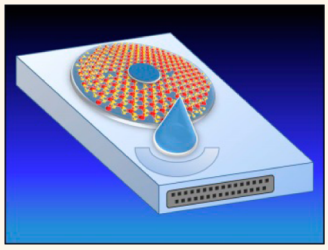
The Virtues of Magnetism

Jan-Ole Joswig, Tommy Lorenz, and Gotthard Seifert*

Physical Chemistry, TU Dresden, 01062 Dresden, Germany

ABSTRACT Dislocations at grain boundaries in semiconducting two-dimensional transition-metal dichalcogenides have been found to be the origin of substantial intrinsic magnetic moments. Here, we introduce a first-principles study by Yakobson and co-workers, published in this issue of *ACS Nano* that shows the influence of grain-boundary tilt angle and doping level on the resulting magnetic moments. This specific property may help in designing new two-dimensional magnetic semiconductors.



In Mozart's late opera *Così fan tutte* from 1790, Despina, the accomplice of thread puller Don Alfonso, instantly heals the two male characters who are pretending to be dying by using the virtues of magnetism. Naturally, she had time enough to praise in length these virtues and their effects on the human body, known also as Mesmerism,[1] beforehand in the finale of the first act. Although magnetism had been known for centuries, its scientific sources were not yet understood at the end of the 18th century, when Lorenzo da Ponte wrote the libretto.

Since then, we have gained a relatively full description of magnetic phenomena: in the 19th century, scientists like Lorentz explained magnetism at the macroscopic scale; in the 20th century, the evolving quantum-mechanical descriptions of matter and its properties made it possible to gain insight into the physics on the atomic scale. Nowadays, we have gone another step further: with the upcoming techniques of tailoring nanomaterials, our ability to tune electronic, optical, and magnetic properties on the atomic scale has led to new breakthroughs.

In this issue of *ACS Nano*, Yakobson and co-workers[2] report on intrinsic magnetism of grain boundaries in two-dimensional (2D) metal dichalcogenides. Although these materials, *e.g.*, MoS_2, have been studied since the 1970s,[3] they rose to greater importance in the past decade, when a simple technique using Scotch tape and other exfoliation methods gave access to single layers of 2D materials. Having a height of less than a nanometer but other dimensions in the micrometer range, these 2D materials can be viewed as part of the nanomaterials family.

Two-dimensional metal dichalcogenides differ substantially from graphene, which is the most studied 2D material.[4] Whereas the latter has a thickness of only one atom, transition-metal dichalcogenide sheets consist of three atomic layers—*e.g.*, sulfur/metal/sulfur—which only have covalent bonds between atoms that are situated in different layers (Figure 1). Through their special accordion-like bonding, these materials have different properties than those of graphene. First and foremost, they are semiconducting, which is a significant advantage when it comes to usage as components in electronic devices, such as single-layer transistors.[5] Second, their mechanical properties differ from those of graphene, as transition metal dichalcogenides show much lower tensile stress upon applied strain.

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Yakobson and co-workers' theoretical study focuses on the 2D transition-metal

* Address correspondence to gotthard.seifert@chemie.tu-dresden.de.

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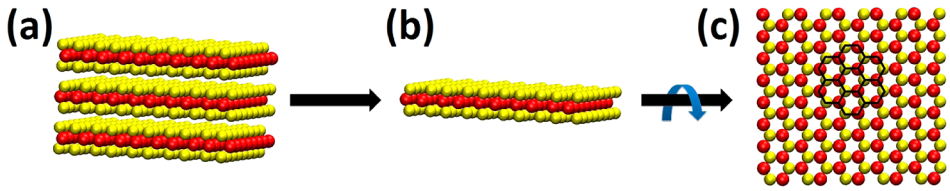

Figure 1. Bulk molybedenum disulfide (MoS_2) (a), a single layer of the material in side view (b) and top view (c), in which the projected hexagons are shown schematically. Molybdenum and sulfur atoms are depicted as red and yellow spheres, respectively.

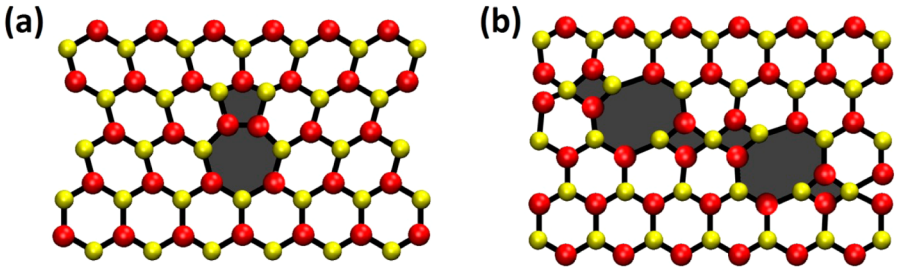

Figure 2. Schematic representation of a (5|7) dislocation (a) and a series of (4|8) dislocations (b) in a top-view projection of two-dimensional molybdenum disulfide (MoS_2). Red and yellow spheres represent Mo atoms and S_2 pairs, respectively.

dichalcogenides MoS_2, $MoSe_2$, WS_2, and WSe_2 (generally MX_2), and the special case of defects at grain boundaries therein.[2] These imperfections can be caused either by missing atoms or by a disadvantageous tilt angle between two perfect 2D parts, and they give rise to surface states unless the dangling bonds are saturated by ring formation. Thus, instead of a perfect (6|6) arrangement (two adjacent six-membered MX_2 rings, whereby the two chalcogen atoms are considered as one ring vertex in projection), the defect has the consequence of producing either (5|7) or (4|8) rings instead, and induces surface states within the band gap of the pristine material.[6] In the (5|7) ring, homoelemental bonds result, whereas in the (4|8) ring, this is not the case.

First-principles calculations of these defected 2D structures—Yakobson and co-workers used spin-polarized density-functional theory to perform this task—revealed that in 2D inorganic materials the spin polarization was highly localized at the dislocations. At a (5|7) dislocation, grain boundaries show ferromagnetic spin ordering, and a typical magnetic moment of 1 μB per dislocation results. The size of the magnetic moment is dependent on the dislocation itself. The authors studied symmetric defects resulting from different tilt angles that are responsible for the dislocations (Figure 2). Below tilts of 32°, the magnetic moment of a molybdenum-rich grain boundary is proportional to the tilt angle. The resulting magnetic moments are 30−45% higher than at graphene zigzag edges; at (4|8) dislocations, a magnetic moment 75% higher than in graphene edges is achieved. Generally, the spin polarization is located on the molybdenum atoms in these cases. Finally, at a tilt angle of 47°, antiferromagnetic (4|8) dislocations are more favorable than (5|7) dislocations. The preference of this 8-fold ring-containing structure is in agreement with recent experimental findings.[7]

The study of Yakobson and co-workers[2] has also put emphasis on the question of how the doping level, *i.e.*, the density of dislocations along a grain boundary, affects the resulting magnetic properties. The amount of grain-boundary dislocations is expected to be small compared to the basal plane area of the 2D material. Nevertheless, Yakobson's calculations show that magnetic response is tunable *via* the doping level. Additionally, they find that charge transport along grain boundaries is fully spin-polarized and that some of their studied systems—depending on the tilt angle—exhibit half-metallic behavior due to crossing of the defect molybdenum 4d states with the Fermi level of the pristine material.

Consequently, there are grain-boundary tilt angles that leave the material semiconducting; this is especially true for low tilt angles. Here, the defect states do not overlap with the Fermi level. Thus, we deal with a magnetic semiconductor, which is also a 2D material. The spin-dependent transport could be regulated by appropriate engineering of the 2D material. Yakobson and co-workers find these magnetic grain boundaries to a different extent in all four of the studied transition-metal dichalcogenides MoS_2, $MoSe_2$, WS_2, and WSe_2, whereas they are not present in graphene, hexagonal boron nitride, or the metallic 1T phase of MoS_2.

The question remains as to whether these magnetic dislocations are experimentally accessible: Wang and co-workers[8] have recently reported on a site-specific electron energy-loss magnetic chiral dichroism method, which enables investigations of the local, *i.e.*, atomic site-specific

magnetic structure. With this newly developed technique, the authors made a step forward in the field of magnetic measurements in comparison to X-ray magnetic circular dichroism and neutron diffraction. Applying it to the system discussed here may test experimentally the local magnetism at grain-boundary dislocations.

Going a step further than experimental proof and looking ahead, technological manipulation of layered materials could result in the ability to tailor the magnetic properties of semiconducting 2D materials. In electronic data storage, the local electron-spin information is unused, but technological handling of 2D magnetic semiconductors could open a gate to potential applications in this area.

To come full circle: In Mozart's *Così fan tutte*, the dressed-up "magnetic doctor" Despina together with her potential mesmeric powers—the virtues of magnetism—is saluted with "the honors that he deserves." Yakobson and co-workers opened the door to new potential applications of nanoscopic 2D magnetic semiconductors, for which we should likewise salute them.

Conflict of Interest: The authors declare no competing financial interest.

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