

Transition Metal Chalcogenides: Ultrathin Inorganic Materials with Tunable Electronic Properties

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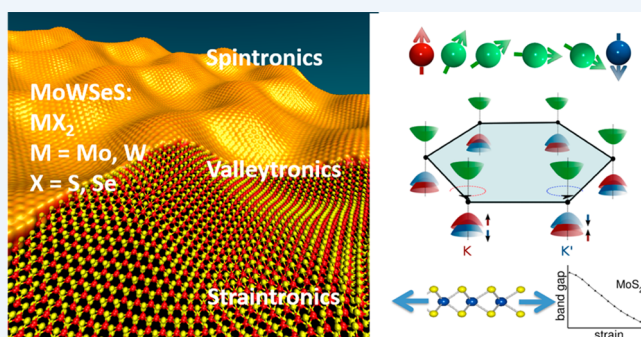
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CONSPICUOUS: After the discovery of graphene and the development of powerful exfoliation techniques, experimental preparation of two-dimensional (2D) crystals can be expected for any layered material that is known to chemistry. Besides graphene and hexagonal boron nitride (h-BN), transition metal chalcogenides (TMC) are among the most studied ultrathin materials. In particular, single-layer MoS_2 , a direct band gap semiconductor with ~ 1.9 eV energy gap, is popular in physics and nanoelectronics, because it nicely complements semimetallic graphene and insulating h-BN monolayer as a construction component for flexible 2D electronics and because it was already successfully applied in the laboratory as basis material for transistors and other electronic and optoelectronic devices.

Two-dimensional crystals are subject to significant quantum confinement: compared with their parent layered 3D material, they show different structural, electronic, and optical properties, such as spontaneous rippling as free-standing monolayer, significant changes of the electronic band structure, giant spin–orbit splitting, and enhanced photoluminescence. Most of those properties are intrinsic for the monolayer and already absent for two-layer stacks of the same 2D crystal. For example, single-layer MoS_2 is a direct band gap semiconductor with spin–orbit splitting of 150 meV in the valence band, while the bilayer of the same material is an indirect band gap semiconductor without observable spin–orbit splitting. All these properties have been observed experimentally and are in excellent agreement with calculations based on density-functional theory.

This Account reports theoretical studies of a subgroup of transition metal dichalcogenides with the composition MX_2 , with $M = \text{Mo}$, or W and $X = \text{Se}$ or S , also referred to as "MoWSeS materials". Results on the electronic structure, quantum confinement, spin–orbit coupling, spontaneous monolayer rippling, and change of electronic properties in the presence of an external electric field are reported. While all materials of the MoWSeS family share the same qualitative properties, their individual values can differ strongly, for example, the spin–orbit splitting in WSe_2 reaches the value of 428 meV, nearly three times that of MoS_2 . Further, we discuss the effect of strain on the electronic properties (straintronics). While MoWSeS single layers are very robust against external electric fields, bilayers show a linear reduction of the band gap, even reaching a semiconductor–metal phase transition, and an increase of the spin–orbit splitting from zero to the monolayer value at rather small fields. Strain is yet another possibility to control the band gap in a linear way, and MoWSeS monolayers become metallic at strain values of $\sim 10\%$. The density-functional based tight-binding model is a useful tool to investigate the electronic and structural properties, including electron conductance, of large MoS_2 structures, which show spontaneous rippling in finite-temperature molecular dynamics simulations. Structural defects in MoS_2 result in anisotropy of the electric conductivity. Finally, DFT predictions on the properties of noble metal dichalcogenides are presented. Most strikingly, 1T PdS_2 is an indirect band gap semiconductor in its monolayer form but becomes metallic as a bilayer.



INTRODUCTION

We are used to associating materials with their fundamental properties: copper is an opaque metal, diamond a transparent insulator, and silicon a gray semiconductor. The atomistic and electronic structures of materials typically remain stable over a large range of temperatures and pressures. Exceptions are known for some electronic phenomena, such as the temperature dependency of the resistance of a semiconductor or of the magnetization of a ferromagnetic material. At first glance, the same is true for layered materials. Closer inspection of systems with sufficiently high crystallinity shows some peculiarities, for

example, strong anisotropy in mechanical and electronic properties. When thinned to individual layers or stacks of a few layers, however, they show phenomena that are unprecedented in materials science, which are subject of this Account.

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A plethora of layered materials is known from nature or synthesis, and for all of them, there is a realistic chance that they can be exfoliated to the monolayer (ML)¹ or directly grown in mono- or few-layer forms. Electronically, these two-dimensional (2D) crystals may be metals, insulators and semiconductors.² Indeed, after the discovery of graphene,³ a large number of 2D crystals have been prepared and investigated, the most prominent ones being hexagonal boron nitride (h-BN) and transition metal chalcogenides (TMCs) of stoichiometry MX_2 . As bulk layered materials, the latter ones exist in 1T (tetragonal, AA stacking), 2H (hexagonal, ABAB stacking), and more rarely in 3R (rhombohedral, ABCABC stacking) polymorphs (Figure 1). In monolayers, where the

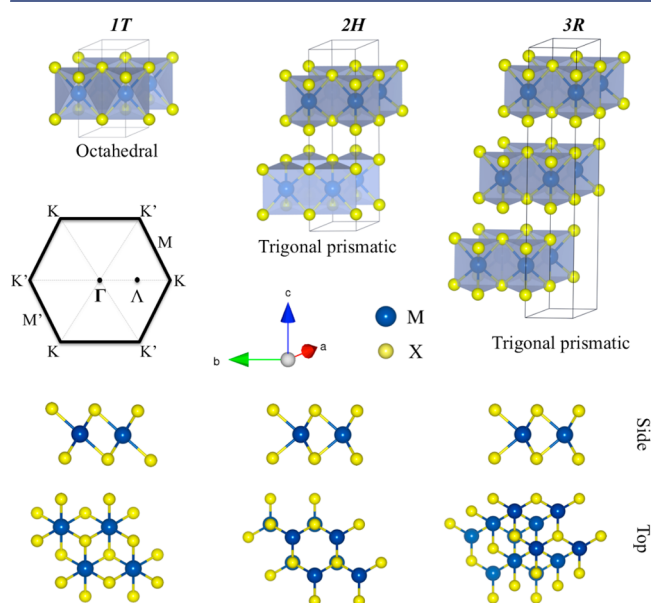


Figure 1. Structure of transition metal chalcogenides (TMCs) of composition MX_2 . Depending on the metal atom, the MX_2 family can crystallize in 1T (tetragonal), 2H (hexagonal), or 3R (rhombohedral) symmetry. For a detailed discussion of the representatives of TMC 2D crystals, see ref 2. The figure also shows the hexagonal Brillouin zone with the high symmetry k points.

stacking is irrelevant, we distinguish only the tetragonal (t) and hexagonal (h) structures. For convenience, the bulk notation (1T and 2H) is also used for monolayers in this Account.

The prototype 2D crystal, graphene, with evidently extraordinarily high mechanical and chemical stability and electron mobility, sensitized scientists to the notion that 2D materials are special. Massless electrons at the Dirac cones offered new physics, and a vast amount of research was carried out in the physics community since the seminal work of Novoselov, Geim, and others.⁴ Particular hope was raised for graphene being an alternative to common semiconductors for electronic applications. However, because graphene does not exhibit an intrinsic band gap and because it is difficult to introduce a sizable one, its application as basis material for transistors appears to be unsuitable. On the other hand, as intrinsic semiconductors, TMCs MX_2 ($M = \text{Mo}$ or W , $X = \text{S}$ or Se , sometimes referred to as “MoWSeS”) are developing as a realistic alternative to three-dimensional (3D) silicon for future nanoelectronic applications, in particular after the first transistor⁵ and further devices⁶ have been demonstrated in the laboratory. Although numerous studies on the properties of

TMCs have been published in the past years, some fundamental electronic properties remain to be precisely determined. For example in single-layer MoS_2 , the prototype TMC, the values for electron mobility^{7–10} and band gap^{11–14} are still a matter of debate.

The electronic properties of MoWSeS materials in their monolayer, thin multilayer, and bulk forms have been studied in great detail. The focus of this Account is the observation that this material class is a particularly sensitive one: when thinned to single layers or stacks of a few layers, both internal and external factors can significantly alter the electronic properties of these 2D crystals. Intrinsic factors are the number of layers, heterostructural stacking and defects, including point defects and grain boundaries, while external factors include electric fields (gate voltages) and mechanical deformation. The high sensitivity of MoWSeS materials, on one hand, is a challenge for experiments, because it is more difficult to control the material's quality and thus to create reproducible results. On the other hand, if these factors are under control, these materials offer the possibility for unprecedented devices, as multifunctional devices can be designed based on grounds of externally triggered electronic property changes.

COMPUTATIONAL ASPECTS

It is important to state that calculations on 2D materials require much care. Density-functional theory (DFT) has become the primary working tool in atomistic materials science, chemistry, and physics. DFT with the presently available density functionals, however, suffers some deficiencies that are important to keep in mind when addressing 2D systems. While the 2D crystal structure, defined by strong chemical interactions, is typically described very accurately, the interlayer interaction, as present in any stacks of 2D crystals including the bulk, is governed by London dispersion interactions (LDI), which are poorly described within DFT. Today, the state of the art is to treat them empirically using a classical force-field like correction term as proposed by Grimme^{15,16} or others.¹⁷ Approaches beyond DFT, for example, the local MP2 approach, confirmed the excellent performance of LDI-corrected DFT in the computationally feasible case of h-BN bilayer and bulk.¹⁸ The LDI influences the interlayer distance but also the interlayer stacking, which may result in significant differences in the electronic properties.¹⁹

Relativistic effects are important, and specific examples will be discussed in more detail below. Relativistic treatment of the core electrons in TMC is crucial. In addition, spin-orbit (SO) interactions can significantly alter the electronic structure, in particular in the case of 2H monolayers.^{20,21} The choice of basis functions is yet another critical issue: plane waves are particularly popular in the physics community and their application requires 3D periodic boundary conditions. Technically, this is possible by including a “vacuum layer”, which must be sufficiently large in order to avoid spurious interlayer interactions.² More importantly, if external fields are present in the Hamiltonian, artifacts due to unphysical periodicity in the direction of the field need to be corrected. Attention must be given to the choice of the k point sampling in the reciprocal lattice: even for larger super cells, the computationally favorable Γ point approximation must be explicitly validated.²² Finally, it must be noted that free-standing 2D materials are not planar but ripple on a scale of ~ 1 nm.^{23,24}

As confirmed for a large number of 2D crystals, DFT yields excellent band structures including effective electron and hole

masses but not necessarily correct band gap values. The underestimation of band gaps is a well-known issue of this theory and can be corrected either by methods beyond DFT, for example, the GW approximation, by quasi-particle models such as the GLLB-SC approach,²⁵ or by model exchange correlation potentials, such as the Tran–Blaha modified Becke–Johnson (TBBJ) potential.²⁶ For the MoWSeS materials, DFT band gaps using the PBE functional²⁷ are typically in good agreement with experiment.¹² The reason is a fortuitous error cancellation: Due to quenched Coulomb screening, 2D materials have appreciable exciton binding energies. Thus, the optical gap, where electrons and holes are subject to Coulomb attraction and which is accessible in photoluminescence experiments, is lower than the transport gap. PBE-DFT results are close to the optical gap; however, band structure calculations give the transport gap, which is significantly higher in experiment and at higher levels of theory, as in the GW approach. Correct predictions of the optical gap must include the exciton binding energy, for example, by using the Bethe–Salpeter equation. These calculations are computationally very demanding, and final converged values for exciton binding energies in MoWSeS materials are still debated.^{11,13,14,28}

When addressing large structures, for example, to investigate dynamic effects, defects, and doping, approximate DFT within the DFTB framework^{29,30} is a useful method. Unfortunately, at present the choice of parameters is limited to a few 2D materials, such as graphene, silicene, and MoS₂. However, we have recently developed parameters for the periodic table that are useful for electronic structure and in particular for electron transport simulations,³¹ for example, using the nonequilibrium Green's function (NEGF) approach in conjunction with the Landauer formula.

INTRINSIC PROPERTIES OF PRISTINE MoWSeS MATERIALS

Strictly speaking, 2D (and 1D) materials cannot exist in free form. This has been concluded based on the experimental observation that for thin film materials the melting point lowers when the thickness is reduced and rationalized by the anharmonic character of the interatomic interactions.³² Thus, the demonstrated existence of 2D materials was at first surprising; however, soon the intrinsic rippling of graphene was observed in experiment³³ and simulation.²³ For 2D materials with more than one atomic layer, as is the case for TMCs and many other 2D crystals, vibrational degrees of freedom normal to the lattice plane are available. However, intrinsic rippling has also been observed in MoS₂, by investigating a ML deposited on a transition electron microscope (TEM) grid,³⁴ and later confirmed by direct Born–Oppenheimer molecular dynamics (BOMD) simulations (Figure 2).²⁴ Investigating the intrinsic rippling of 2D materials is interesting beyond academic curiosity, since it has

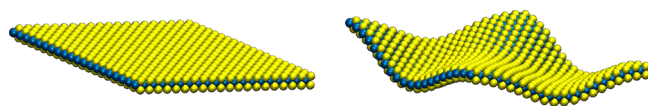


Figure 2. Snapshots of a BOMD simulation of MoS₂ ML after 1 ps (left) and 25 ps (right). Periodic boundary conditions have been applied; the simulation temperature was 300 K. Courtesy of Dr. Pere Miró. Data is taken from ref 24.

consequences for the electronic structure. For MoS₂, at 300 K, the band gap can be reduced by up to 400 meV.²⁴ We are currently investigating the rippling of a range of 2D materials, its temperature dependence, and the influence of flat and nanostructured substrates.

One of the interesting phenomena in MX₂ TMCs is the change of the band structure when the material is thinned from bulk to the ML. As shown in Figure 3, MoS₂ bulk has an

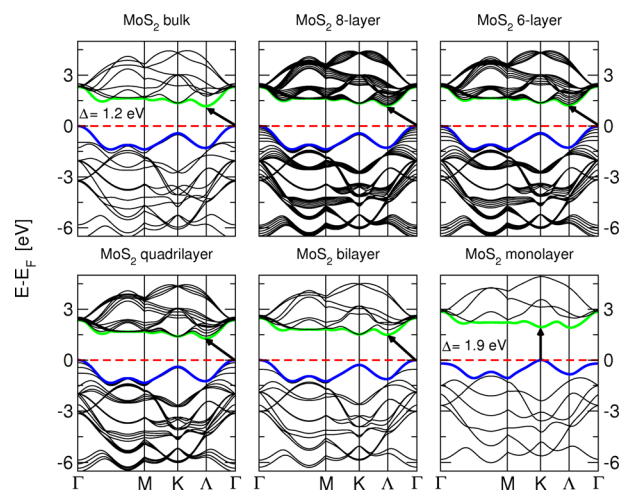


Figure 3. Band structure of MoS₂ in bulk, multilayer, bilayer, and monolayer forms. The Fermi level is indicated by a red dashed line. The top valence band is indicated in blue, the lowest-energy conduction band in green. Lowest-energy electron transitions are indicated by arrows. Results (neglecting spin–orbit interactions) are taken from ref 12.

indirect band gap with an electron transition between the Γ and a point located halfway between K and Γ , commonly called the Λ point. When the material is thinned, the valence band valley at the Γ point decreases, while the conduction band valley at the Λ point increases. When ultimately the material goes from bilayer (BL) to ML, the valence band maximum (VBM) and the conduction band minimum (CBM) are both located at the K point, leading to a direct band gap semiconductor.¹² This effect was first reported by Mak et al.,³⁵ who observed a strong increase of photoluminescence intensity upon going from BL to ML MoS₂, and experimentally confirmed and rationalized on grounds of DFT calculations by Splendiani et al.³⁶ We have shown that this effect is not restricted to MoS₂, but observed in all MoWSeS materials.¹²

It was at first glance surprising that 2H-MX₂ MLs exhibit giant SO splittings. The photoluminescence spectrum of MoS₂ reported by Splendiani et al. showed two excitons,³⁶ which differ by 50 nm; the difference in energy is caused by the large SO splitting in the K valley of the valence band. These giant SO splittings have been analyzed theoretically by Zhu et al.³⁷ and range from 150 meV for MoS₂ up to 453 meV for layers that include heavier elements such as WSe₂.²¹ The appearance of SO splittings is rationalized in Figure 4. In the bulk and also in the 2H BL, inversion symmetry centers are found between the layers. Thus, spatial inversion and time inversion is present at the electronic valleys, and the energy levels of the two spin polarizations are degenerate. Indeed, even for WSe₂, the SO splitting values are negligible.²⁰ In contrast, the inversion symmetry is absent in the MLs. Now, SO coupling affects the energy levels at the K valleys of the valence band, resulting in

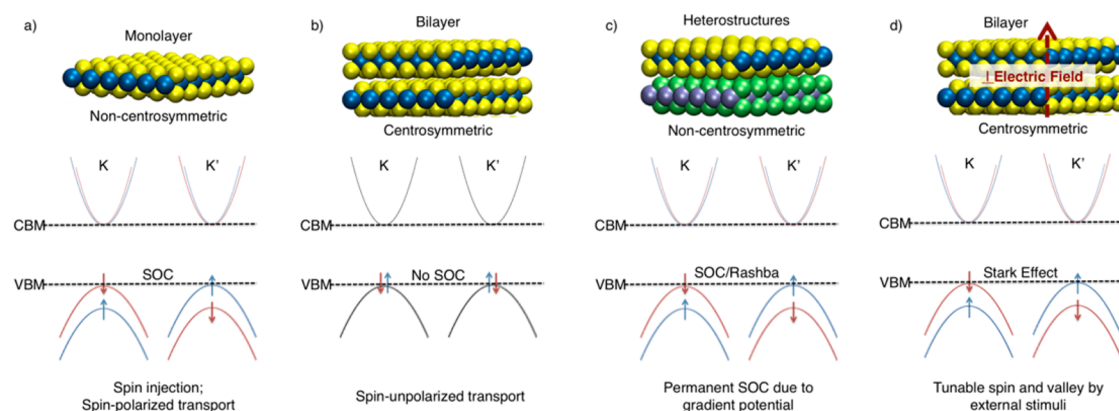


Figure 4. Effect of spin–orbit interactions in 2H-MX₂ mono- and bilayers. (a) Due to lack of inversion symmetry, giant SO coupling is observed for the ML, as result of time inversion at K and K' = -K. (b) The inversion symmetry is restored in the BL, and the SO splitting disappears due to spatial inversion. (c) In a heterostructured BL, the symmetry is again broken due to a chemical potential gradient normal to the planes and SO splitting reappears (Rashba splitting). (d) The symmetry can also be broken by external fields that are applied normal to the layer, as shown here for an electric field (Stark effect). Courtesy of Dr. Agnieszka Kuc, Jacobs University Bremen.

giant SO splittings. This symmetry-based effect is obviously very sensitive, and any break of symmetry, for example, caused by mechanical factors, such as by shear stress, will affect the electronic structure of the system. It is also possible to introduce SO splitting in bilayers and other multilayers with even layer numbers by a potential gradient: One way is to use different layer compositions, for example, as present in heterostructures with two different MX₂ layers, where the chemical potential gradient breaks the inversion symmetry. For mixed stacks of MoWSeS layers, this so-called Rashba effect results in SO splitting values close to those of the ML with largest intrinsic SO splitting.²⁰ Another way to break the inversion symmetry is the presence of an external field, as can be realized via a gate voltage or by ionic liquid gating. Relatively small electric fields are necessary to achieve maximum SO splittings,³⁸ as will be discussed in more detail below.

As summarized in Table 1, the band gaps of MX₂ TMCs, at least at the DFT level, vary between 1.74 and 0.86 eV, and

Table 1. Electronic Band Gaps (Δ), Spin–Orbit Splittings at the K Valley in the Valence Band (Δ_{SO}), and Effective Electron (m_e^*) and hole (m_h^*) Masses of TMC MX₂ Monolayers (M = Mo or W, X = S, Se, or Te)^a

	Δ (eV)	Δ_{SO} (meV)	m_e^*/m_0	m_h^*/m_0
MoS ₂	1.62 (1.28)	147	0.449	-0.537
MoSe ₂	1.40 (0.86)	176	0.557	-0.616
MoTe ₂	0.97 (0.74)	190	0.541	-0.618
WS ₂	1.74 (1.37)	395	0.276	-0.351
WSe ₂	1.43 (0.99)	428	0.439	-0.369
WTe ₂	0.86 (0.60)	480	0.398	-0.300

^aResults, taken from ref 20, have been calculated using the TBBJ model density functional including scalar relativistic effects and SO couplings. Corresponding bulk values are given in parentheses.

confirm that these materials are intrinsic semiconductors. The chalcogen atoms have the strongest influence on the band gap size, with heavier atoms yielding smaller values, while exchange of Mo and W has only a minor effect. The situation is different when looking at SO splittings, which are dominated by the choice of metal atoms with much larger values caused by the heavier tungsten. Effective masses of electrons and holes show a less pronounced trend; however, here also the transition metal

shows the largest influence, with MoX₂ having in general higher effective masses than the WX₂ counterparts.

The sensitivity of the interlayer interaction raises the question how the properties of these ML materials change if they are deposited on a substrate or on a ML of different composition. MoS₂-substrate interactions have been studied by Dolui et al., who discuss the origin of n- and p-type doping in MoS₂ deposited on SiO₂. Interestingly, in the defect-free case, the electronic density-of-states (DOS) arising from the MoS₂ ML is not affected by the presence of the substrate.³⁹ The situation is different for heterostructures of different TMC MX₂ layers, as originally discussed by the Terrones and the Krasheninnikov groups.^{40,41} Here, many systems show direct band gap characteristics, and the large structure variety that is possible by combining two MX₂ MLs offers a wide range of possible band gaps in heterostructured 2H-MX₂ BL systems.⁴⁰ On the other hand, the optical properties of the ML are only slightly affected when heterostructures are formed.⁴¹ Our calculations are in line with this latter observation, as the SO splitting at the VBM in heterostructured 2H-MX₂ BL systems is very close to the SO splitting value in the layer with the heavier elements.²⁰

For finite structures, for example, for TMC platelets that can be synthesized using colloidal chemistry,⁴² quantum confinement as a function of the platelet diameter is observed. Lateral quantum confinement depends on the electronic structure of the edges (boundary conditions) and on the lateral size. Edge effects strongly depend on the environment for group 6 TMCs, which makes the analysis difficult. On the other hand, for group 4 1T-MX₂ flakes, M = Ti, Zr, or Hf, the theoretical analysis is easier, because the edge geometry is well-defined; as a consequence, the stoichiometry of the perfect flake is M_nX_{2n-2}, independent of flake size and shape. This results in four excess electrons that are distributed over the flake, concentrated on the basal plane as shown in Figure 5. Increasing the flake size dilutes the effect of those excess electrons, and eventually the properties converge to those of the 2D crystal.⁴³

■ STRAINTRONICS IN MoWSeS MONOLAYERS

The extraordinary mechanical properties of layered TMCs are reflected in their excellent tribological properties. Nanoparticles of MoS₂ and WS₂ are employed as high-performance

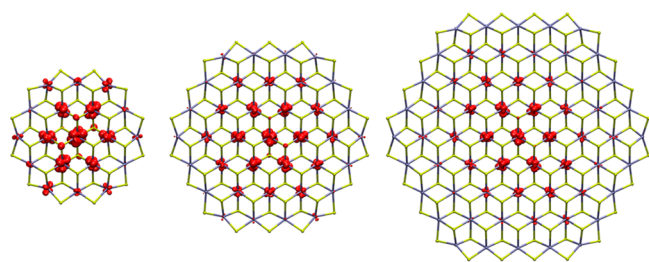


Figure 5. Electronic structure of 1T-MX₂ nanoflakes. The distribution of the four excess electrons (see text) are shown for a small ($n = 19$), medium ($n = 30$), and large ($n = 43$) Ti_{*n*}S_{2*n*-2} model.

lubricants.^{44,45} TMC layers exhibit very high tensile strength and a linear strain–stress relation until nearly the rupture point, which has been found at elongations of more than 10% for WS₂ nanotubes.⁴⁶ We have found a similar stability in MoWSeS monolayers with respect to tensile and biaxial isotropic stress.⁴⁷ It is interesting to note that in 2H-MX₂ ML, the spatial extension results mainly from an increase of the X–M–X bond angles, and only a relatively small change of the M–X bond lengths is observed.⁴⁷ However, because this change increases the distance between the metal atoms and the d-band of the metals governs the electronic structure, strong electro-mechanical effects occur. Unidirectional strain has been realized in experiment, for example, in large-diameter WS₂ nanotubes.⁴⁶ Bidirectional strain can be implemented, though with more difficulty, by substrate heating or by nanoindentation with AFM tips. For the MoS₂ example, which performs similarly to the other MoWSeS materials in this case, the evolution of the band gap as a function of uni- and bidirectional strain is visualized in Figure 6.^{47,48} At equilibrium, MoS₂ is a direct band gap

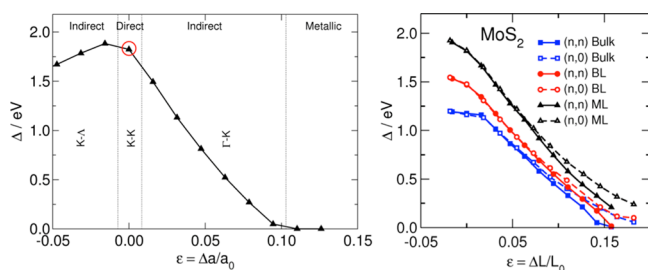


Figure 6. Straintronics in MoS₂ monolayer. (left) band gap of MoS₂ ML as a function of bidirectional strain, plotted over the change of the lattice constant (hexagonal lattice). Locations of the fundamental band gap within the Brillouin zone are indicated. (right) Evolution of the band gap as a function of tensile strain in MoS₂ ML, BL, and bulk. Strain is applied along armchair (n,n) and zigzag ($n,0$) direction, respectively. Values are taken from refs 47 and 48.

semiconductor. Bidirectional strain linearly reduces the band gap by approximately 200 meV per % of strain (Figure 6). After $\sim 10\%$ elongation, the system changes its character from being semiconducting to metallic. NEGF-DFTB calculations confirmed the authenticity of the metallic state. When the material expands, the VBM changes from the K to the Γ point, and the system becomes an indirect gap semiconductor. Similar behavior is found for bidirectional compression; however, here the CBM changes and the reduction of band gap is less than upon expansion. For unidirectional strain, the band gap change is less pronounced and similar along armchair and zigzag directions. Band gap reduction upon tensile strain has been observed also for MoS₂ BL and bulk.^{47,48} Shear stress has

been reported to significantly alter the electronic properties in MX₂ (M = Mo or W, X = S, Se, or Te) monolayers,⁴⁹ and it remains to be investigated how this affects the SOC in mono- and bilayer forms.

TUNING PROPERTIES OF MoWSeS MATERIALS WITH ELECTRIC FIELDS (GATING)

Gate voltages are a common way to control electronic devices, and this concept is particularly useful in 2D electronics. A gate voltage creates an electric (E) field, which is oriented perpendicular to the 2D crystal plane. This field has direct impact on the electrons, because it shifts the electronic levels and polarizes the electronic structure, causing a dipole moment normal to the layer. In 2D crystals, the electric field can have more pronounced effects. For example, the MoS₂ nanoribbon band gap decreases as a function of an external electric field; however, this effect is significantly influenced by edge states, and thus this is not an intrinsic property of the 2D crystal.⁵⁰ The effect of the external field decreases with ribbon width,⁵¹ and the electronic band gaps of MoWSeS MLs have almost no dependency on external E fields up to significant field strengths of more than 2 V/Å, even though a pronounced dipole moment normal to the layer arises.²¹ For larger fields, the band gap decreases almost linearly, and after 6 V/Å for sulfides (4 V/Å for selenides), a semiconductor–metal transition is observed (Figure 7). However, such field strengths are at least 1 order of magnitude higher than those that are common in state-of-the-art experiments including ionic liquid gating.⁵²

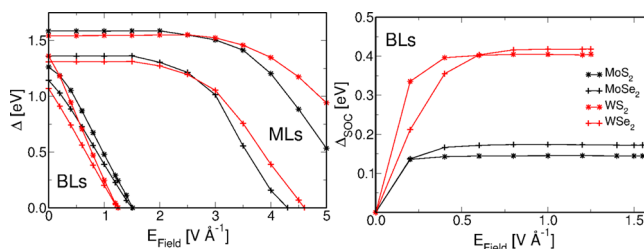


Figure 7. Effect of an external electric field normal to MoWSeS mono- and bilayers. The band gap evolution as a function of the applied E field for MoWSeS MLs and BLs (left), and the evolution of SO splitting of the valence band K valleys for MoWSeS BLs (right) are shown. Values are taken from refs 21 and 53.

The situation is different for the BLs. Here, two effects are observed: First, for all MoWSeS materials, the band gap decreases, almost linearly, with external electric fields. Moreover, the external E field breaks the inversion symmetry, and a SO splitting quickly arises and saturates at values that match those of the corresponding MLs (Figure 7).⁵³ In the literature, the sensitivity of the band gap decrease is reported in controversy: Ramasubramaniam et al.⁵⁴ reported a semiconductor–metal transition at about three times smaller field compared with other calculations;^{19,53} however, as analyzed by Liu et al., this is probably due to an incorrect structure model that was subject to unphysical symmetry constraints.¹⁹

DEFECTS IN MoWSeS MATERIALS

Materials contain defects. Defects have implications on the mechanical as well as on the electronic properties, and in general, as suggested by the terminology, their presence is not appreciated. In most materials, small defect concentrations do not alter the properties. There are well-known exceptions

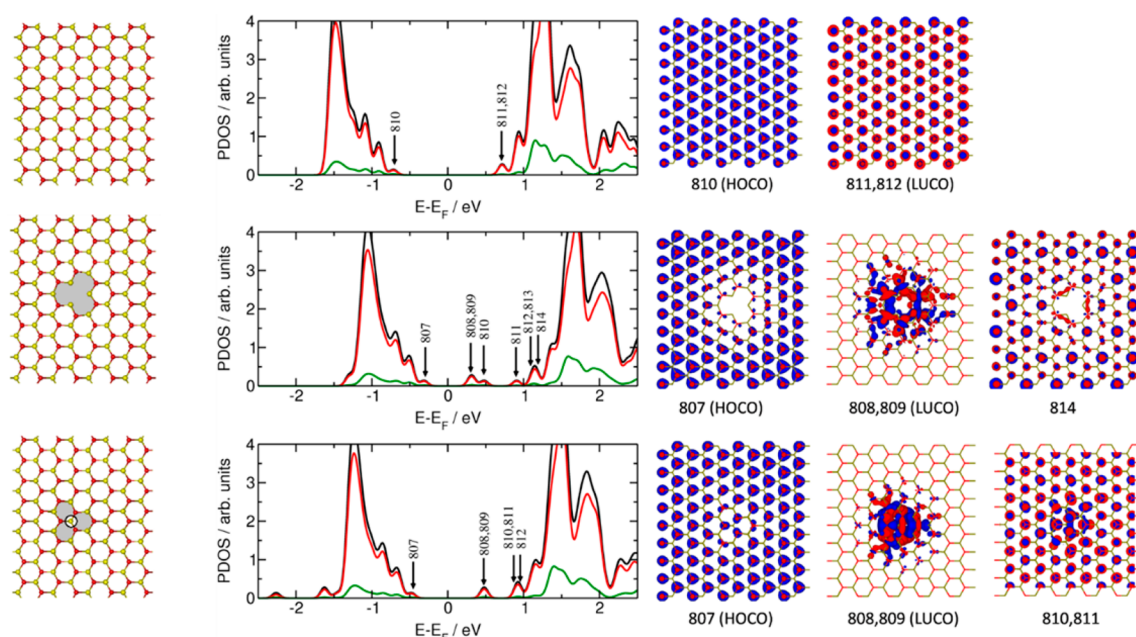


Figure 8. Point defects in MoS₂ monolayer: pristine MoS₂ ML (top), MoS₂ with Mo vacancy (center), and MoS₂ with S vacancy (bottom). The total (black) and projected density-of-states (PDOS) (Mo 4d, red, and S 3p, green) are shown next to the structure. On the right, the frontier crystal orbitals are depicted, that is, the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCCO), which is a delocalized state for the pristine monolayer but a localized color center for the doped structures. For the latter ones, the next delocalized states that can contribute to electronic conduction are illustrated, and energetically they are found at energies similar to the CBM of the pristine monolayer (see PDOS plots). Calculations have been carried out at the DFTB level and results are taken from ref 57.

where defects significantly influence the properties. A very important one is the doping of semiconductors, where concentrations in the parts per billion range significantly alter the room temperature electronic conductivity. Other examples are the color change by impurities in precious stones such as diamond and also in heterogeneous catalysis on surfaces.

It is very difficult to produce defect-free 2D TMC structures. Exfoliated material inherits the defects of the bulk system, for example, topological or stoichiometric defects, while material grown by chemical vapor deposition or other deposition techniques^{55,56} is typically rich in grain boundaries. Thus, the influence of defects on the properties of 2D materials is an important research topic.

We have studied the role of structural defects on the electronic structure of MoS₂. Point defects (missing Mo or S atoms), missing MoS₂ units, and rotated bonds have been considered. Grain boundaries have been modeled as linear chains of defects and extended defect structures. All defect models create a local distortion to the lattice, but at longer scale, they do not significantly influence the structure of the material.⁵⁷ From investigations on WS₂ nanotubes, it is known, however, that point defects can strongly affect the mechanical stability, because under tensile strain their appearance triggers a zipper-like rupture mechanism.⁴⁶ Defects have also a significant influence on the electronic structure of MoS₂ monolayers, because they introduce states in the forbidden region of the band gap. At low concentration, however, states arising from local defects act as color centers as their corresponding orbitals are located around the defect site. Thus, even though the states are close to the Fermi level, they do not make the material metallic (Figure 8).

This is confirmed by explicit electron transport calculations using the NEGF-DFTB approach. Indeed, no transport channels around the state energies of the localized defect

orbitals are opened, indicating that MoS₂ retains its semiconducting character.⁵⁷ However, it is important to note that the extension of the electronic disturbance caused by point defects, such as shown in Figure 8, exceeds a diameter of 1 nm. Thus, in samples with moderate defect concentrations, bands arising from those states are likely to appear. This phenomenon will have significant influence on the properties of the material and is currently subject to more detailed investigations in our group.

2H-MX₂ TMC MLs exhibit hexagonal symmetry, and thus, within the single crystal, they could have direction-dependent transport properties. Our NEGF-DFTB calculations imply that for pristine MoS₂ the electron transport along armchair and zigzag directions is very similar. However, once defects are incorporated into the material, the transport becomes direction dependent.⁵⁷ This effect also requires further investigations; in particular the role of the defect concentration is not yet well understood.

■ MATERIALS BEYOND MoWSe

Chemistry offers a very rich choice of layered materials, and most of them are likely to exist in their monolayer forms.^{1,2} To illustrate the necessity of exploring the large diversity of 2D materials, we move to noble metal dichalcogenides with Pd and Pt metal centers. Both crystallize in layered form, PtX₂ in 1T-MX₂ (see Figure 1) and PdX₂ in an orthorhombic (2O, i.e., pyrite) form as was already reported by Grønbold and co-workers in the 1950s.⁵⁸ Unfortunately, to date neither of them has yet been prepared in their monolayer forms. Our first-principles calculations predict the 1T phase as the most stable at the monolayer level and show that these monolayers are semiconducting with indirect band gaps between 1.1 and 1.7 eV.⁵⁹ PdS₂ is a particularly interesting representative of this group, because it changes its character from semiconducting

(1.11 eV band gap) to metallic when going from monolayer to bilayer. The metallic character has been confirmed by explicit electron conductance calculations using the NEGF approach.⁵⁹ Thus, PdS₂ offers the possibility to manufacture ultrathin applications based on a single material that can be used for electrodes and device.

CONCLUSION AND PERSPECTIVES

Two-dimensional materials offer properties that are interesting for many applications that exceed the well-known examples in lubrication and catalysis. It is particularly interesting that these materials are very sensitive to stacking, particle size, and defect type and concentration. Moreover, external factors as electromagnetic fields and strain have a significant influence on the electronic structure. Thus, 2D crystals meet the ultimate frontier of materials science: with tools of materials science, it is impossible to make them even thinner. However, the electronic properties of these materials can be tailored by intrinsic factors; thus new perspectives in chemistry, materials science, and physics are offered.⁶⁰ This is reflected in the emerging research directions spin-, strain-, and valleytronics that are currently en vogue for two-dimensional materials including and beyond graphene.

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Notes

The authors declare no competing financial interest.

Biography

Thomas Heine graduated in physics from TU Dresden under the guidance of Gotthard Seifert, with research stages in Montréal (Dennis R. Salahub) and Exeter (Patrick Fowler). After postdoctoral stages in Bologna (Francesco Zerbetto) and Geneva (Jacques Weber), he obtained the *venia legendi* in Physical Chemistry at TU Dresden. In 2008, he was appointed as Associated Professor of Theoretical Physics/Theoretical Materials Science at Jacobs University and was promoted to Full Professor in 2011. His research interests include molecular framework compounds, two-dimensional materials, theoretical spectroscopy, and the development of methods and software for materials science.

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