Giant valley drifts in uniaxially strained monolayer MoS₂

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Using first-principles calculations, we study the electronic structure of monolayer MoS₂ under uniaxial strain. We show that the energy valleys drift far off the corners of the Brillouin zone (K points), about 12 times the amount observed in graphene. Therefore, it is essential to take this effect into consideration for a correct identification of the band gap. The system remains a direct band gap semiconductor up to 4% uniaxial strain, while the size of the band gap decreases from 1.73 to 1.54 eV. We also demonstrate that the splitting of the valence bands due to inversion symmetry breaking and spin-orbit coupling is not sensitive to strain.

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I. INTRODUCTION

MoS₂ has a layered hexagonal structure with space group P6₃/mmc, where each layer possesses a sandwich structure with the Mo atoms located between two layers of S atoms. The atoms are bonded covalently within a layer, while the layers interact via weak van der Waals forces, which renders the material properties extremely anisotropic. As the number of layers is reduced, MoS₂ undergoes a transition from an indirect into a direct band gap semiconductor, which leads to a large increase of the luminescence quantum efficiency. Monolayer MoS₂ is a semiconductor with a direct band gap of 1.8 eV and thus a promising candidate for electronic, optoelectronic, and photovoltaic applications.^{1–4} The formation of suspended monolayer MoS₂ has been demonstrated recently and its properties have been investigated both experimentally and theoretically.^{5–8} The material shows a room-temperature mobility of up to 200 cm² V⁻¹ s⁻¹, which is comparable to that of graphene nanoribbons.⁵ Work on suspended few-layer MoS₂ has demonstrated a surprisingly high Young's modulus of 0.33 TPa, which is lower than that of graphene (0.8–1.0 TPa) but higher than that of graphene oxide (0.2 TPa) and hexagonal boron nitride (0.25 TPa).⁹

Strain engineering for a long time is used successfully to improve the performance of conventional metal-oxide-semiconductor field-effect transistors. In graphene-based systems strain has revealed interesting effects on the electronic properties^{10–17} and also in monolayer MoS₂ it is attracting great attention in recent years.^{18–32} One of the most remarkable observations is the fact that strain can be used to transform monolayer MoS₂ from a semiconductor into a metal. In order to obtain further insight into the evolution of the electronic properties under uniaxial strain, we employ in the present work first-principles calculations. We will show that the conduction band minima and valence band maxima drift strongly off the corners of the Brillouin zone. The system remains a direct band gap semiconductor up to 4% strain, while the band gap decreases from 1.73 to 1.54 eV.

II. COMPUTATIONAL DETAILS

Our density functional theory calculations are carried out using the QUANTUM-ESPRESSO code.³³ The local density approximation for the exchange-correlation functional and norm-conserving pseudopotentials are used. Moreover, we

employ a kinetic energy cutoff of 952 eV for the wave functions and a 16 × 16 × 1 k-mesh.

Uniaxial strain along the x axis (i.e., the zigzag direction) is expressed via the two dimensional strain tensor $\hat{\epsilon} = [\epsilon, 0; 0, -\nu\epsilon]$, where ν is Poisson's ratio. For strain along an arbitrary direction the strain tensor has to be rotated as $\hat{\epsilon}' = R^{-1}\hat{\epsilon}R$, where R is the rotation matrix. Similar to graphene, uniaxial strain breaks the hexagonal symmetry, so that for an arbitrary strain direction the point group is reduced from D_{3h} to C_{2h} . Only the C_2 rotation and the in-plane mirror symmetry are retained. For strain along the $\theta = 0^\circ$ and 30° directions additional mirror planes emerge, resulting in a D_{2d} symmetry. The lattice and the direction of the applied strain are illustrated in Fig. 1(a). By the hexagonal symmetry, only strain directions between $\theta = 0^\circ$ and 30° are of interest, where we focus on $\theta = 0^\circ, 15^\circ$, and 30° . In Figs. 1(b)–1(d) the Brillouin zone is shown for these cases, where for clarity an exaggerated strain of $\epsilon = 20\%$ is used. The six corners of the Brillouin zone still correspond to the K points, but their relative locations in the reciprocal lattice are changed.

III. RESULTS AND DISCUSSION

As a starting point, we relax monolayer MoS₂, including the spin-orbit coupling and adopting a vacuum layer of 16 Å thickness, to obtain the structure without strain (3.171 Å in-plane lattice constant and 3.168 Å distance between the S layers). Without spin-orbit coupling the lattice constant converges to 3.166 Å, i.e., there is only a small effect on the structure. Under strain we relax the atomic coordinates until the forces have declined below 0.003 eV/Å and minimize the stress vertical to the strain direction with respect to Poisson's ratio. For small strain we obtain $\nu = 0.31$, which agrees with previous calculations.^{21,27,34,35}

For the relaxed systems, we calculate the band structures along high symmetry directions that correspond to the Γ -K-M- Γ path for unstrained monolayer MoS₂. We note that there are more high symmetry paths though. Ignoring the spin degree of freedom, for $\theta = 0^\circ$ there are two groups of K points, $\bar{K}_1 = \{K_1, K_4\}$ and $\bar{K}_2 = \{K_2, K_3, K_5, K_6\}$, and two groups of M points, $\bar{M}_1 = \{M_1, M_3, M_4, M_6\}$ and $\bar{M}_2 = \{M_2, M_5\}$. As a result, there are three inequivalent paths: Γ - $\bar{K}_1$ - $\bar{M}_1$ - Γ , Γ - $\bar{K}_2$ - $\bar{M}_2$ - Γ , and Γ - $\bar{K}_2$ - $\bar{M}_1$ - Γ . A similar situation appears for $\theta = 30^\circ$, whereas for an arbitrary angle between $\theta = 0^\circ$ and 30° , due to the C_2 rotation symmetry, both the K and M points can

FIG. 1. (Color online) (a) Unit cell of MoS₂ without strain. Brillouin zone under uniaxial strain along the (b) $\theta = 0^\circ$, (c) $\theta = 15^\circ$, and (d) $\theta = 30^\circ$ directions. The red arrow in (a) defines the direction of the applied strain.

be divided into three groups, which leads to six inequivalent paths. For strain along the $\theta = 0^\circ$ direction we choose the Γ - K_1 - M_1 - Γ and Γ - K_2 - M_2 - Γ paths as examples, see Fig. 2(c).

The band structure is addressed in Fig. 2(a), where solid lines represent the system without strain and dashed lines

FIG. 2. (Color online) (a) Band structures of monolayer MoS₂ without strain and under uniaxial strain ($\theta = 0^\circ$). (b) Zoom of the valence bands near the K point. (c) Brillouin zone.

FIG. 3. (Color online) Color map of the band structure (a) without strain as well as under uniaxial strain along the (b) $\theta = 0^\circ$, (c) $\theta = 15^\circ$, and (d) $\theta = 30^\circ$ directions. Zero energy (dark red) corresponds to the valence band maximum. The lower left and upper right corners of the color maps are the points $(-1, -1) \times 2\pi/a_0$ and $(1, 1) \times 2\pi/a_0$ of the reciprocal space, where a_0 is the lattice constant of the unstrained system.

represent the Γ - K_1 - M_1 - Γ (red) and Γ - K_2 - M_2 - Γ (green) paths for $\theta = 0^\circ$. According to Ref. 21, the critical strain along the zigzag and armchair direction beyond which monolayer MoS₂ becomes elastically unstable amounts to 36% and 28%, respectively. In the following the strain is set to 4% unless stated otherwise. It is found that the energy of the valence bands is enhanced almost in the entire Brillouin zone, while the conduction band minimum near the K point shifts slightly to lower energy, i.e., the energy gap decreases under strain. By closely checking the bands near the K point, see the zoomed panel in Fig. 2(b), we find that the valence band maximum along the Γ - K_1 - M_1 - Γ path drifts off the K point, whereas along the Γ - K_2 - M_2 - Γ path it is still located exactly at K. The same effect appears for the conduction band minimum. It is also found that the shift of the highest occupied band at the Γ point is larger than at the K point, which implies that stronger strain will transform the direct into an indirect band gap.

To further investigate the drifts of the band maxima and minima, we show color maps of the band structure in Fig. 3 for the highest occupied bands. The solid lines represent the Brillouin zone boundaries. Without strain [Fig. 3(a)] we observe a six-fold rotation symmetry. The valence band maxima are located exactly at the K points. On the other hand, when strain is applied [Figs. 3(b)–3(d)] it is obvious that the valence band maxima are displaced from the corners of the Brillouin zone, due to the distortion of the latter. For strain along an arbitrary angle it therefore is not possible to find

FIG. 4. (Color online) Color map of the band structure near the K_2 point (a) without strain as well as under uniaxial strain along the (b) $\theta = 0^\circ$, (c) $\theta = 15^\circ$, and (d) $\theta = 30^\circ$ directions. Zero energy (dark red) corresponds to the valence band maximum. The lower left and upper right corners of the color maps are the points $(-0.06, -0.06) \times 2\pi/a_0 + K_2$ and $(0.06, 0.06) \times 2\pi/a_0 + K_2$ of the reciprocal space.

the true band gap along the standard high symmetry paths. The additional mirror symmetry for strain along the zigzag [Fig. 3(b)] and armchair [Fig. 3(d)] directions is reflected by the energy maps, whereas for $\theta = 15^\circ$ [Fig. 3(c)] this symmetry is absent. As compared to the value of -0.204 eV in Fig. 3(a), Figs. 3(b)–3(d) show clearly enhanced energies of -0.015 , -0.009 , and -0.006 eV, respectively, in the center of the Brillouin zone. The enhancement is stronger when θ approaches 30° . Since the conduction band minima are located near the K points, the systems remain direct band gap semiconductors up to 4% uniaxial strain, where a transition to an indirect band gap is easiest achieved for uniaxial strain along the armchair direction. We notice that the critical strain for such a transition is larger than found previously,^{19,21} as we take into account the spin-orbit coupling.

Due to the broken inversion symmetry, the two highest occupied bands show a significant splitting, except for the high symmetry points of the Brillouin zone. Without strain the maximum is located at the K point (0.151 eV), whereas under strain it is displaced, similar to the valence band maximum. It is found that the amount of splitting is insensitive to the strain, as it originates from the spin-orbit coupling, changing only slightly to 0.154 eV.

A zoomed view of the vicinity of the K_2 point is shown in Fig. 4. We clearly see a strong trigonal distortion around the valence band maximum. This feature is different from graphene, in which case the low-energy dispersion is isotropic up to

FIG. 5. (Color online) Energy difference between the highest valence and lowest conduction bands near the K_2 point (a) without strain as well as under uniaxial strain along the (b) $\theta = 0^\circ$, (c) $\theta = 15^\circ$, and (d) $\theta = 30^\circ$ directions. The maps cover the same area as in Fig. 4.

1 eV.³⁶ Without strain the valence band maximum coincides with the K_2 point, whereas for strain along the $\theta = 0^\circ$ direction it moves out of the Brillouin zone along the x axis. For $\theta = 15^\circ$ and $\theta = 30^\circ$ the dashed lines enclose an angle of 2θ with the x axis. A similar effect has been observed in graphene,¹¹ as it shares the two dimensional hexagonal structure, but the displacement is much enhanced in monolayer MoS₂. Per percent of strain it amounts to nearly $7.5 \times 10^{-3} (2\pi/a_0)/\%$, in contrast to $0.6 \times 10^{-3} (2\pi/a'_0)/\%$ in graphene (where a'_0 is the graphene lattice constant). This much more pronounced effect can be attributed to the larger Poisson's ratio of MoS₂ (0.31) as compared to that of graphene (0.16), which results in larger distortions of the Brillouin zone. The valley drifts have direct effects on valleytronics applications, which also applies to the strong coupling between the spin and valley degrees of freedom.⁷ As the valley degree of freedom is used to characterize the charge carriers,³⁷ large valley shifts will induce decoherence and thus limit the performance of devices. In addition, the intervalley scattering and thus the transport properties, for example weak localization effects, are modified. An analysis of graphene by the tight-binding method^{12,17} has attributed the drift to changes in the hopping amplitudes and to the lattice deformation. A similar model could also describe the valley drifts in MoS₂, if an accurate parametrization was obtained for the variation of the hopping amplitudes under strain.

According to Fig. 5, the band gap changes from 1.734 eV in the case without strain to 1.546, 1.543, and 1.540 eV for uniaxial strain along the $\theta = 0^\circ$, 15° , and 30° directions,

respectively, which demonstrates that there is only a weak dependence on the strain angle. The magnitude of the band gap reduction, 50 meV/%, is in good agreement with the experimental values of 45³⁰ and 48 meV/%.³¹ In previous calculations a much larger value of 100 meV/% was found,^{19–21} which is explained by the fact that our band gap remains direct up to 4% uniaxial strain and demonstrates the importance of including the spin-orbit coupling in the calculations. It has been reported that the band gap reduces faster (200 meV/%) under biaxial strain.^{19–21,24,25} Uniaxial tensile strain increases the Mo-Mo and Mo-S bond lengths and decreases the distance between the S layers due to Poisson contraction. Therefore, the orbital hybridizations and widths of the d bands are reduced. Because the bands near the Fermi energy are composed mainly of Mo 4d and S 3p atomic orbitals, this results in a smaller band gap.²⁹ As compared to graphene,³⁸ the effect of strain on the electronic properties of monolayer MoS₂ is more complex, as the band structure in the vicinity of the Fermi energy is richer due to the sandwich structure and stronger spin-orbit coupling. By examining the lowest conduction and highest valence bands, we find three separatrix lines (boundaries of Fermi lines with different topologies).

IV. CONCLUSION

In conclusion, we have studied the electronic band structure of monolayer MoS₂ under uniaxial strain. It is found that the valence band maxima and conduction band minima are displaced significantly in the reciprocal space, much more than in related compounds, particularly in graphene. Therefore, care must be taken to extract correct band gaps. Our results show that the size of the band gap decreases from 1.73 eV without strain to 1.54 eV in the case of 4% uniaxial strain, where the splitting of the valence bands is not sensitive to the amount and direction of strain. In previous first-principles studies on MoS₂ under uniaxial strain the spin-orbit coupling has not been included, yielding a critical strain for the transition from a direct into an indirect band gap of ~1%. According to our results the system remains a direct gap semiconductor up to 4% strain.

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