Enhanced electron–phonon scattering in Janus MoSSe

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Abstract
Electron–phonon (e–ph) interaction in monolayer Janus MoSSe has been investigated using ab initio approach. We find that the asymmetric structure induced net dipole moment in MoSSe introduce an enhanced e–ph interaction compared to the symmetric MoS2. Through the mode resolved scattering analysis, we demonstrate that the out-of-plane optical mode in MoSSe contributing to the total e–ph scattering rates are much more than MoS2. Around the band edges, the maximum mean free paths (MFPs) of both electrons and holes along zigzag (ZZ) direction are found to be 4 nm in MoSSe, while the MFPs along armchair directions are significantly shorter than along ZZ direction, meaning the highly anisotropic transport properties in MoSSe.

1. Introduction
Transition metal dichalcogenides (TMDs) MX2 (M = transition metal; X = chalcogen) have attracted more attention in two-dimensional (2D) families due to their unique mechanical and electronic properties [1—4]. The 2D TMDs are semiconductors with strong spin–orbit coupling (SOC), and their spin and valley are coupled, which plays an important role in valleytronic applications. More TMDs can be obtained via changing chalcogen (such as S, Se, Te) and transition metals (Mo, W, Nb, V) [5]. Besides, different MoS2 based morphologies have been successfully synthesized, such as MoS2 nanorods [6], nanopetals [7], nanopowder [8] and nanotubes [9]. Recently, a new monolayer 2D TMDs Janus MoS2, with out-of-plane asymmetry, has been successfully fabricated [10, 11]. The out-of-plane asymmetry introduce a intrinsic vertical electric field which is absent in symmetry MX2. The vertical electric filed cause a Rashba spin–orbit interaction (SOI), shedding a light on future spintronics [12, 13]. In addition, the vertical electric field also introduce piezoelectric effects, and can be tuned by strain [14]. The MoSSe based heterostructures exhibit unique electronic and optical properties and the Rashba SOI varies with the interlayer distances [15, 16]. Moreover, the large band offset reduce the valley polarization dramatically and hence increase the valley lifetime of the heterostructures.

The carrier’s lifetime and the hot carrier cooling process in materials are dependent strongly on the electron–phonon (e–ph) interaction [17—25]. The carrier relaxation dynamics of several TMDs are investigated experimentally and theoretically [26—30], which mainly focus on the spin dependent e–ph interaction. Although synthesized successfully, Janus MoS2 structures have been studied mostly on the electronic structures [15, 16]. In this paper, the e–ph interaction including scattering and lifetime of MoS2 are investigated in detail. We also discuss the Rashba spin–orbit coupling and out-of-plane electric field induced scattering characteristics and compared with MoS2. Moreover, the mean free paths (MFPs) of MoS2 are computed and mapped in the Brillouin zone.

2. Methods
The ground state calculations are performed using density-functional theory [31] with the generalized gradient approximation [32], as implemented in the Quantum ESPRESSO code [33, 34]. Norm-conserving fully
relativistic pseudopotential \[35\] and a kinetic energy cutoff 120 Ry are employed. The van der Waals corrections are included via PBE \[36\] in the calculations of relaxation. Electronic and phonon states are computed using a \(24 \times 24 \times 1\) \(k\)-point mesh and a \(8 \times 8 \times 1\) \(q\)-point mesh, and then we interpolate to a fine mesh with \(400 \times 400 \times 1\) \(k\) and \(q\) points to obtain the \(e\)-\(ph\) matrix elements based on maximally localized Wannier functions implemented in EPW code \[37\]–\[39\].

The real and imaginary parts of the electron self-energy are given by \[40\]:

\[
\Sigma^{e-ph}_{\nu\nu'} = \sum_{q,\nu,\nu'} |g^{\nu\nu'}_{n,m}(k, q)|^2 \left[ \frac{n(\varepsilon_{q,n}) + f(\varepsilon_{m,k+q})}{\varepsilon_{n,k} - \varepsilon_{m,k+q} + i\hbar \omega_{q\nu'}} - \frac{n(\varepsilon_{q,n}) + 1 - f(\varepsilon_{m,k+q})}{\varepsilon_{n,k} - \varepsilon_{m,k+q} - i\hbar \omega_{q\nu'}} \right],
\]

where \(\varepsilon_{m,k+q}\) and \(\hbar \omega_{q\nu'}\) are the electron energy in band \(\nu\) and state \(k\) and phonon energy in band \(\nu'\) and state \(q\), respectively. \(n(\varepsilon_{q,n})\) is the Bose occupation factor and \(f(\varepsilon_{m,k+q})\) is Fermi occupancy function, and we take 300 K to evaluate them. \(\eta\) is the Gaussian broadening parameter. The \(e\)-\(ph\) scattering rate \(\Gamma^{e-ph}_{n,k}\) is inverse with the relaxation time and directly connected to the imaginary part of electron self-energy as \(\Gamma^{e-ph}_{n,k} = 1/\tau^{e-ph}_{n,k} = 2/\hbar \text{Im}(\Sigma^{e-ph}_{n,k})\).

3. Results and discussion

The crystal structure and the corresponding electric dipole moments of monolayer Janus MoSSe are illustrated in figure 1. The relaxed lattice parameter is \(a = b = 3.25\) Å in conjunction with a 2.43 Å S-Mo bond length and a 2.54 Å Se-Mo bond length, which agree well with the results in \[10\]. Owing to the different electronegativity, the electrons locating around S and Se atoms are less than Mo atoms, and thus the dipole moments direction is from S and Se atoms to Mo atoms. Additionally, the mirror asymmetry of the chemical bonding in MoSSe brings about an out-of-plane net dipole moment which is absent in symmetric molybdenum disulfide structures, as shown in the lower panel of figure 1.

The out-of-plane dipole moment in Janus MoSSe cause a Rashba splitting in the valence band (VB) maxima at \(\Gamma\) point which is absent in the symmetric MoS\(_2\), as shown in figures 2(c) and (f). The Rashba splitting in MoSSe gives rise to a energy shift along the momentum vector \(k\), which would yield a additional phase space for \(e\)-\(ph\) scattering. Meanwhile, there exist SOC induced splittings at the conduction and the valence band edge in Janus MoSSe and symmetric MoS\(_2\), and the splittings \(\lambda_{\text{Kc}}\) and \(\lambda_{\text{Kv}}\) in MoSSe are larger than that in MoS\(_2\) due to the increased atomic number of Se. The \(\lambda_{\text{Kc}}\) in MoSSe is 13 meV while is only 3 meV in MoS\(_2\), and the \(\lambda_{\text{Kv}}\) is as well larger than 14\% compared to MoS\(_2\), which agrees well with previous results \[12\]. For MoSSe, the VB holds a local maximum around the \(\Gamma\) point with the energy 112 meV lower than VBM while larger than the lower VB at K point. The local maximum at \(\Gamma\) point in VB for MoS\(_2\) is just equal to the lower VB at K (both are 148 meV lower than VBM). More importantly, the conduction and the valence band edges hold opposite spin orientation as shown figure S1 is available online at stacks.iop.org/NJP/21/113040/mmmedia, which means the electrons scatter from the upper to the lower conduction band and from the lower to the upper valence band at the K point would be a intravalley spin-flip process \[29\].

![Figure 1. MoS\(_2\) monolayer and dipole moments. \(P_{\text{S-Mo}}\) (\(P_{\text{Se-Mo}}\)) represents the moments from S (Se) to Mo, and net in-plane (out-of-plane) dipole moments are denoted as \(P_{//}\) \((P_{\perp})\).](image-url)
The significant SOC-induced splittings for the conduction and the valence bands in both MoSSe and MoS\(_2\) would bring about different scattering rates for electrons and holes. Figure 3 illustrates the scattering rates of MoSSe and MoS\(_2\). For holes in the VB of MoSSe shown in figure 3(a), only intravalley scattering is possible within the energy range from \(E_\Gamma\) to the VBM, which dominated by the longitudinal optical (LO) phonon mode 1 and 2 (figure S2). Below the energy of 112 meV (\(E_\Gamma\)) and 169 meV (\(E_{Kv2}\)), \(\Gamma\) valley and \(Kv2\) valley participate in the scattering, and the scattering rate mainly originates from the longitudinal acoustic (LA) and the highest out-of-plane optical (ZO) phonon modes. For MoS\(_2\), due to the nearly identical energy of \(E_\Gamma\) and \(E_{Kv2}\), \(\Gamma\) valley and \(Kv2\) valley contribute to the scattering simultaneously when the energy is lower than 14.8 meV (e.g. \(E_\Gamma\) and \(E_{Kv2}\)), and LA and ZO\(_2\) phonon modes start to contribute to the scattering, while above \(E_\Gamma\) and \(E_{Kv2}\), LO\(_2\) mode dominates the scattering. Intervalley scattering occurs for holes and electrons through spin-flip [41] or overcoming the SOC splitting. The band edges at state \(K\) and state \(K'\) have the same energy but with opposite spins (figure S1), and thus the intervalley scattering between these states must undergo spin-flip process which highly unlikely to happen [42]. The SOC splitting in MoSSe is 169 meV and the energy difference between the VBM and maximum at \(\Gamma\) is 112 meV, both dramatically greater than the maximum phonon energy of 55 meV (figure S3), meaning that the scattering processes in VB between \(\Gamma\) state and VBM or between \(Kv2\) state and VBM are not possible. MoS\(_2\) holds the same situation as MoSSe for VB except that the intervalley scattering could occur since the energies \(E_\Gamma\) and \(E_{Kv2}\) are almost degenerated. Consequently, the upper state \(Kv1\) in VB (e.g. VBM) gives rise to a locked spin-valley state with low scattering rate as shown in figures 3(a) and (c), and the corresponding relaxation time at VBM for MoSSe and MoS\(_2\) is about 48 fs and 273 fs, respectively. Overall, scattering rate of MoSSe for VB larger than that in MoS\(_2\), which is determined by the e–ph coupling strength and energy differences between the involved edge states. The largest scattering rate in figure 3(a) actually is composed of two branches due to the Rashba splitting while it is degenerated in MoS\(_2\) (figure 3(c)). Contrary to the holes, the electrons in CB exhibit strong e–ph scattering, as shown in figures 3(b) and (d), which brings about slower dynamics for electrons at the edge of the CB compared with holes. There is a valley at Q point with the energy of 132 meV higher than CBM in MoSSe and 114 meV in MoS\(_2\), as shown in figures 3(b) and (d) with \(E_{Qc1}\) where the intervalley scattering play a role. Around the CB edge at K point, the SOC splitting for MoSSe and MoS\(_2\) are 13

![Figure 2. Electronic band structures of MoSSe (a) and MoS\(_2\) (d). (b), (c) and (e), (f) are magnified views of the CBM and the maxima of the valence band at \(\Gamma\) point, respectively.](image-url)
and 3 meV, respectively, both are substantially smaller than the maximum phonon energy mentioned above. Thus, the electrons can easily decay from the upper energy level \( E_{Kc2} \) at \( K \) point to \( E_{Kc1} \) at \( K' \) point through intervalley scattering. The predicted lifetime of MoSSe at CBM is 43 fs while it is 128 fs in MoS2, because of a smaller SOC splitting in MoS2 at CB edge. From the mode-resolved scattering rate (figure S2), we expect that below the energy \( E_{Qc1} \), LO1 phonon mode dominates the scattering in MoSSe while LA and LO2 modes are the main source of the scattering. Here we focus only on the e–ph scattering while the electron–electron scattering is not included, since it is dominant in the total scattering with the energy range far away from the band edges [28].

The e–ph scattering rates can be mapped in the Brillouin zone (BZ) to analyse the transport properties along the crystallographic directions. The mean free paths (MFPs) \( L_{n,k} \) characterize the carriers moving along the direction \( k \) in band \( n \), and can be obtained as \( L_{n,k} = \frac{1}{v_{n,k} \cdot \tau_{n,k}} \) where \( v_{n,k} \) and \( \tau_{n,k} \) is the carrier velocities and e–ph relaxation times. Figure 4 shows the MFPs of MoSSe and MoS2 for holes and electrons moving along zigzag (ZZ) and armchair (AM) directions within 0.5 eV of the band edges. Around the band edges, both holes and electrons move along only AM directions. For MoSSe, the MFPs for both hot holes and hot electron along ZZ direction are between 4 and 5 nm around the band edges. While in MoS2, the MFPs of hot holes as long as 20 nm, even for the hot electrons they are two times larger than in MoSSe. As mentioned above, the out-of-plane electric dipole moments in MoSSe introduce an extra force for carriers compared to the asymmetric MoS2, and thus the out-of-plane vibration of the ZO1 mode in MoSSe couples strongly with the carriers. The strong e–ph coupling results in the scattering rate originating from the ZO1 mode in MoSSe significantly larger than that in MoS2 as observed in figure S2. Consequently, the short MFPs of MoSSe here are attributed to the out-of-plane dipole moments. Our results also indicate that the MFPs of hot holes in MoSSe and MoS2 are larger that hot electrons, which means hot holes transport more easily than hot electrons, agrees well with the results of the mobility analysis in [28, 43–46]. Furthermore, the MFPs along AM direction are much shorter than along ZZ direction, meaning the highly anisotropic propagation of hot carriers in MoSSe and MoS2. For both hot electrons and hot holes, we predict that the ZZ direction would be the best choice to extract hot carriers due to the longer MFPs within the energy range of 0.5 eV around the band edge. Our results further suggest that hot carriers hold significant difference in transport distance along ZZ and AM direction within an energy range \( \sim 0.2 \) for holes and \( \sim 0.35 \) for electrons, which gives a guide to design the one dimensional MoSSe based devices.

Figure 3. The scattering rate of MoSSe and MoS2. (a)/(c) and (b)/(d) are holes and electrons for MoSSe and MoS2, respectively. The VBM and CBM are set to 0 in (a)/(c) and (b)/(d). Note that the different scales of scattering rate in (a)/(c) and (b)/(d).
4. Conclusions

In summary, we demonstrate the crucial role of out-of-plane dipole moment in e–ph interaction and transport properties in Janus MoSSe induced by mirror asymmetry, and compared the results to MoS2. Our results show that the increased atomic number of Se in MoSSe induce a stronger spin–orbit splittings than MoS2, making the scattering rates different in the two structures. The scattering rates in MoSSe are much larger than in MoS2 for both conduction and valence band. Through the vibration mode resolved analysis, we find the out-of-plane mode ZO1 contributes more scattering rate in MoSSe than in MoS2 with the energy of 0.5 eV around the band edge. We predict the MFPs in MoSSe are much shorter than MoS2 due to the strong ZO1 scattering, and around the band edge, both hot holes and hot electrons hold much longer MFPs along ZZ direction than along AM direction. The findings here are of interest in designing MoSSe based nanodevices.

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