Photoluminescence Studies of Excitonic Complexes in Atomically Thin Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} Alloys

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Transition metal dichalcogenides show new emergent properties at monolayer thickness, notably strong Coulomb and electron-phonon interactions enabling new insight into physics of many body effects. Here, we report photoluminescence and reflectivity contrast measurements of excitons (X) and trions (T) and the Raman spectra of phonons in monolayers of Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} alloys with sulfur mole content from y = 0 up to y = 1. Binary MoSe\textsubscript{2} and ternary Mo(S\textsubscript{y}Se\textsubscript{2−y})\textsubscript{2} alloys exhibit contrasting behavior in the temperature evolution of excitons and trions photoluminescence intensity from T = 7 − 295 K. In MoSe\textsubscript{2} a trion dominates photoluminescence spectra at low temperatures but exciton dominates photoluminescence at higher temperature. In contrast, in ternary Mo(S\textsubscript{y}Se\textsubscript{2−y})\textsubscript{2} alloys and MoS\textsubscript{2} trions dominate photoluminescence spectra at all measured temperatures, with the trion to exciton photoluminescence intensity ratio increasing with sulfur content. We attribute the strong increase of the trion photoluminescence intensity in Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} monolayers with increase of sulfur mole content to the significant increase of the two-dimensional electron gas concentration and also to the strong exciton-trion coupling mediated by an optical phonon. We also demonstrate that increasing sulfur content in Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} alloys stabilizes total photoluminescence intensity at high temperature.

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1. Introduction

There is currently significant interest in two-dimensional semiconductors based on transition metal dichalcogenides (TMDCs), such as WSe\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, MoS\textsubscript{2}, following the demonstration of the indirect-to-direct bandgap transition and strong spin and valley coupling in a single monolayer (ML) [1–10]. In MLs of TMDCs the bottom of the conduction band and the top of the valence band are located at the K points of two-dimensional (2D) hexagonal Brillouin zone. The strong spin–orbit coupling and lack of inversion symmetry lead to valley-contrasting strong spin splitting of valence and conduction bands [4–12]. The direct energy gap in the visible spectral range and the coupling of the spin and valley degree of freedom make TMDCs very promising for photonics and spintronic applications [3–21]. The confinement to a single layer and reduced dielectric screening lead to strong many body effects mediated by Coulomb interactions. In monolayers of TMDCs excitons, bound electron–hole pairs (X), exhibit very high binding energies of a few hundreds of meV [22–28]. In the presence of access carriers charged excitons, trions (T), consisting of two electrons and one hole, or two holes and one electron are reported [29–32] in optical spectra of TMDCs MLs. In selenides, MoSe\textsubscript{2} and WS\textsubscript{2} the photoluminescence intensity of a trion is high at low temperatures but rapidly disappear from the PL spectra with the increase of temperature [32].

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We present detailed temperature dependent (T = 7 − 295 K) photoluminescence (PL) studies of excitons and trions in binary, MoSe\textsubscript{2} and MoS\textsubscript{2} ternary Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} MLs with compositions y = 0.1, 0.2, 0.3, and 0.5. Additionally, we performed complementary measurements of reflectivity contrast (RC) and the Raman scattering spectra of all MLs. Binary MoSe\textsubscript{2} and ternary Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} alloys exhibit very different temperature evolution of the exciton and trion PL intensity. In MoSe\textsubscript{2} trion dominates in PL spectra at low temperatures but strongly decreases in intensity with the increase of temperature range. In contrast, in PL spectra of ternary Mo(S\textsubscript{y}Se\textsubscript{1−y})\textsubscript{2} and binary MoS\textsubscript{2} MLs trions dominate in PL spectra at all measured temperatures (T = 7 − 295 K). Confinement to a single layer Coulomb and reduced dielectric screening yields also to strong binding energy of charged excitons in TMDCs [30–33]. In selenides MoSe\textsubscript{2} and WS\textsubscript{2} binding energy of an additional electron or hole to a neutral exciton is equal to 30 meV and is comparable with energies of optical phonons [33–36] which leads to strong coupling of the exciton and trion by exchange of an optical phonon [37]. In MoSe\textsubscript{2} the A\textsubscript{1′} optical phonon energy, 29.8 meV [33], resonances with the trion binding energy equal 30 meV [33]. In MoS\textsubscript{2} the A\textsubscript{1′} phonon energy of 51 meV [33] strongly exceeds those in MoSe\textsubscript{2}. For that reason incorporation of sulfur atoms into MoSe\textsubscript{2} host lattice results in significant increase of the A\textsubscript{1′} phonon energy [36]. We found that the high temperature trion to exciton PL intensity ratio (I\textsubscript{T}/I\textsubscript{X}) increase with sulfur mole content. We relate this effect to the substantial increase of two-dimensional electron gas (2DEG) concentration and also to the increase of the exciton-trion coupling mediated by the A\textsubscript{1′} optical phonon. We also demonstrate that increasing sulfur con-
tent in \( \text{Mo(S}_y\text{Se}_{1-y})_2 \) alloys stabilizes high temperature total PL. With the temperature growth from 6 K to 295 K the total PL in MoSe\(_2\) decreases about four orders of magnitude whereas in MoS\(_{1.0}\text{Se}_{1.0}\) only about 5 times.

2. Samples and experiment

We studied MLs of binary MoSe\(_2\) and MoS\(_2\), and ternary Mo(S\(_y\)Se\(_{1-y}\))\(_2\) alloys elaborated by mechanical exfoliation from single crystals on SiO\(_2\) (300 nm)/Si substrate. The thicknesses of the mono- to few-layer flakes were established using optical contrast, the Raman spectroscopy and subsequently by observation of efficient photoluminescence. Bulk mixed crystals were grown by chemical vapor transport technique (CVT). Prior to the crystal growth the powdered compounds of the series were prepared from the elements (Mo: 99.99%, S: 99.999%, Se: 99.995%) by reaction at 1000°C for 10 days in evacuated quartz ampoules. The S and Se materials were added in such manner that the S content \( y \) changing relatively to the Se content increases from 0 to 0.5 with a content step size \( \Delta y = 0.1 \). The chemical transport was achieved with \( I_2 \) as a transport agent in the amount of about 5 mg/cm\(^2\).

The samples were mounted on the cold-finger of a non-vibrating closed cycle cryostat, where temperature can be varied from 7 to 300 K. For temperature-dependent PL experiments a 532 nm line of a diode-pumped solid state laser was used for excitation. The laser beam was focused on the sample under normal incidence using a high resolution, long distance microscope objective (NA = 0.65). The diameter of excitation spot was equal to \( \approx 1.5 \) \( \mu \)m. The spectra were analyzed with a 0.5 m focal length spectrometer and a 600 lines/mm grating. A Peltier-cooled Si charge coupled device was used as a detector. The RC and Raman spectra were measured in the same setup. In RC experiments a filament lamp was used as a light source. The polarization-resolved Raman scattering measurements were performed at room temperature in backscattering geometry with a 2400 groves/mm grating. The Raman signal was excited with \( \sigma^+ \) circularly polarized light and detected separately in \( \sigma^+ \) and \( \sigma^- \) polarizations.

3. Results and discussion

Figure 1 shows the evolution of the unpolarized Raman spectra of the Mo(S\(_y\)Se\(_{1-y}\))\(_2\) monolayers measured at \( T = 295 \) K with concentration of sulfur allowing for the determination of phonon frequencies. For the binary MoSe\(_2\), the frequencies of the first order Raman lines are equal to 240.6 cm\(^{-1}\) and 286 cm\(^{-1}\). They are assigned to the out-of-plane \( A'_1 \) and in-plane \( E'_2 \) modes, respectively. As the composition \( y \) slightly increases, we can identify in the Raman spectra additional features in the range 200–280 cm\(^{-1}\). The presence of a sulfur atom in the host lattice of MoSe\(_2\) induces vibrations with out of plane weight in the vicinity of \( A'_1 \) mode, resulting in characteristic splitting into two branches denoted as \( A'_1^* \) and \( A'^* \).

The splitting is directly related to the different distribution of the chalcogenide atoms within the Mo(S\(_y\)Se\(_{1-y}\))\(_2\) layers. As it is seen in Fig. 1, the \( A'_1^* \) (Se–Se) and \( A'^* \) (Se–S) phonons evolve in a different manner as a function increasing S content \( y \). Based on their intensities, we have divided them into two groups [33–36]. The first group, at lower frequencies, corresponds to the Se–Se configuration, whereas the second group at higher frequencies is likely related to the Se–S vibration [33–36]. Among mixed Se–S branch, we can identify at least three components, shifting to higher frequency upon increasing \( y \). They are well resolved for 0.1 < \( y < 0.2 \), when the 2Se\(_2\) + 1SeS, 2Se\(_2\) + 1S\(_2\) or 1Se\(_2\) + 2SeS arrangements are the most probable [33–36]. By contrast, Se–Se branch shifts to lower frequency. In bulk alloys, studied in our recent papers, this branch disappears from the Raman spectra when the sulfur content exceeds \( y = 0.5 \) [36].

![Figure 1](image-url) The Raman spectra of all studied MLs recorded at \( T = 300 \) K.

Figure 2 presents examples of comparative RC and PL spectra of the studied MLs for MoSe\(_2\), Mo(S\(_0.3\)Se\(_{0.7}\))\(_2\), Mo(S\(_0.5\)Se\(_{0.5}\))\(_2\) and MoS\(_2\) at two temperatures \( T = 10 \) K and \( T = 120 \) K. In PL experiments the laser excitation power is relatively low (\( P = 100 \) \( \mu \)W) to avoid heating of the ML. At low temperature (\( T = 10 \) K) PL and RC spectra two distinct transitions, corresponding to the exciton and trion are recorded. Their energy positions are in a good agreement with the previous reports [29–32]. In PL spectra of MoS\(_2\) an additional line (denoted as \( L \), see also Fig. 3) is detected in the lower energy sector. The nature of this line is still under debate [1, 3] and is beyond the scope of this work. In PL spectra of all studied MLs at \( T = 10 \) K the PL intensity of the trion exceeds this of the exciton. Contrary to the PL spectrum, in the RC spectrum of MoSe\(_2\) and Mo(S\(_0.3\)Se\(_{0.7}\))\(_2\) the exciton resonance is stronger than this of the trion. In RC spectra
of Mo(S$_{0.5}$Se$_{0.5}$)$_2$, the trion and exciton resonances are comparable and only in binary MoS$_2$ the trion resonance is stronger than that of exciton. The reason is that the strength of optical amplitude of the exciton and trion resonances in reflectivity are determined by respective density of states, whereas the PL intensity is contributed additionally by a state occupation factor. At low temperatures the excess carriers and photocreated electron–hole pairs thermalize into the same locations corresponding to minima of the potential fluctuations in the monolayer, leading to the increase of the probability of trion formation, which is observed as an increase of the trion emission relative to the exciton emission.

Fig. 2. Examples of comparative PL and RC spectra recorded at $T = 10$ K and $T = 120$ K for MLs of: (a) and (b) — MoSe$_2$, (c) and (d) — Mo(S$_{0.5}$Se$_{0.5}$)$_2$, (e) and (f) — MoS$_2$.

The comparison of RC and PL spectra of Mo(S$_{0.1}$Se$_{0.9}$)$_2$ and Mo(S$_{0.2}$Se$_{0.8}$)$_2$ MLs are not presented as they exhibit the same relation as those of monolayers with low sulfur concentrations, MoSe$_2$ and Mo(S$_{0.3}$Se$_{0.7}$)$_2$. The energy positions of the exciton and trion in monolayers of Mo(S$_y$Se$_{1-y}$)$_2$ alloys shift to higher energies with the increase of the sulfur mole content with characteristic band gap bowing deviating from a strictly linear extrapolation between the binary bandgaps (not presented).

Figure 3 presents evolution of PL spectra as a function of temperature for all studied MLs. The corresponding spectrum for each temperature is normalized to one. The complementary Fig. 4 presents temperature dependence of the integrated PL intensity of excitons and trions, and the total integrated PL intensity for all monolayers, except binary MoS$_2$, as in this sample only the trion line is well resolved in the PL spectra at all measured temperatures. The common feature observed in PL spectra of all studied MLs is that at low temperatures the PL intensity of the trion exceeds that of the exciton, and that PL intensities of both lines decrease with increasing temperature but with substantially different rates for different MLs.

In binary MoSe$_2$ at $T = 7$ K the PL intensity of the trion is about 50 times stronger than that of the exciton. With temperature growth the exciton PL increases relatively to the trion PL, with the latter showing a dramatic reduction by about four orders of magnitude in the range from 7 K to 295 K. The PL intensity of X exceeds that of T at temperature above 140 K. The temperature evolution of PL spectra of ternary Mo(S$_y$Se$_{1-y}$)$_2$ alloys exhibit gradual change from MoSe$_2$ with increase of the sulfur mole content. The most intriguing change is observed in temperature evolution of the trion to exciton PL intensities ratio ($I_T/I_X$) presented in Fig. 5. Two regimes of high and low temperature are distinguished. At low temperatures, below $T < 100$ K, the PL intensity of T is much higher than of X for all ternary samples but no evident correlation between $I_T/I_X$ ratio and increase
of sulfur content is observed. At higher temperatures $T > 100$ K the $I_T/I_X$ ratio in ternary Mo(S$_y$S$_{1−y}$)$_2$ MLs exceeds this of MoSe$_2$ and increases with the increase of the sulfur mole content. In all Mo(S$_y$S$_{1−y}$)$_2$ MLs we observe that the trion dominates emission at all measured temperatures. In binary MoS$_2$ the intensity only the trion line is distinguished in PL spectra at all measured temperatures. The exciton line is only hardly distinguished in PL spectra at all measured temperatures. The line $L$ observed at low temperatures of PL spectra of MoS$_2$ is beyond the scope of this paper.

Fig. 5. The temperature dependence of the trion to exciton PL intensity ratio $I_T/I_X$ in monolayers of Mo(S$_y$S$_{1−y}$)$_2$ alloys. In the inset the PL spectra of all studied samples recorded at $T = 20$ K are compared: (1) MoSe$_2$, (2) Mo(S$_{0.4}$Se$_{0.6}$)$_2$, (3) Mo(S$_{0.2}$Se$_{0.8}$)$_2$, (4) Mo(S$_{0.3}$Se$_{0.7}$)$_2$, (5) Mo(S$_{0.5}$Se$_{0.5}$)$_2$.

We attribute the observed increase in the trion emission in Mo(S$_y$S$_{1−y}$)$_2$ monolayers with the growth of the sulfur mole content to two effects: (1) the increase of the exciton–trion coupling mediated by optical phonon, (2) the growth of the 2D electron concentration. With the growth of the sulfur content the energy of the out of plane optical phonon $A'_1$ increases (Fig. 1), which results in the increase of the exciton–trion coupling mediated by this phonon. Our interpretation is based on the recent work of Jones et al. [37], in which they demonstrated an efficient luminescence upconversion process from a trion to an exciton resonance in monolayer WSe$_2$, producing spontaneous anti-Stokes emission with an energy gain of 30 meV. They attributed this effect to a double resonant Raman scattering, where the incident and scattered photons are in resonance with the trion and the neutral exciton, respectively. Coupling between the trion and the exciton is realized by exchange of the out of plane optical phonon $A'_1$. In WSe$_2$ the optical phonon $A'_1$ energy of 31 meV exceeds the trion binding energy equal to 30 meV. In contrast, in MoSe$_2$ MLs, studied in this paper, the energy of $A'_1$ optical phonon, equal to 29.8 meV, is slightly lower than the trion binding energy, equal to 30 meV, which results in weaker exciton–trion coupling, especially at higher temperatures, when excitons have additional kinetic energy proportional to $kT$. The increase of the $A'_1$ optical phonon energy in Mo(S$_y$S$_{1−y}$)$_2$ alloys, for small sulfur content $y < 0.3$, results in almost linear increase of high temperature $I_T/I_X$ ratio as a function of phonon energy $E_{ph}$, measured from the trion binding energy $E_T$ (not shown). For the higher sulfur content $y \geq 0.3$ we observed abrupt increase of $I_T/I_X$ ratio. We suggest that this abrupt increase is related to significant increase of 2DEG concentration in Mo(S$_y$S$_{1−y}$)$_2$ monolayers with increase of sulfur content. As reported in Refs. [3, 29] there is a substantial difference in the intrinsic two-dimensional electron gas concentration in MoSe$_2$ and MoS$_2$ monolayers in vacuum. In MoSe$_2$ MLs the background 2DEG concentration is of order $10^{10}$ cm$^{-2}$ [29], whereas in MoS$_2$ MLs it is of order of $10^{12}$ cm$^{-2}$ [3]. Hence one should expect the strong increase of the 2DEG concentration in Mo(S$_y$S$_{1−y}$)$_2$ MLs with the increase of the sulfur mole content.

![Fig. 6](image-url) Fig. 6. The photoluminescence spectra recorded at $T = 295$ K in ambient and vacuum for (a) MoSe$_2$, (b) Mo(S$_{0.2}$Se$_{0.8}$)$_2$, (c) Mo(S$_{0.5}$Se$_{0.7}$)$_2$ and (d) Mo(S$_{0.5}$Se$_{0.5}$)$_2$.
sulfur mole content. It is well established that under ambient conditions physiosorbed $O_2$ and $H_2O$ molecules deplete $n$-type materials such as MoS$_2$ and MoSe$_2$, much more than conventional electric field gating [38, 39]. In Fig. 6 we compare the PL spectra recorded at $T = 295 \, K$ in ambient and vacuum conditions for different monolayers: (a) MoSe$_2$, (b) Mo(S$_{0.2}$Se$_{0.8}$)$_2$, (c) Mo(S$_{0.3}$Se$_{0.7}$)$_2$ and (d) Mo(S$_{0.5}$Se$_{0.5}$)$_2$. The experiments are performed under the same conditions for all samples. As is clearly seen, under ambient condition for all monolayers the maximum of PL intensity is detected at the exciton, whereas in vacuum the maximum PL intensity shifts gradually from the exciton to trion in MoSe$_2$ and ternary Mo(S$_{0.5}$Se$_{0.5}$)$_2$. This observation confirms qualitatively the increase of 2DEG concentration with the increase of sulfur mole content up to $y = 1$. We found significant difference in temperature evolution of the exciton and trion PL intensity of binary MoSe$_2$ and ternary Mo(S$_y$Se$_{1-y}$)$_2$ monolayers. In MoSe$_2$ trion dominates in PL spectra at low temperatures but significantly decreases in intensity with increase of temperature. In contrast, in ternary Mo(S$_y$Se$_{1-y}$)$_2$ alloys we observe robust trion emission, dominating PL spectra at all measured temperatures. Moreover, the high temperature trion to exciton PL intensity ratio increases with sulfur content. We attribute these observation to strong increase of the exciton–trion coupling and to the increase of two-dimensional electron gas concentration with increase of sulfur content.

4. Conclusion

In summary we report observation of robust triions in temperature dependent photoluminescence and reflectivity contrast studies of Mo(S$_y$Se$_{1-y}$)$_2$ monolayers with sulfur mole content up to $y = 1$. We found significant difference in temperature evolution of the exciton and trion PL intensity of binary MoSe$_2$ and ternary Mo(S$_y$Se$_{1-y}$)$_2$ monolayers. In MoSe$_2$ trion dominates in PL spectra at low temperatures but significantly decreases in intensity with increase of temperature. In contrast, in ternary Mo(S$_y$Se$_{1-y}$)$_2$ alloys we observe robust trion emission, dominating PL spectra at all measured temperatures. Moreover, the high temperature trion to exciton PL intensity ratio increases with sulfur content. We attribute these observation to strong increase of the exciton–trion coupling and to the increase of two-dimensional electron gas concentration with increase of sulfur content.

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