Fast relaxation of photo-excited carriers in 2D transition metal dichalcogenides
Mark Danovich, Igor L. Aleiner, Neil D. Drummond, Vladimir I. Fal’ko

Abstract—We predict a fast relaxation of photo-excited carriers in monolayer transition metal dichalcogenides (TMDCs), which is mediated by the emission of longitudinal optical (LO) and homopolar (HP) phonons. By evaluating Born effective charges for MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$, we find that, due to the polar coupling of electrons with LO phonons, and the homopolar phonons lattice deformation potential, the cooling times for hot electrons and holes from excitation energies of several hundred meV are at ps-scale.

Index Terms—TMDCs, Optoelectronics, Ultrafast relaxation

I. INTRODUCTION

MONOLAYER transition metal dichalcogenides (TMDCs) offer a unique possibility to create nm-thin optoelectronic devices [1]–[9], in particular when used in van der Waals heterostructures with other two-dimensional (2D) crystals [10]. The optoelectronic functionality of TMDCs is determined by their high-efficiency optical absorption in the visible optical range [11] as well as the fact that their monolayers are direct-band-gap 2D materials. Because of their promise for optoelectronics, it is important to understand the process of cooling (energy relaxation) of photo-excited carriers in TMDCs. In this paper we show that photo-excited carriers can emit $\Gamma$-point optical phonons at a sub-ps time scale. Such a high speed of relaxation of electrons and holes excited to energies $> 150$ meV above the band edge arises from polar coupling to the longitudinal optical (LO) phonons, and the deformation potential induced by the out of plane homopolar (HP) phonon mode. In the theory reported in this Letter, we analyze the phonon-mediated cooling of hot electrons/holes in TMDCs, taking into account two phonon modes coupled to the intra-band intra-valley relaxation processes: the in-plane LO phonon and the out of plane HP vibrational mode [12]. Density functional theory (DFT) modeling produces electron (hole) couplings to the corner of the Brillouin zone (K-point) phonons, which are weaker by at least an order of magnitude [13]–[17]. We also note that advance DFT methods have shown that the energy difference between the $Q$ and $K$ valleys in the conduction band in MoS$_2$ and MoSe$_2$ are large enough to exclude $K \rightarrow Q$ scattering from our considerations [15], [18].

II. CARRIER-PHONON INTERACTION

The carrier-phonon interaction in TMDCs is given by the Hamiltonian

$$ H_{e-ph} = \sum_{\mu = LO, HP} g_{\mu, q} c_{\mu q}^\dagger c_{\mu q} (a_{\mu, -q} + a_{\mu, q}), $$

(1)

where $c_{\mu q}^\dagger$ ($c_{\mu q}$) are the creation (annihilation) operators for a charge carrier (electron or hole) in the vicinity of one of the valleys, $(K$ or $K')$, near the corners of the hexagonal Brillouin zone of the 2D crystal [19], [20], with $\vec{k}$ measured from the valley center (see Fig. 1). The operators $a_{\mu, q}$ are the phonon creation (annihilation) operators for mode $\mu = LO$ or HP with wavevector $\vec{q}$, where $|q| \ll |K|$. The two phonon modes accounted for in the relaxation process are shown in Fig. 1.

The LO mode, which corresponds to the irreducible representation $E'$ of the symmetry group $D_{3h}$ of the crystal, couples to the charge carriers through the polarization induced by the lattice deformation, $\vec{P} = Z \vec{u}$, where $Z$ is the Born charge, $\vec{u}$

![Fig. 1. Sketch of the energy relaxation of photo-excited carriers in the valence (v) and conduction (c) bands of TMDCs through phonon emission. The use of the parabolic approximation in the description of electron and hole dispersion in each valley ($K$ or $K'$) sets a constraint, $E \leq 0.25 eV$ on the excitation energies of the charge carriers. The insets show side view of the atomic displacements in the LO and HP modes.](image)

1TMDCs have 6 optical modes denoted by the irreducible representations of the point group $D_{3h}$, $\{A_1, A_2, E, E', E''\}$, and 3 acoustical modes denoted by LA, TA, and ZA, where LA and TA are in-plane longitudinal and transverse modes, and ZA is the out-of-plane mode. We neglect the transverse optical and acoustical modes due to their weak coupling at the $\Gamma$ point, $q \rightarrow 0$.}

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is the relative displacement of the two sublattices in the LO vibration, $A$ is the unit cell area, and $e$ is the electron charge.

To estimate the Born charge we used DFT [22] to calculate the Born effective charges of the atoms in the lattice of monolayer TMDCs. The latter are defined by the response of the atomic displacements in a unit cell to a homogeneous electric field. Hence, we write

$$Z = Z_{xx} = Z_{yy}, \quad Z_{ij} = \frac{1}{e} \frac{\partial F_{ij}(s)}{\partial E_{i}}, \quad E = 0,$$ (2)

where $F(s)$ is the force acting on atom $s$ at its zero-field equilibrium position. We used the CASTEP plane-wave basis code [23], [24] to calculate the Born effective charge tensors for MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$; see Table I. We used the Perdew–Burke–Ernzerhof [27] (PBE) exchange–correlation functional, norm-conserving pseudopotentials, a plane-wave cutoff energy of $\sim 816$ eV, a $97 \times 97$ Monkhorst–Pack grid of $k$-points, and, for the in-plane components of the Born effective charge tensors) an artificial (out-of-plane) periodicity of $\sim 16$ Å. We verified that our results are converged with respect to these parameters. For the out-of-plane component we found a significant dependence on the artificial periodicity, which we removed by extrapolating to infinite layer separation.

The LO phonon coupling (the same for electrons and holes) is given by

$$g_{LO} = \frac{i}{A} \sqrt{\frac{\hbar}{2MN\hbar\omega_{LO}}} \frac{2\pi Z\epsilon^2}{1 + qr_s},$$ (3)

where $N$ is the number of unit cells, $M_r$ is the reduced mass of the two sublattices, and $\omega_{LO}$ is the LO phonon frequency.

3Note that Eq. (2) is evaluated using Eqs. (40) and (42) of Ref. [25]. To evaluate Eq. (42) of Ref. [25], derivatives of the Kohn–Sham orbitals with respect to the atomic positions and with respect to the wavevector are required. The latter are evaluated within the parallel-transport gauge by minimizing the functional in Eq. (70) of Ref. [26].

4Starting from the electrostatic interaction energy in 2D, $E = \frac{1}{2} \int d^2r\, \sigma(\mathbf{r})\sigma(\mathbf{r}) + \frac{1}{2} \int d^2\mathbf{r} P_{1p}^2 + P_{1p}$, with $\sigma(\mathbf{r}) = e\rho(\mathbf{r}) - \mathbf{V} \cdot P_{1p}(\mathbf{r})$, where $\rho(\mathbf{r})$ is the 2D carrier density, $P_{1p}$ is the optical phonon induced polarization, $P_{1p}$ is the remaining in-plane polarization, and $\mathbf{V}$ is the in-plane rigidity. Assuming the adiabatic approximation, we Fourier transform the integrand, and integrate out $P_{1p}$, we obtain the dielectric screening $1/\hbar\omega_{LO} k_r$, which is the remaining in-plane polarization, and the carrier-phonon coupling is obtained from the term containing $\rho_{\mathbf{q},\mu}^\phi P_{1p,\phi}$, which are the Fourier components of the electron density and the optical phonon induced polarization vector.

The dielectric screening of the electric field of LO mode deformations is described [3], [28] by the factor $1/(1 + qr_s)$, where $r_s$ is a length scale defined by $r_s = a_z(\epsilon_{||} - 1)/2$, where $a_z$ and $\epsilon_{||}$ are the z-axis lattice constant and in-plane dielectric constant of a bulk crystal of the corresponding TMDC [21], [28]. The values used for the screening lengths are taken from the DFT calculated 2D polarizabilities in Ref. [21].

The homopolar (HP) mode (which corresponds to the irreducible representation $A_1^3$ of the symmetry group $D_{3h}$) couples with the carriers through the lattice deformation potential

$$g_{HP}^2 = \sqrt{\frac{\hbar}{2MN\hbar\omega_{HP}}} D^\alpha, \quad \alpha = c \text{ or } v,$$ (4)

where $M$ is the total atomic mass within the unit cell, $\omega_{HP}$ is the HP phonon frequency, and we distinguish electrons in the conduction band ($c$) and holes in the valence band ($v$). Here we follow the definitions given in Refs. [13], [14], [18] for the coupling and, below, we use the deformation potentials for the HP phonon mode reported in Ref. [13].

### III. SCATTERING RATES

The emission of both LO and HP phonons by a photoexcited electron/ hole with initial momentum $k_i$ measured from the center of the corresponding $(K$ or $K')$ valley, is characterized by the rate calculated using the Fermi golden rule,

$$\tau^{-1} = \frac{2\pi}{\hbar} \sum_{\mathbf{q},\mu} |\langle f | H_{e-ph} | i \rangle|^2 \delta(E_f - E_i).$$
This yields
\[ \tau_{LO,\alpha}^{-1} = \tau_{\alpha}^{-1} f \left( \frac{E_\alpha}{\hbar\omega_{LO}}, k_\alpha r_\star \right), \quad \alpha = c \text{ or } v \]
\[ \tau_{\alpha}^{-1} = \frac{2\pi^2 Z^2 E_B m_\alpha a_B^2 E_B}{\hbar M_\alpha^2 A \hbar\omega_{LO}}, \quad f = \frac{1}{\pi} \frac{k_\alpha}{k_i} \left( \frac{u^+}{1 + u k_\alpha r_\star^2} \right)^2 \sqrt{1 - \left[ \frac{E_\alpha}{2k_\alpha} (u + \frac{1}{u}) \right]^2}; \]
\[ u_\pm = \frac{k_\alpha}{k_i} \left( 1 \pm \sqrt{1 - \frac{k_\alpha^2}{k_i^2}} \right); \quad k_\alpha = \sqrt{\frac{2m_\alpha \hbar\omega_{LO}}{\hbar}}; \]
\[ \tau_{HP,\alpha}^{-1} = \frac{m_\alpha AD_\alpha^2}{2M_\alpha^2 \hbar \omega_{HP}}. \tag{5b} \]

Note that these scattering rates are valid only for carrier energies above the corresponding optical phonon energy. Furthermore, the rate of emission of the HP phonon is independent of the carrier energy, due to the constant coupling coefficient and the constant density of states for 2D carriers with parabolic dispersion. For the LO phonon mode we express the scattering rate in terms of a dimensionless integral by performing a change of variables, defining the dimensionless variable \( u = q/k_{c(v)} \), where \( k_{c(v)} \) is the carrier wavevector corresponding to an energy of \( \hbar\omega_{LO} \), and \( a_B \) and \( E_B \) are the Bohr radius and energy. In Table II we list the values of the parameter \( \tau_{c(v)}^{-1} \) for various TMDCs, and in Fig. 2 we show the shape of the function \( f \) for different carrier energies \( E_{c(v)} \). The decrease of this scattering rate upon increasing \( r_\star \) or excitation energy can be understood from the diagram depicting the kinematic phase space for a carrier emitting an optical phonon.

Comparing the values of \( \tau_{c(v)}^{-1} \) and \( \tau_{HP,c(v)}^{-1} \) in Eqs. (5a), (5b), and Table II, we see that emission of the LO phonon mode with \( r_\star = 0 \), dominates in the relaxation over the HP phonon. The two rates become comparable for sufficiently large carrier energies or sufficiently large \( r_\star \) values. Asymptotically, we have for the LO phonon, \( \tau_{LO,\alpha}^{-1} \sim 1/(r_\star \sqrt{E}) \); therefore, the boundary between the two modes is given by
\[ \frac{r_\star \sqrt{m E}}{\hbar} \sim 4\pi Z^2 \frac{a_0^2 E_B^2}{M_\alpha^2 A \hbar\omega_{LO}} \quad \text{or} \quad E_{c(v)} \sim \frac{2m_\alpha \hbar\omega_{LO}}{\hbar}; \]
so that we can determine the relaxation time as a function of the initial carrier energy \( E \) as
\[ t(E) = \int_0^E \frac{d\epsilon}{\frac{\hbar\omega_{LO}}{\tau_{LO}(E)} + \frac{\hbar\omega_{HP}}{\tau_{HP}(E)}}. \tag{6b} \]
For hot carriers excited to the energy \( E \gg \hbar\omega_{LO/HP} \), Eqs. (5a), (5b) yield \( \tau_{LO}^{-1} \propto 1/\sqrt{E} \) (also see Fig. 2) and \( \tau_{HP}^{-1} \) is a constant, so that we find an analytical asymptotic form for the cooling time of charge carriers from the initial energy \( E \) to the bottom of the band,
\[ t(E) \approx aE - b\sqrt{E} + c. \tag{6c} \]

The fitted values of the parameters \( a, b \) and \( c \) for the conduction and valence bands relaxation times are listed in Table II and correspond to the numerically obtained [29] relaxation time curves shown in Fig. 3 for the conduction (c) and valence (v) bands.

V. CONCLUSION

We calculated the scattering rates and relaxation times of photo-excited carriers in TMDCs due to optical phonon emission. We obtained relaxation times of a few ps for all the materials studied, with MoSe\textsubscript{2} and MoS\textsubscript{2} having the shortest relaxation times.

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This parameter was derived by equating \( \tau_{LO,\alpha}^{-1} \sim \tau_{HP,\alpha}^{-1} \), and using the asymptotic form of \( \tau_{\alpha}^{-1} \) for large carrier energies. The corresponding values are, 13, 18, 15 and 57 for electrons and 20, 21, 27, and 31 for holes in MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, and WSe\textsubscript{2}, respectively.
sub-ps relaxation times for all carrier energies up to 0.25 eV, which is determined by their respective unit cell Born charges, $Z_{\text{MoSe}_2} = -1.80$ and $Z_{\text{MoS}_2} = -1.08$, and respective optical deformation potentials (Table I). For $\text{WS}_2$ and $\text{WSe}_2$, we find smaller unit cell Born charges, $Z_{\text{WS}_2} = -0.47$ and $Z_{\text{WSe}_2} = -1.08$, and smaller HP deformation potentials, resulting in longer relaxation times. However, for these two 2D materials, an additional channel of $K \rightarrow Q$ intervalley relaxation is possible, due to a smaller $E_{KQ}^c$ splitting than in Mo-based dichalcogenides, so that the rates shown in Eq. (5) give only the lower bound for the speed of relaxation in $\text{WS}_2$ and $\text{WSe}_2$. The introduction of a dielectric environment through a substrate or full encapsulation, will have two main effects on the calculated relaxation times. First, the electric potential induced by the LO phonon will be reduced in the long wavelength limit by the dielectric constant of the environment $\epsilon_{\text{env}}$, therefore reducing the LO phonon coupling by a factor of $\epsilon_{\text{env}}$. The HP phonon mode on the other hand will not be affected in such a way, as its coupling mechanism does not involve an electric field. Second, carriers in the TMDC monolayer can emit phonons in the substrate, thus increasing the total scattering rate. The obtained fast carrier cooling rates and the subsequent formation of excitons which can radiatively recombine and emit light, can lead to high quantum efficiencies, crucial for the range of optoelectronics device applications utilizing TMDCs, including light emitters, photodetectors, and novel valletronic devices.

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For example, full encapsulation by hexagonal Boron Nitride results in $\epsilon_{\text{env}} = \sqrt{\epsilon_{\text{BN}}} \approx 4.4$.


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