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Photocarrier-phonon relaxation in highly excited monolayer transition-metal dichalcogenides

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ABSTRACT

We formulate a microscopic model describing interaction between photoinjected carriers and optical phonons in monolayer transition-metal dichalcogenides which are an important example of 2D direct-bandgap semiconductors. The model takes account of the spin-valley structure of the conduction and valence bands. The evolution equations for the carrier and phonon quasi-temperatures are derived and the carrier-phonon relaxation time is estimated. We present the experimental pump-probe results for monolayer WSe_2 conforming the theoretical prediction.

1. Introduction

Monolayer transition-metal dichalcogenides (TMDs for short) demonstrate many remarkable properties that hold much promise for optoelectronics and photonics applications [1,2]. One of the most important *physical* problems in this field is ultrafast nonlinear dynamics of carriers in atomically thin semiconductors under high levels of optical excitation.

On the basis of general properties of ultrafast relaxation processes in semiconductors, one can assume that the transfer of the excess energy of hot photocarriers to the thermal bath follows through thermalization between the carriers and optical phonons [3]. The aim of the paper is to formulate a microscopic model describing this process in monolayer TMDs. To do it at the fundamental mechano-statistical level, we use the so-called Non-Equilibrium Statistical Operator Method (NSOM) [4,5] which allows one to calculate measurable quantities on a microscopic basis and provides an account of the specific spin-valley band structure in 2D TMDs. As an illustration of this aspect, we estimate the carrier-phonon relaxation time in TMDs and present the corresponding experimental results for monolayer WSe_2.

2. The relaxation model

Since the strong Coulomb interaction leads to fast thermalization of the hot electrons and holes, on a longer time scale the state of the carrier's subsystem can be characterized by some quasi-temperature $T_c(t)$ and quasi-chemical potentials $\mu_i(t)$, where $i = e, h$. Here we shall restrict our consideration to the assumption that the optical phonon subsystem also can be characterized by a unique quasi-temperature $T_{ph}(t)$. More general models will be briefly discussed in Section 4.

Within the above assumptions, equations of evolution for $T_c(t)$ and $T_{ph}(t)$ can be derived in a rather general form using the NSOM [4,5]. In this method the quasi-temperature $T_S(t)$ of a subsystem S is determined from the self-consistency condition $\langle H_S\rangle^t = \langle H_S\rangle^t_{\rm rel}$, where the average of the subsystem's Hamiltonian, $\langle H_S\rangle^t$, is calculated with the true nonequilibrium statistical operator $\varrho(t)$, while the average $\langle H_S\rangle^t_{\rm rel}$ is calculated with the so-called relevant statistical operator $\varrho_{\rm rel}(t)$ which is an equilibrium-like distribution at time t. In the case under consideration, we have

$$\varrho_{\rm rel}(t) = Z^{-1}(t)\exp\left\{-\beta_c(t)[H_c - \mu_e(t)N_e - \mu_h(t)N_h] - \beta_{ph}(t)H_{ph}\right\}. \quad (1)$$

Here $Z(t)$ is the normalization factor, H_c and H_{ph} are the Hamiltonians of the carriers and phonons, N_e and N_h are the number operators for electrons and holes. We also introduce the notation $\beta_c(t) = 1/k_BT_c(t)$, $\beta_{ph}(t) = 1/k_BT_{ph}(t)$. The self-consistency conditions for the quasi-chemical potentials $\mu_{e(h)}(t)$ can be written as $n = \langle N_{e(h)}\rangle^t_{\rm rel}/A$, where n is the surface density of the photogenerated electrons (holes), and A is the sample area.

Statistical distributions like (1) are frequently met in the theory of relaxation processes and usually it is assumed that the Hamiltonians of the subsystems do not include the interaction term. Unfortunately, in this case the distribution (1) has the disadvantage that it does not converge to the equilibrium Gibbs distribution when the temperatures of the subsystems become equal. As shown in Ref. [5], one way around this problem is to redefine the Hamiltonians of the subsystems. In the

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context of the carrier-phonon system, the Hamiltonians H_c and H_{ph} in Eq. (1) are to be interpreted as

$$H_c = H_c^{(0)} + \alpha H_{int}, \quad H_{ph} = H_{ph}^{(0)} + (1-\alpha)H_{int}, \tag{2}$$

where $H_c^{(0)}$ and $H_{ph}^{(0)}$ describe *free* carriers and phonons, respectively, and H_{int} is the interaction term. The parameter α satisfies $0 \le \alpha \le 1$ and determines the fractions of the interaction energy assigned to the subsystems.

According to the NSOM, the operator (1) can be used to construct the true statistical operator of the system, $\varrho(t)$, and then to derive the evolution equations for $\langle H_c\rangle^t$ and $\langle H_{ph}\rangle^t$ (see Section 7.1 in Ref. [5]):

$$\frac{d\langle H_c\rangle^t}{dt} = \mathcal{L}(t)\left[\beta_c(t) - \beta_{ph}(t)\right], \quad \frac{d\langle H_{ph}\rangle^t}{dt} = -\mathcal{L}(t)\left[\beta_c(t) - \beta_{ph}(t)\right], \tag{3}$$

where $\mathcal{L}(t)$ is the so-called *kinetic coefficient*. In the weak coupling limit, it does not depend on the value of the parameter α and can be written as [5]

$$\mathcal{L}(t) = \int_{-\infty}^{0} dt_1 e^{\eta t_1} \int_0^1 dx \mathrm{Tr}\{J[\varrho_{\mathrm{rel}}^{(0)}(t)]^x J(t_1)[\varrho_{\mathrm{rel}}^{(0)}(t)]^{(1-x)}\}, \quad \eta \to +0. \tag{4}$$

Here $\varrho_{\mathrm{rel}}^{(0)}(t)$ is the relevant distribution (1) in which the Hamiltonians H_c and H_{ph} are replaced by $H_c^{(0)}$ and $H_{ph}^{(0)}$, $J = [H_{int}, H_{ph}^{(0)}]/i\hbar$ is the energy flux operator, and $J(t_1)$ is a Heisenberg picture operator for noninteracting subsystems. To compute the kinetic coefficient explicitly, we take $H_c^{(0)}$, $H_{ph}^{(0)}$, and H_{int} in the standard form:

$$H_c^{(0)} = \sum_{\mathbf{k}i} \varepsilon_{\mathbf{k}i} c_{\mathbf{k}i}^\dagger c_{\mathbf{k}i}, \quad H_{ph}^{(0)} = \sum_{\mathbf{q}\lambda} E_{\mathbf{q}\lambda} b_{\mathbf{q}\lambda}^\dagger b_{\mathbf{q}\lambda}, \tag{5}$$

$$H_{int} = \sum_{\mathbf{k}\mathbf{q}i\lambda} W_{\mathbf{q}\lambda}^i a_{\mathbf{k}+\mathbf{q}i}^\dagger a_{\mathbf{k}i}(b_{\mathbf{q}\lambda} + b_{-\mathbf{q}\lambda}^\dagger). \tag{6}$$

In order to have a compact notation, we assume the index i to specify the type of the carries (electrons or holes) and, when necessary, the spin state. The index λ refers to the phonon branches, and $E_{\mathbf{q}\lambda} = \hbar\omega_{\mathbf{q}\lambda}$ is the phonon energy. With the above expressions for the Hamiltonians, Eq. (4) gives

$$\begin{aligned}\mathcal{L}(t) = \frac{\pi}{\hbar}\sum_{\mathbf{k}\mathbf{q}i\lambda} E_{\mathbf{q}\lambda}^2 |W_{\mathbf{q}\lambda}^i|^2 \Bigg\{ & \frac{e^{(\beta_{ph}-\beta_c)E_{\mathbf{q}\lambda}} - 1}{(\beta_{ph}-\beta_c)E_{\mathbf{q}\lambda}} \\ & \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q}i} - \varepsilon_{\mathbf{k}i} - E_{\mathbf{q}\lambda}) n_{\mathbf{k}i}(1 - n_{\mathbf{k}+\mathbf{q}i}) N_{\mathbf{q}\lambda} \\ & + \frac{e^{(\beta_c-\beta_{ph})E_{\mathbf{q}\lambda}} - 1}{(\beta_c-\beta_{ph})E_{\mathbf{q}\lambda}} \delta(\varepsilon_{\mathbf{k}-\mathbf{q}i} - \varepsilon_{\mathbf{k}i} + E_{\mathbf{q}\lambda}) n_{\mathbf{k}i}(1 - n_{\mathbf{k}-\mathbf{q}i})(1 + N_{\mathbf{q}\lambda}) \Bigg\}.\end{aligned} \tag{7}$$

For the carriers, the number occupation function $n_{\mathbf{k}i}(t) = \langle c_{\mathbf{k}i}^\dagger c_{\mathbf{k}i}\rangle^t$ resembles a time-dependent Fermi-Dirac distribution

$$f_i(\varepsilon; t) = \{\exp\{\beta_c(t)[\varepsilon - \mu_i(t)]\} + 1\}^{-1}, \tag{8}$$

where ε is the energy of the quasi-particle state. The phonon number occupation function $N_{\mathbf{q}\lambda}(t) = \langle b_{\mathbf{q}\lambda}^\dagger b_{\mathbf{q}\lambda}\rangle^t$ coincides with a time-dependent Planck distribution

$$N_{\mathbf{q}\lambda}(t) = \left\{\exp[\beta_{ph}(t)E_{\mathbf{q}\lambda}] - 1\right\}^{-1}. \tag{9}$$

Now the energy balance Eq. (3) can be transformed into relaxations equations for the quasi-temperatures $T_c(t)$ and $T_{ph}(t)$. We use for this purpose the self-consistency conditions $\langle H_c\rangle^t = \langle H_c\rangle_{\mathrm{rel}}^t$ and $\langle H_{ph}\rangle^t = \langle H_{ph}\rangle_{\mathrm{rel}}^t$, where the averages on the right-hand sides are to be calculated with the relevant statistical operator (1). In the weak coupling limit, one may replace H_c and H_{ph} with $H_c^{(0)}$ and $H_{ph}^{(0)}$, so that Eq. (3) are rewritten as

$$C_c(t)\frac{d\beta_c(t)}{dt} = \mathcal{L}(t)\left[\beta_c(t) - \beta_{ph}(t)\right], \quad C_{ph}(t)\frac{d\beta_{ph}(t)}{dt} = -C_c(t)\frac{d\beta_c(t)}{dt}, \tag{10}$$

where we have introduced the time-dependent "heat capacities"

$$C_c(t) = \partial\langle H_c^{(0)}\rangle^t/\partial\beta_c(t), \quad C_{ph}(t) = \partial\langle H_{ph}^{(0)}\rangle^t/\partial\beta_{ph}(t). \tag{11}$$

It should be remembered, however, that these capacities are negative since the energies are differentiated with respect to the inverse temperatures.

To complete the formulation of the model, we now consider the quasi-chemical potentials $\mu_e(t)$ and $\mu_h(t)$ which determine to a large degree the statistical properties of hot photocarriers. Let $n(t)$ be the surface density of electrons (holes) in a 2D semiconductor. Then the quasi-chemical potentials are determined by the relations

$$n(t) = \int \nu_i(\varepsilon) f_i(\varepsilon; t), \quad i = e, h, \tag{12}$$

where $\nu_i(\varepsilon)$ are the 2D density of states functions. Since the electron-hole recombination time is expected to be much greater than the carrier-phonon relaxation time [3], in what follows it is assumed that the carrier density n does not depend on time and is determined by the initial pump excitation.

The electronic structure of monolayer TMDs near the Fermi energy can be modelled by two degenerate parabolic conduction and valence bands (valleys) around the K and K' points in the 2D Brillouin zone (see, e.g., Ref. [2] and references therein). Taking also into account that the spin degeneracy is splitted at each valley by the spin-orbit interactions [2], Eq. (12) is rewritten as

$$n = \frac{m_i^*}{\pi\hbar^2}\left(\int_0^\infty f_i(\varepsilon)d\varepsilon + \int_{\Delta_i}^\infty f_i(\varepsilon)d\varepsilon\right), \quad i = e, h, \tag{13}$$

where Δ_e (Δ_h) stands for the conduction (valence) band spin-orbit splitting. As is customary in the electron-hole picture, the one-particle energies and the quasi-chemical potentials are measured from the edge of the bands. Now the evaluation of the right-hand side of Eq. (13) reduces to performing standard integrals. After some manipulations we obtain explicit expressions for the quasi-chemical potentials (the time argument is omitted for brevity):

$$\mu_i = \beta_c^{-1}\ln\left\{\left[\frac{1}{4}(e^{\beta_c\Delta_i} - 1)^2 + e^{\beta_c(\tilde{\varepsilon}_i + \Delta_i)}\right]^{1/2} - \frac{1}{2}(e^{\beta_c\Delta_i} + 1)\right\}, \tag{14}$$

where $\tilde{\varepsilon}_i = n\pi\hbar^2/m_i^*$. In principle, Eq. (10), together with Eqs. (7)–(9), (11), and (14), form a closed model for calculating the time evolution of the carrier and phonon quasi-temperatures with some initial conditions and a given carrier density n. Here we shall obtain a rough estimate of the carrier-phonon relaxation time using our Eq. (10). First we note that $\Delta\beta(t) = \beta_c(t) - \beta_{ph}(t)$ satisfies the equation $d\Delta\beta(t)/dt = -\Delta\beta(t)/\tau(t)$ with

$$\tau^{-1}(t) = \mathcal{L}(t)|C_c^{-1}(t) + C_{ph}^{-1}(t)|. \tag{15}$$

Obviously $\Delta\beta(t)$ decreases exponentially at $t \to \infty$ with the characteristic time $\tau_r = \tau(\infty)$. This quantity may be considered as a reasonable estimate of the carrier-phonon relaxation time. To calculate τ_r explicitly, we use typical values of relevant parameters for monolayer TMDs, which are currently available in the literature [2]: $m_e^* \approx m_h^* \approx 0.4m_0$, where m_0 is the electron mass, $\Delta_e \approx 30$ meV, $\Delta_h \approx 450$ meV. For the carrier-phonon interaction amplitude $W_{\mathbf{q}\lambda}^i$ appearing in Eq. (7), we take the functional form proposed in Refs. [6,7]. Assuming that the energy of almost dispersionless optical phonons does not vary significantly from one branch to another, we choose $E_{\mathbf{q}\lambda} \approx 50$ meV [6]. The final carrier and phonon quasi-temperatures are assumed to be close to room temperature, so that, in calculating τ_r, we take $T_c = T_{ph} = 300$ K. Finally, the carrier density is taken to be $n \approx 10^{14}$ cm^{-2}. With the above assumptions, explicit calculation of the asymptotic value of the quantity (15) gives $\tau_r \approx 1$ ps. It is of the same order of magnitude as carrier-phonon relaxation times for many other highly photoexcited polar semiconductors [3].

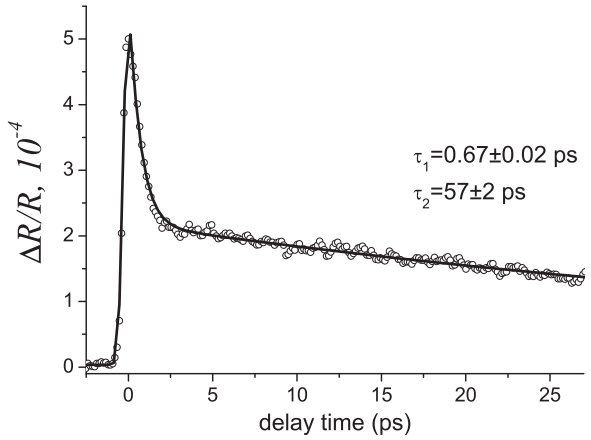

Fig. 1. The time-resolved reflectivity changes in monolayer WSe_2 (points) and data fitting within the two-time relaxation model.

3. Experimental results for monolayer WSe_2

The two-color pump-probe experiment was performed at room temperature to measure the relaxation time for hot photocarriers in monolayer WSe_2 using the amplified Ti-sapphire laser and frequency doubler (Avesta-Project) with the wavelengths of 800 and 400 nm and pulse widths of 50 and 150 fs for the probe and pump beams, respectively. Monolayer WSe_2 flakes were prepared by mechanical exfoliation on a Si/SiO_2 substrate from bulk samples fabricated by the chemical vapor transport method (analogous to the one described in Ref. [8]). The single layer thickness was confirmed by AFM and photoluminescence. The photon energy of the pump (ε_{400} = 3.1 eV) far exceeded the band gap in monolayer WSe_2, whereas the photon energy of the probe (ε_{800} = 1.5 eV) was close to the band gap. The focusing of the beams was performed in a confocal geometry with ×40 objective (NA=0.65), the laser spot diameter was about 10 μm both for the pump and the probe. This gives the fluence Φ_{400} = 2 mJ/cm^2 for the pump and Φ_{800} = 13 mJ/cm^2 for the probe. The repetition rate of the system was 3 kHz.

The differential reflectivity of a monolayer WSe_2 is presented in Fig. 1. The experimental data were fitted within the two-time relaxation model which is commonly used for direct band semiconductors [9]. The resulting values of the relaxation times are $\tau_1 = 0.67 \pm 0.02$ ps and $\tau_2 = 57 \pm 2$ ps. It is natural to identify τ_1 with the carrier-phonon relaxation time τ_r introduced in Section 2. In support of this interpretation we can give a simple estimate for the photoinjected carrier density in the experimental conditions. We shall use the so-called single-photon absorption model [10] in which nonlinear effects, such as saturation of absorption, are not taken into account. For a monolayer with the thickness d_{ML} this model gives $n = d_{ML}\alpha_{400}(1 - R_{400})\Phi_{400}/\varepsilon_{400}$, where α_{400} is the absorption coefficient, and R_{400} is the reflection coefficient determined by the refractive index at the pump frequency. In the case of WSe_2, d_{ML} = 0.85 nm, $\alpha_{400} = 5.5\cdot10^5$ cm^{-1}, R_{400} = 0.47. Then we find that $n = 1.13\cdot10^{14}$ cm^{-2}. This estimate of the carrier density is close to the value used in the previous section.

4. Concluding remarks

The carrier-phonon relaxation model proposed in this paper takes into account the spin-valley band structure which is the characteristic feature of 2D TMDs, but there are open questions still to be answered as well as some problems to be solved. For instance, the role of collective effects remains obscure. Note in this connection a giant bandgap renormalization observed in WS_2 at high electron-hole densities [11]. Another problem to be analyzed is the importance of the selective transfer of energy to the phonon modes, which can produce a slower cooling down of the carriers [3].

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