{-+})^* = M_{\mathbf{kK}}^{+-}$.

Furthermore, we assume that the electrons are scattered by the Coulomb impurities, thus $V_q = 2\pi e^2/\varepsilon|\mathbf{q}|$. We also

assume that electrons are photoexcited across the band gap Δ to the states $\mathbf{k}$ in the vicinity of the band minimum $vk \ll \Delta$. In this case, the expression for electron energies in the bands can be simplified as $E_{\mathbf{k}} \approx \Delta/2 + \varepsilon_{\mathbf{k}}$, $\varepsilon_{\mathbf{k}} = k^2/2m$, where m is an effective mass. In the same approximation, one can also set $u_{\mathbf{k}} \approx 1$, and $v_{\mathbf{k}} \approx 0$. Usually $p_i \gg 2a + k' - k$, and the matrix element squared can be expanded as

$$|M^{-+}_{\mathbf{k}'\mathbf{k}}|^2 \approx |M(\mathbf{p}_i)|^2 + \frac{\partial |M(\mathbf{p}_i)|^2}{\partial (p_i)_\alpha}(2a_\alpha + \Delta k_\alpha) + \frac{1}{2}\frac{\partial^2 |M(\mathbf{p}_i)|^2}{\partial (p_i)_\alpha \partial (p_i)_\beta}(2a_\alpha + \Delta k_\alpha)(2a_\beta + \Delta k_\beta), \tag{14}$$

where $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$. The PGE stems from the correction determined by the cross term in Eq. (14):

$$\delta|M^{-+}_{\mathbf{k}'\mathbf{k}}|^2 = \frac{\partial^2 |M(\mathbf{p}_i)|^2}{\partial (p_i)_\alpha \partial (p_i)_\beta}(a_\alpha \Delta k_\beta + a_\beta \Delta k_\alpha). \tag{15}$$

For the Coulomb impurities $|M(\mathbf{p}_i)|^2 = n_i V_p^2$, where $p = |\mathbf{p}_i|$ and $V_p = 2\pi e^2/p$, we find

$$\delta|M^{-+}_{\mathbf{k}'\mathbf{k}}|^2 = 2n_{imp}\frac{\partial^2 V_p^2}{\partial^2 p}\frac{(\mathbf{a}\cdot\mathbf{p}_i)(\Delta\mathbf{k}\cdot\mathbf{p}_i)}{p^2} + 2\frac{n_{imp}}{p}\frac{\partial V_p^2}{\partial p}\left((\mathbf{a}\cdot\Delta\mathbf{k}) - \frac{(\mathbf{a}\cdot\mathbf{p}_i)(\Delta\mathbf{k}\cdot\mathbf{p}_i)}{p^2}\right). \tag{16}$$

The correction to the intervalley scattering probability, which contributes to the PGE current, reads

$$\delta W^{-+}_{\mathbf{K}\mathbf{k}} = 2\pi\langle\delta|M^{-+}_{\mathbf{k}'\mathbf{k}}|^2\rangle\delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}}), \tag{17}$$

where $\langle ...\rangle$ means the averaging (sum over positions $\mathbf{p}_i$) over nearest three passive valleys K', $\varepsilon_{\mathbf{k}} = \hbar^2 k^2/2m$ is an electron dispersion in active "+" valley, whereas $\varepsilon_{\mathbf{k}'} = \hbar^2 k'^2/2m$ is an electron dispersion in all $i = 1, 2, 3$ passive "−" valleys counted from their centers $\mathbf{k}' = 0$. Since $\varepsilon_{\mathbf{k}'}$ does not depend on the valley position $\mathbf{p}_i$, it is possible to take the sum over $\mathbf{p}_i$ in Eq. (16). Furthermore, the components of the PGE current Eq. (5) are determined by the single parameter λ. Therefore, it is possible to consider only j_x. Thus, keeping only a_x component in Eq. (16) and taking into account that $\mathbf{p}_1 = p(-1, 0)$ and $\mathbf{p}_{2,3} = p(1/2, \pm\sqrt{3}/2)$, we find from Eq. (16)

$$\left|M^{(1)}_{\mathbf{k}'\mathbf{k}}\right|^2 = 6n_{imp}V_p^2\frac{a_x(k'_x - k_x)}{p^2},$$

$$\left|M^{(2,3)}_{\mathbf{k}'\mathbf{k}}\right|^2 = \pm 4\sqrt{3}n_{imp}V_p^2\frac{a_x(k'_y - k_y)}{p^2},$$

and, finally,

$$\langle\delta|M^{-+}_{\mathbf{k}'\mathbf{k}}|^2\rangle = \sum_{\mathbf{p}_i}\delta|M^{-+}_{\mathbf{k}'\mathbf{k}}|^2 = 6n_{imp}V_p^2\frac{a_x(k'_x - k_x)}{p^2}. \tag{18}$$

C. Interband generation rate and PGE current in *p*-type TMD monolayer

The interband generation rate, describing the absorption of the electromagnetic field, reads

$$g_{\mathbf{k}} = 2\pi|M_{cv}|^2\delta(\omega - \Delta - 2\varepsilon_{\mathbf{k}})\theta[\Delta/2 - |\mu| + \varepsilon_{\mathbf{k}}], \tag{19}$$

where M_{cv} is the interband matrix element accounting for the valley selectivity as $M_{cv} = (\sigma + \eta)M_0$, where $\sigma = \pm 1$ is a circularity of the external EM field pumping and $\eta = \pm 1$ is a valley index; Δ is a TMD monolayer band gap, and ω is frequency of the pumping EM field. For simplicity, we assume $M_0 = M(\mathbf{k} = 0)$ to be independent of the electron momentum under interband pumping. The $\theta[x]$-function factor is the occupation factor of the initial state in the valence band, and $|\mu|$ is the absolute value of the Fermi energy level counted from the band gap center, see Fig. 1. It plays an essential role in p-doped case, when $|\mu| > \Delta/2$ and describes the Moss-Burstein effect. If the Fermi level lies within the band gap, $|\mu| < \Delta/2$. This case corresponds to the intrinsic regime at zero temperature, and $\theta[...] = 1$ in Eq. (19). (An intrinsic TMD monolayer is considered in the next section.)

Combining together Eqs. (8), (17), (18), and (19), we find the PGE current in the form (restoring $\hbar$)

$$j_x = 2e\frac{\tau_R}{\tau_i}\frac{a_x}{\hbar p^2}(\hbar\omega - \Delta)N_e. \tag{20}$$

Here, $|\mathbf{p}_i| = p \sim 2\pi/a_0$ is a reciprocal wavevector defining the passive valleys K' positions (without strain), a_0 is a lattice constant, $\tau_i^{-1} = mn_i V_p^2/\hbar^3$ is an electron-impurity scattering time, $N = \frac{1}{2}|M_0|^2 m\tau_R\theta[\omega - 2|\mu|]$ is a photoelectron density ($|\mu| > \Delta/2$), and $a_x = -\Xi(u_{yy} - u_{xx})$ is a pseudovector potential describing the strain and possessing the dimension of a wavevector. Comparing Eq. (20) with a phenomenological expression Eq. (5), we find

$$\lambda = 2e\frac{\Xi}{\hbar p^2}\frac{\tau_R}{\tau_i}(\hbar\omega - \Delta). \tag{21}$$

This is the main result for the case of a p-type semiconducting monolayer with weak intraband energy relaxation, when the energy relaxation time $\tau_\epsilon \gg \tau_R, W^{-1}_{\mathbf{k}\mathbf{K}}$.

D. Intrinsic semiconducting layer with nonlinear recombination

Contrary to the previous case, let us now assume that $\tau_\epsilon \ll \tau_R, W^{-1}_{\mathbf{k}\mathbf{K}}$. Thus, we consider an intrinsic monolayer (see Fig. 3) with fast intraband energy relaxation.

The distribution functions of photoelectrons and photoholes are set as quasiequilibrium Maxwell distribution functions of the form $\propto Ae^{-\varepsilon_{\mathbf{k}}/T}$, where A is a constant, that will be expressed via stationary nonequilibrium particle densities. Thus, the stationary electron $f^{\pm}_{\mathbf{k}}$ and hole $\phi^{\pm}_{\mathbf{k}}$ distribution functions can be written as

$$f^{\pm}_{\mathbf{k}} = \frac{2\pi\hbar}{m_c T}N^{\pm}e^{-\varepsilon^e_{\mathbf{k}}/T}, \quad \phi^{\pm}_{\mathbf{k}} = \frac{2\pi\hbar}{m_v T}P^{\pm}e^{-\varepsilon^h_{\mathbf{k}}/T}, \tag{22}$$

where $N^{\pm}$ and $P^{\pm}$ are the electron and hole densities in active/passive valleys. Their values can be found from a Boltzmann-type system of equations, describing the balance of generation/recombination processes and intervalley relax-

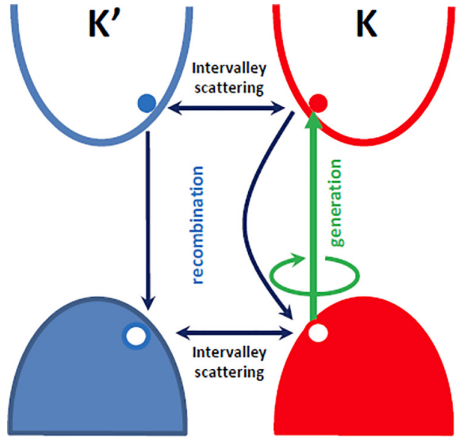

FIG. 3. The two-valley band structure of MoS2 monolayer and the draft of electron transitions describing the valleys-selective interband pumping, the interband recombination, and intervalley relaxation processes for intrinsic TMD monolayer.

ation:

$$\sum_{\mathbf{k}_1} W^R_{\mathbf{k}\mathbf{k}_1} f^+_{\mathbf{k}} \phi^+_{\mathbf{k}_1} = g_{\mathbf{k}} + \sum_{\mathbf{K}'} (W^{+-}_{\mathbf{k}\mathbf{K}'} f^-_{\mathbf{K}'} - W^{-+}_{\mathbf{K}'\mathbf{k}} f^+_{\mathbf{k}}),$$
$$\sum_{\mathbf{K}_1} W^R_{\mathbf{K}\mathbf{K}_1} f^-_{\mathbf{K}} \phi^-_{\mathbf{K}_1} = \sum_{\mathbf{k}'} (W^{-+}_{\mathbf{K}\mathbf{k}'} f^+_{\mathbf{k}'} - W^{+-}_{\mathbf{k}'\mathbf{K}} f^-_{\mathbf{K}}). \quad (23)$$

The left-hand sides describe the interband two-particle nonlinear recombination processes in a given valley, while the other terms are analogs to Eq. (6). For an arbitrary relation between the recombination lifetimes and the intervalley relaxation processes, the system of equations Eq. (23) can be solved if we consider the strain-induced part of intervalley relaxation probability, namely

$$\delta W^{+-}_{\mathbf{k}\mathbf{K}'} = W^{+-}_{\mathbf{k}\mathbf{K}'} - W^0_{\mathbf{k}\mathbf{K}'} = 2\pi\delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \times [|V(\mathbf{k}' + \mathbf{p}_i - \mathbf{k} + 2\mathbf{a})|^2 - |V(\mathbf{k}' + \mathbf{p}_i - \mathbf{k})|^2], \quad (24)$$

as a small perturbation. Excluding the strain-induced part of intervalley relaxation, and taking the recombination probability in the form $W^R_{\mathbf{k}\mathbf{k}_1} = W^R = \text{const}$, and then integrating over $\mathbf{k}$, $\mathbf{K}$ in Eq. (23), we find the balance equations

$$\alpha N^+ P^+ = G - \frac{N^+ - N^-}{\tau_v},$$
$$\alpha N^- P^- = -\frac{N^- - N^+}{\tau_v}, \quad (25)$$

where

$$\alpha = \frac{(2\pi\hbar)^2}{m_c m_v T^2} W^R \sum_{\mathbf{k}\mathbf{k}_1} e^{-\varepsilon^e_{\mathbf{k}}/T} e^{-\varepsilon^h_{\mathbf{k}_1}/T},$$
$$\frac{1}{\tau_v} = \frac{2\pi\hbar}{m_c T} \sum_{\mathbf{k}\mathbf{K}} W^0_{\mathbf{k}\mathbf{K}} e^{-\varepsilon^e_{\mathbf{k}}/T}. \quad (26)$$

Equations (25) together with the particle-density conservation under optical pumping, $N^+ + N^- = P^+ + P^-$ and $N^+ = P^+$ determine the nonequilibrium particle densities $N^\pm$ and $P^\pm$, which enter the photoinduced distribution functions [Eq. (22)].

Furthermore, the strain-induced anisotropic corrections $\delta f^\pm_{\mathbf{k}}$ and $\delta\phi^\pm_{\mathbf{k}}$ satisfy the equations

$$\delta f^+_{\mathbf{k}} W^R \sum_{\mathbf{k}_1} \phi^+_{\mathbf{k}_1} + f^+_{\mathbf{k}} W^R \sum_{\mathbf{k}_1} \delta\phi^+_{\mathbf{k}_1} = \sum_{\mathbf{K}'} (\delta W^{+-}_{\mathbf{k}\mathbf{K}'} f^-_{\mathbf{K}'} - \delta W^{-+}_{\mathbf{K}'\mathbf{k}} f^+_{\mathbf{k}}),$$
$$\delta f^-_{\mathbf{K}} W^R \sum_{\mathbf{K}_1} \phi^-_{\mathbf{K}_1} + f^-_{\mathbf{K}} W^R \sum_{\mathbf{K}_1} \delta\phi^-_{\mathbf{K}_1} = \sum_{\mathbf{k}'} (\delta W^{-+}_{\mathbf{K}\mathbf{k}'} f^+_{\mathbf{k}'} - \delta W^{+-}_{\mathbf{k}'\mathbf{K}} f^-_{\mathbf{K}}). \quad (27)$$

The second terms in the left-hand sides of these equations are zero due to the anisotropy of the corrections $\delta\phi^\pm_{\mathbf{k}_1}$. Thus, we come up with simplified equations

$$\delta f^+_{\mathbf{k}} = \tau^+_R \sum_{\mathbf{K}'} (\delta W^{+-}_{\mathbf{k}\mathbf{K}'} f^-_{\mathbf{K}'} - \delta W^{-+}_{\mathbf{K}'\mathbf{k}} f^+_{\mathbf{k}}),$$
$$\delta f^-_{\mathbf{K}} = \tau^-_R \sum_{\mathbf{k}'} (\delta W^{-+}_{\mathbf{K}\mathbf{k}'} f^+_{\mathbf{k}'} - \delta W^{+-}_{\mathbf{k}'\mathbf{K}} f^-_{\mathbf{K}}), \quad (28)$$

where $(\tau^\pm_R)^{-1} = W^R \sum_{\mathbf{k}_1} \phi^\pm_{\mathbf{k}_1}$ are the intravalley recombination times, which are determined by the light intensity via the nonequilibrium hole densities [found from Eq. (22)]. Combining together Eqs. (22), (28), and the current densities in the pumped valley $\mathbf{j}^+ = e\sum_{\mathbf{k}} \mathbf{v}^+_{\mathbf{k}} \delta f^+_{\mathbf{k}}$, and the passive valley $\mathbf{j}^- = e\sum_{\mathbf{K}} \mathbf{v}^-_{\mathbf{K}} \delta f^-_{\mathbf{K}}$, we arrive at the total current density in the form

$$\mathbf{j} = -\frac{e}{3}\frac{2\pi\hbar}{m_c T} \sum_{\mathbf{k},\mathbf{K}} (\tau^+_R \mathbf{v}^+_{\mathbf{k}} - \tau_R{}^- \mathbf{v}^-_{\mathbf{K}}) \times (N^+ \delta W^{-+}_{\mathbf{K}\mathbf{k}} - N^- \delta W^{+-}_{\mathbf{k}\mathbf{K}}) e^{-\varepsilon_{\mathbf{k}}/T}. \quad (29)$$

Furthermore, taking into account that $\delta W^{-+}_{\mathbf{K}\mathbf{k}} = \delta W^{+-}_{\mathbf{k}\mathbf{K}}$ [as it follows from Eq. (24)], yields

$$\mathbf{j} = -\frac{e}{3}\frac{2\pi\hbar\Delta N}{m_c T} \sum_{\mathbf{k},\mathbf{K}} (\tau^+_R \mathbf{v}^+_{\mathbf{k}} - \tau^-_R \mathbf{v}^-_{\mathbf{K}}) \delta W^{-+}_{\mathbf{K}\mathbf{k}} e^{-\varepsilon_{\mathbf{k}}/T}, \quad (30)$$

where $\Delta N = N^+ - N^-$. Using the linear-in-strain correction to $\delta W^{-+}_{\mathbf{K}\mathbf{k}}$, given by Eqs. (17) and (18), we find

$$\lambda = 2e\frac{\Xi}{\hbar p^2} \left(\frac{\tau^+_R + \tau^-_R}{2\tau_i}\right) (2T), \quad (31)$$

which describes the PGE effect in intrinsic TMD monolayers.

IV. DISCUSSION

Let us discuss the main results of this paper: Eqs. (21) and (31), describing p-doped and intrinsic semiconductors, respectively. In both the cases, the PGE effect is directly proportional to a large factor $\tau_R/\tau_i \gg 1$. The difference is that in the case of a p-type TMD monolayer, the recombination time is determined by the equilibrium hole density $\tau_R^{-1} \sim P^0$, and can be controlled by the gate voltage. Contrary, in the case of an intrinsic TMD monolayer, the recombination times

τ_R^+ and τ_R^- are determined by the nonequilibrium photoinduced hole densities in the valleys and directly depend on the intensity of the light-generating charge photocarriers.

The second characteristic of expressions Eqs. (21) and (31) is their dependence on the mean of electron energy. In the p-doped case, we assumed that the intravalley-intraband energy relaxation is weak, and the corresponding expression Eqs. (21) is directly proportional to the kinetic energy of photoelectrons, given by the factor $(\hbar\omega - \Delta)/2$. In the case of fast-energy relaxation, the PGE current is determined by the mean value of equilibrium electron energy, given by the temperature T.

It should be noted that the developed theory is based on the two-band model, Eq. (9). The band structure of a TMD monolayer is more complex than two bands. The hole and electron bands are strongly split by the spin-orbit coupling, they have strong warping, etc. The account of these effects in the consideration of the intervalley relaxation processes may require a more complex study (the account for the specific spin-related intervalley scattering mechanisms for the PGE effect). Then, the PGE may demonstrate more complex dependencies on the TMD monolayer parameters, however, we believe that the key behavior has been captured in this manuscript. Nevertheless, the present theory can be directly applicable when the external EM field frequency exceeds the spin-orbit splitting of the bands.

In the present consideration we also ignored the excitonic effects. If the light frequency is less than the material band gap $\omega < \Delta$, the bound excitons are formed and, being neutral particles, they do not provide the PGE current. If $\omega > \Delta$, the electron-hole pairs are excited and the Coulomb interaction between electron and hole modifies their wavefunctions. It, in turn, modifies the intervalley impurity-induced scattering matrix elements, and we believe that the only difference that appears is the Sommerfeld factor [24]. Nevertheless, we assume that this factor does not essentially affect the condition of existence or absence of the PGE effect we considered.

V. CONCLUSION

We developed the theory of the photogalvanic effect driven not by an external vector field but by the scalar generalized force determined by the valley electron population difference that may occur in TMD monolayers. We showed that the effect arises under the action of a uniform strain field applied to the monolayer. We considered two different cases: (i) a p-doped and (ii) intrinsic monolayer (n-type can be considered in full analogy with the p-type). In the (i) case, we used the linear theory of recombination processes, while for (ii) the nonlinear recombination theory was applied. Furthermore, we scrutinized the intervalley electron relaxation due to electron scattering off Coulomb impurity potential as a microscopic mechanism of the effect under study.

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