

Phonon softening and direct to indirect band gap crossover in strained single-layer MoSe₂S. Horzum,^{1,2,*} H. Sahin,^{1,†} S. Cahangirov,^{3,‡} P. Cudazzo,^{3,§} A. Rubio,^{3,||} T. Serin,^{2,¶} and F. M. Peeters^{1,**}¹*Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium*²*Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Ankara, Turkey*³*Nano-Bio Spectroscopy group, Departamento Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPIC, Av. Tolosa 72, E-20018 San Sebastián, Spain*

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Motivated by recent experimental observations of Tongay *et al.* [*Nano Lett.* **12**, 5576 (2012)] we show how the electronic properties and Raman characteristics of single layer MoSe₂ are affected by elastic biaxial strain. We found that with increasing strain: (1) the E' and E'' Raman peaks (E_{2g} and E_{1g} in bulk) exhibit significant redshifts (up to ~ 30 cm⁻¹), (2) the position of the A'_1 peak remains at ~ 180 cm⁻¹ (A_{1g} in bulk) and does not change considerably with further strain, (3) the dispersion of low energy flexural phonons crosses over from quadratic to linear, and (4) the electronic band structure undergoes a direct to indirect band gap crossover under $\sim 3\%$ biaxial tensile strain. Thus the application of strain appears to be a promising approach for a rapid and reversible tuning of the electronic, vibrational, and optical properties of single layer MoSe₂ and similar MX₂ dichalcogenides.

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I. INTRODUCTION

The discovery of graphene^{1,2} is expected to play an important role in future nanoscience and nanotechnology applications. Recent advances in nanoscale growth and mechanical exfoliation techniques have led not only to the fabrication of high-quality graphenes but also the emergence of several new classes of two-dimensional (2D) structures such as ultrathin transition metal dichalcogenides (TMDs). Just like graphene TMDs have hexagonal crystal structure composed of layers of metal atoms (M) sandwiched between layers of chalcogen atoms (X) with stoichiometry MX₂. TMDs have electronic semiconducting or metallic properties and most of bulk TMDs possess indirect band gaps of the order 1–2 eV.³ The synthesis of several TMDs has been realized experimentally^{4–7} and the stability and electronic properties of various single layer dichalcogenides was recently reported.⁸ Recent studies of several semiconducting TMDs such as MoS₂, WS₂, MoTe₂, and MoSe₂ have shown that the band gap increases and transforms to a direct band gap with decreasing number of layers.^{7,9–11} These sizable band gaps make them well suited for electronic applications such as transistors, photodetectors, and electroluminescent devices. Another unique feature of two-dimensional ultrathin materials is the possibility to apply large reversible elastic strain. It has been shown that graphene can be strained up to 20% of its ideal structure with only small changes in its electronic band structure, which is in contrast to TMDs.^{12–15}

The most recent efforts have been directed towards the synthesis and manipulation of molybdenum diselenide (MoSe₂) single layers. In addition to preliminary reports on synthesis of few-layer MX₂ structures,^{16,17} Tongay *et al.* demonstrated that a single layer of MoSe₂ possesses a direct optical gap of 1.55 eV and exhibits good thermal stability.¹⁸ However, to our knowledge, no research exists addressing the question of how electronic properties and lattice dynamics of single layer MoSe₂ are affected by strain. In the present work we investigate the effect of biaxial strain on the electronic and vibrational properties of single layer MoSe₂ structures. Our

calculations revealed that applying biaxial strain is able to tune the Raman characteristics and electronic band structure of single layer MoSe₂. We expect that this study will offer new opportunities for strain-engineered nanoscale optoelectronic device applications.

II. COMPUTATIONAL METHODOLOGY

Calculations of physical properties of equilibrium and strained structures were carried out in the framework of density functional theory (DFT), using the plane-wave self-consistent field (PWSCF) code as implemented in the QUANTUM-ESPRESSO package.¹⁹ The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation potential.²⁰ A plane-wave kinetic energy cutoff of 40 Ry and density cutoff of 400 Ry were used. Brillouin zone integration was performed using a shifted $27 \times 27 \times 1$ Monkhorst-Pack mesh.²¹ To eliminate the interaction emerging from periodic boundary conditions calculations are performed with a large unit cell including 12 Å vacuum space between adjacent MoSe₂ single layers. Ground states and total energies of all systems were obtained after full geometry relaxation with forces on the atoms smaller than 0.02 eV/Å. Phonon frequencies and phonon eigenvectors were calculated in a $4 \times 4 \times 1$ \mathbf{q} grid using the density functional perturbation theory (DFPT).²²

III. RESULTS AND DISCUSSION**A. Single layer MoSe₂**

Atomically thin MoSe₂ is the most recently synthesized member of the ultrathin transition metal dichalcogenides. A single layer structure of MoSe₂ can be viewed as a three-layer stacking of Mo and Se atoms, wherein molybdenum atoms are sandwiched between layers of trigonally arranged selenium atoms. In this configuration, known as 1H structure, each Mo atom is coordinated to six Se atoms. In the equilibrium geometry of the single layer MoSe₂, the Mo-Se distance, the

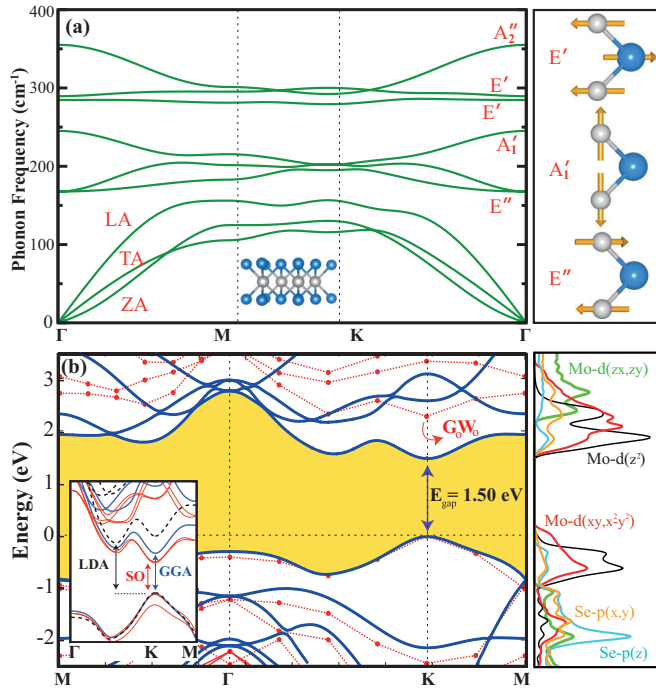


FIG. 1. (Color online) (a) Phonon dispersion for single layer MoSe₂ and displacement directions of Raman-active modes. Inset: Side view of atomic structure of MoSe₂. (b) Electronic band structure and partial density of states calculated within GGA and G_0W_0 . The energies are relative to the Fermi level (i.e. $E_F = 0$). Inset: Comparison of the band edges calculated by GGA, GGA + SO, and LDA.

Se-Se distance, and the lattice constant of the hexagonal unit cell are calculated to be 2.528, 3.293, and $|a| = 3.321$ Å, respectively. Thus, in comparison with single layer MoS₂ having lattice constant 3.12 Å, MoSe₂ has a larger atomic structure due to the larger atomic radius of the Se atoms. In Fig. 1(a) we present the calculated phonon dispersion and vibrational characteristics of Raman-active modes of single layer MoSe₂. It is seen that the frequencies of all phonon branches in the whole Brillouin zone have positive values, i.e., MoSe₂ crystal can remain stable by generating the required restoring force against atomic distortions. Although the synthesis of single layers of MoSe₂ have been achieved only on various substrates so far, energy optimization and phonon dispersion calculations show that freestanding MoSe₂ monolayers are quite stable.

The calculated band structure shown in Fig. 1(b) shows that the single layer MoSe₂ is a semiconductor with a direct band gap at the K high symmetry point. The top of the valence band is mainly composed of Mo- $d_{(x^2-y^2)}$ orbitals and, albeit small, also by Mo- $d_{(xy,yz,zx)}$ and Se- $p_{(x,y)}$ orbitals. Though the electrons occupying 4d and 5s shells of a neutral Mo atom are treated as valence electrons, 5s states have a negligible contribution even away from the Fermi level. However, it is seen that all Mo- d , Se- $p_{(x,y)}$, and Se- $p_{(z)}$ orbitals are hybridized to form the conduction band edge. Note that the x and y component of the orbitals have the same energy due to the two-dimensional lattice symmetry. Due to the presence of another minimum in the conduction band edge between the Γ and K points

we also used local density approximation (LDA) for the exchange correlation functional. Tongay *et al.*¹⁸ demonstrated that such a neighboring conduction band dip is quite sensitive to temperature-induced strain and layer-layer interaction. The lattice constant of a single-layer MoSe₂ is found to be smaller (3.22 Å) in LDA because of the overestimation of the strength of the covalent bonds. The inset of Fig. 1(b) shows a zoom of both LDA, GGA, and GGA + SO band structures along the Γ - K - M path in the Brillouin zone. We see a splitting of the band edges at the vicinity of K point when including spin-orbit (SO) interactions. Interestingly, LDA predicts that single layer MoSe₂ is an indirect semiconductor where the top of the valence band is at the K point, and the bottom of the conduction band is found to be between the Γ and K points. It appears that the physically correct description of single layer MoSe₂ structure that was reported experimentally as a semiconductor¹⁸ with a direct band gap is achieved by using the GGA functionals. Therefore, in the rest of our study PBE calculations will be employed.

Although our PBE calculation captures the qualitative nature of the band edge states it underestimates the band gap. To correct the band gap we use the G_0W_0 approximation^{23–25} as implemented in the VASP package.^{26,27} It was shown before that this kind of calculation has to be converged with respect to the vacuum spacing.^{28,29} We calculate the quasiparticle shifts using $(12 \times 12 \times 1)$ k -point grid with vacuum spacings of 15, 20, 25, and 30 Å and then extrapolate them to infinity in a similar fashion as done in Ref. 28. Our G_0W_0 calculation results in a band gap value of 2.33 eV. Note that excitonic effects are pronounced in 2D materials as MoSe₂ and we need to calculate the binding energy of the exciton in order to estimate the optical gap.^{29–34} Due to the parabolic shape of the conduction and valence bands, we assume that the exciton has the Mott-Wannier character and the effective mass approximation can be used. Hole and electron effective masses calculated from the band structure are $m_h^* = 0.65$ and $m_e^* = 0.53$ (in units of electron mass). Moreover, we account for the effective electron-hole interaction of the system using the model introduced by Cudazzo *et al.*³⁴ Using parameters reported by Ref. 30 we find the binding energy of the exciton 0.7 eV, which is in agreement with the value obtained by solving the Bethe-Salpeter equation.^{30,32} Combining this with our result from G_0W_0 calculation we estimate the optical gap to be 1.63 eV, which is close to the reported experimental value of 1.56 eV.

B. Lattice dynamics and phonon softening

While bulk MoSe₂ crystal has the D_{6h} point group symmetry, it turns into D_{3h} for a single layer structure. Just like in MoS₂,³⁵ lattice vibrations of single layer MoSe₂ is characterized by nine phonon branches including three acoustic and six optical branches. Analysis of lattice dynamics shows that the decomposition of the vibration representation of optical modes at the Γ point is $\Gamma = 2E'' + A_1' + 2E' + A_2'$. While LA and TA acoustic branches have linear dispersion, the frequency of the out of plane flexural (ZA) mode has a quadratic dispersion in the vicinity of $q = 0$. Near to the Γ point the in-plane sound velocity of the LA and TA modes are found to be 1.5×10^3 and 0.9×10^3 m/s, respectively. It

is also seen that differing from graphene’s phonon dispersion the acoustic and optical modes are well separated from each other. Differing from MoS₂ and WS₂ structures in which the A₁’ mode is the highest Raman-active mode, in MoSe₂ the A₁’ mode is located in between the E’ and E’’ modes. In Fig. 1(a) the atomic displacements of the Raman-active modes are presented. Interestingly, although recent Raman spectroscopy measurements of Tongay *et al.*¹⁸ revealed that only one characteristic Raman peak of single-layer MoSe₂ E_{2g} is observable at 240 cm⁻¹, our symmetry analysis predicts the existence of two more Raman-active modes. Significantly decreased intensity of Raman peak around 290 cm⁻¹ can be explained by considering the coupling of in-plane counterphase vibration of MoSe₂ with the SiO₂/Si substrate. Moreover, in experiment the disappearance of E’’ (E_{1g} in bulk) Raman shift around 170 cm⁻¹ is due to the inactivity of this vibrational mode to normally incident light.

Recent experiments on graphene and other few-layer materials have revealed that the application of biaxial and uniaxial tensile stress is possible by using flexible substrates. We will investigate now how the lattice dynamics of single layer MoSe₂ is affected by biaxial strain.

Figure 2 shows phonon dispersion curves and the evolution of Raman peaks as a function of applied strain. Below 1% strain, the E’ branch of single layer MoSe₂ experiences ~10 cm⁻¹ softening which is larger than that of the E_g mode (diatomic corresponding to E’) of graphene.^{36–38} It is seen that the low-energy flexural phonons (ZA) of unstrained single layer MoSe₂ turns almost in a linear dependence under 7%

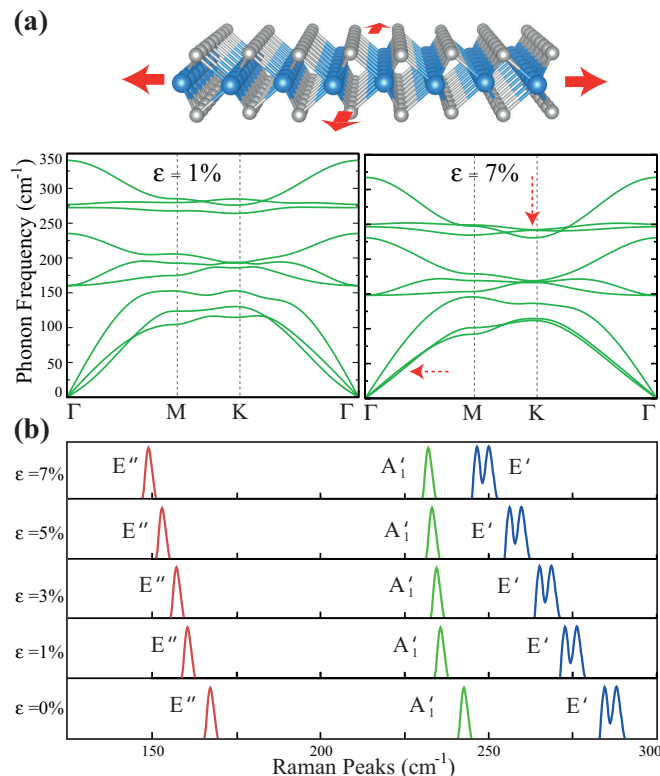


FIG. 2. (Color online) (a) Phonon dispersions for 1% and 7% strained single layer MoSe₂. (b) Evolution of the Raman-active modes as a function of applied strain.

strain. Such a change in phonon dispersion implies a significant decrease in scattering of electrons by the flexural phonons and an increase in electron mobility for strained MoSe₂. For the E’ mode there is a small splitting at the Γ point, as in slightly polar materials such as MoS₂ and WS₂.³⁵ It is also seen that due to the weakening of the covalent bonds under strain the E’ and E’’ modes (that correspond to the E_{1g} and E_{2g} in bulk MoSe₂, respectively) exhibit significant redshifts of about ~30 cm⁻¹. Especially, at the K point, the highest optical mode dips even below the band corresponding to the E’ mode. Another remarkable point is the A₁’ mode (corresponding to the A_{1g} in bulk) that vibrates perpendicular to the applied strain which experiences a smaller softening and is almost pinned to ~231 cm⁻¹ for strain values higher than 1%. Similar direction-dependent softening behavior was observed for various types of materials.^{39,40}

C. Strain-induced direct-to-indirect band gap crossover

In addition to strain-induced changes in the lattice dynamics, the electronic properties of single layer MoSe₂ may exhibit surprising deviations. Existence of a band gap even in the monolayer structure shows strong bonding nature and the covalent character of MoSe₂ layers. Though the covalent bonds formed from valance electrons of Mo and Se atoms are not broken by elastic strain, the strength of the bond is weakened with the increasing distance. Therefore band energies and dispersion can be expected to be strongly dependent on tensile strain. Evolution of the electronic band dispersion under finite biaxial strain ($\epsilon = 1\text{--}7\%$) is shown in Fig. 3. It is clearly seen that the band edges at the Γ and K symmetry points are influenced significantly by biaxial tensile strain. Up to 3% strain, single layer MoSe₂ remains a direct band gap semiconductor with both the top of the valence band and the bottom of the conduction band located at the K point. However, when ~3% strain is applied, as a result of the band shifting at the K point, two valence band edges with the same energy appear in the

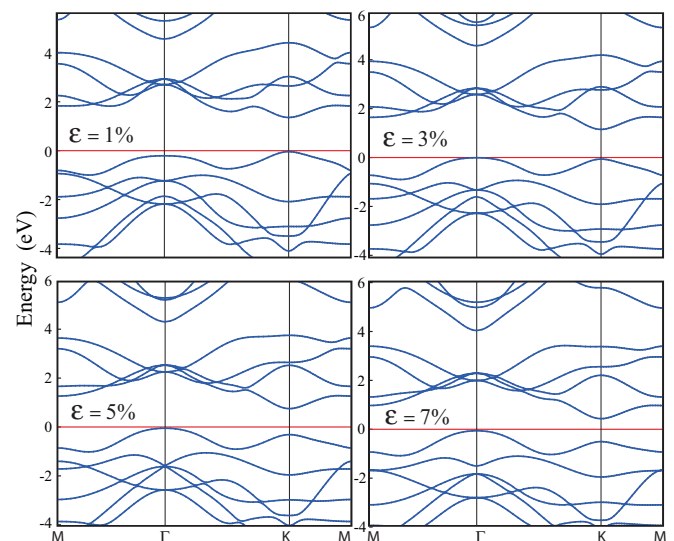


FIG. 3. (Color online) Evolution of the electronic band dispersion of single layer MoSe₂ as a function of strain. Fermi level shown by red line is set to zero in the energy spectrum.

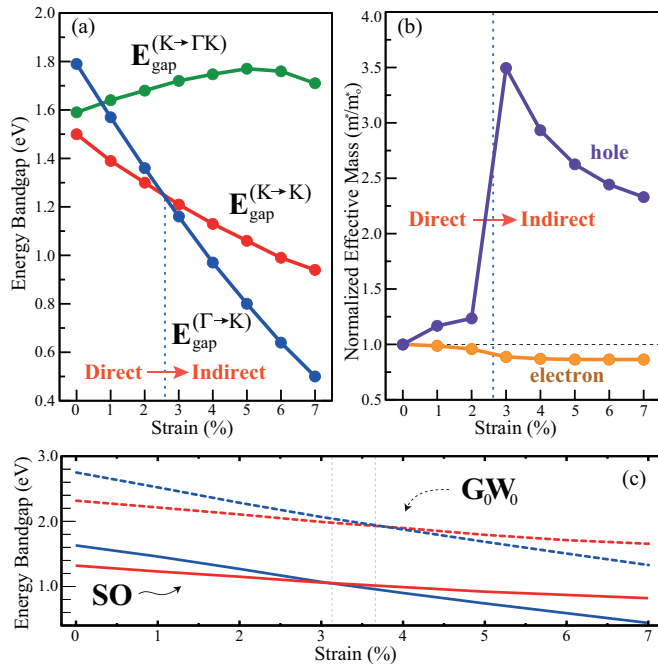


FIG. 4. (Color online) Evolution of (a) direct and indirect energy band gaps, (b) electron and hole effective mass, normalized to unstrained value (m_e^*/m_{e0}^* and m_h^*/m_{h0}^*), under biaxial tensile strain. (c) Energy band gaps calculated by using PBE + SO and PBE + G_0W_0 are shown by solid and dashed lines, respectively. Red, green, and blue colors are used for transitions $K \rightarrow K$, $K \rightarrow \Gamma K$, and $\Gamma \rightarrow K$, respectively.

Brillouin zone while the conduction band edge remains fixed in its original position. Here, with $\sim 3\%$ strain one has both a direct ($K \rightarrow K$) and an indirect ($\Gamma \rightarrow K$) band gap.

Such an interesting electronic structure may result in the presence of two types of holes having different effective masses and the coexistence of direct and indirect band transitions in the optical spectra. We also found that increasing further the strain results in the separation (and shifting) of the uppermost valence band towards the conduction band accompanied by the lowering of the conduction band dip at the K point. Moreover, the second conduction band edge located (between Γ and K) very close to the dip of the conduction band at the K point moves upwards in energy. In addition, band edges of MoS_2 also experiences similar effects with increasing tensile strain.^{12,13} The evolution of direct ($K \rightarrow K$) and indirect ($K \rightarrow \Gamma K$ and $\Gamma \rightarrow K$) energy band gaps under tensile stress are presented in Fig. 4(a-b). Both direct and indirect band gaps decrease monotonically with increasing strain, however the rate of decrease is faster for the indirect band gap. Note that the variation of band gaps with increasing strain has the same qualitative behavior for PBE,

PBE + SO, and PBE + G_0W_0 calculations (see Fig. 4(c)). Although, the effect of spin-orbit coupling is significant, the evolution of the gap with applied strain and other properties are clearly captured by PBE calculation. We predict that the direct-to-indirect crossover takes place at 3–4% strain.

As a consequence of the strain-dependent transition of the valence band edge from the K to Γ point the effective mass of the holes (and electrons) propagating through the single layer MoSe_2 lattice changes dramatically. From Fig. 4(b) it is seen that while the mass of the electrons at the band edge does not change notably, the hole mass shows significant deviations under strain. Since the valence band edge is sharpened by biaxial strain, the effective mass of the holes is decreased and after the band gap crossover holes belong to the uppermost valence band at the Γ point inversely affected by increasing strain. Note that the holes under 7% strain are ~ 2 times heavier than that for unstrained single layer MoSe_2 .

In summary, motivated by the recent experimental study of Tongay *et al.*¹⁸ on single layer MoSe_2 we investigated the electronic properties and lattice dynamics of single layer MoSe_2 as a function of biaxial strain. We showed that GGA describes more accurately the electronic structure of single layer MoSe_2 and that LDA predicts the wrong nature of the band gap. We found that monolayer MoSe_2 has four Raman-active characteristic modes: Among these, the modes having counterphase in-plane motion are significantly modified by strain and they soften by increasing strain. Redshift in the position of these resonant Raman peaks are predicted to be $\sim 30 \text{ cm}^{-1}$. However the A'_1 branch (corresponds to the A_{1g} in bulk) is negligibly influenced by strain. Moreover, the linear dispersion of flexural mode in strained MoSe_2 implies a reduced scattering of electrons from these ZA phonons. Our findings also revealed that the electronic band structure of single layer MoSe_2 also undergoes substantial changes under biaxial tensile strain. While the direct band gap linearly decreases up to $\sim 3\%$ tensile strain, a direct to indirect band gap crossover occurs when strain is further increased. Moreover the appearance of a positive curvature at the K point in the phonon spectra and possible metallicity for higher strain values suggests superconductivity in highly strained single layer MoSe_2 . Our findings indicate that the band gap of single layer MoSe_2 can be tuned reversibly by biaxial strain and is able to capture a broad range of the solar spectrum.

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*seyda.horzumsahin@ua.ac.be

†hasan.sahin@ua.ac.be

‡seycan@gmail.com

§pierluigi.cudazzo@ehu.es

¶angel.rubio@ehu.es

¶tulay.serin@eng.ankara.edu.tr

*francois.peeters@ua.ac.be

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