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The Interface between Gd and Monolayer MoS$_2$: A First-Principles Study

Xuejing Zhang$^1$, Wenbo Mi$^1$, Xiaocha Wang$^2$, Yingchun Cheng$^3$ & Udo Schwingenschlögl$^3$

$^1$Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparation Technology, Faculty of Science, Tianjin University, Tianjin 300072, China, $^2$Tianjin Key Laboratory of Film Electronic & Communicate Devices, School of Electronics Information Engineering, Tianjin University of Technology, Tianjin 300191, China, $^3$PSE Division, KAUST, Thuwal 23955-6900, Kingdom of Saudi Arabia.

Monolayer transition metal dichalcogenides, especially MoS$_2$, have promising prospects in many fields due to their exotic electronic, optical, chemical and thermal properties$^{1-4}$. Unlike gapless graphene, monolayer MoS$_2$ has a direct optical band gap of 1.8 eV$^5$, which is key for field effect transistors, photodetectors and electroluminescent devices$^6-9$. On the other hand, the low electron mobility hampers high performance applications. Interfaces often are more crucial to nanoelectronics than the involved semiconductors themselves$^{10,11}$. Based on density functional theory, Gan et al. have shown that the chemical bonds formed at the MoS$_2$/TiC interface result in conductive MoS$_2$ upwards into the conduction band. At the surface and interface the Gd f states shift to lower energy and new surface/interface Gd d states appear at the Fermi energy, which are strongly hybridized with the Mo 4d states and thus lead to a high spin-polarization (ferromagnetically ordered Mo magnetic moments of 0.15 $\mu_B$). Gd therefore is an interesting candidate for spin injection into monolayer MoS$_2$.

We analyze the electronic structure of interfaces between two-, four- and six-layer Gd(0001) and monolayer MoS$_2$ by first-principles calculations. Strong chemical bonds shift the Fermi energy of MoS$_2$ upwards into the conduction band. At the surface and interface the Gd f states shift to lower energy and new surface/interface Gd d states appear at the Fermi energy, which are strongly hybridized with the Mo 4d states and thus lead to a high spin-polarization (ferromagnetically ordered Mo magnetic moments of 0.15 $\mu_B$). Gd therefore is an interesting candidate for spin injection into monolayer MoS$_2$.

Methods

Our first-principles calculations are performed using the projector-augmented wave method as implemented in the Vienna Ab-initio Simulation Package$^{20,21}$. For the exchange-correlation potential we use the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof$^{22}$. Due to strong on-site Coulomb repulsion of the localized Gd 4f electrons, the rotationally invariant GGA + U method is employed with $U = 7.7$ eV and $J = 0.7$ eV$^2$. The two-layer Gd/MoS$_2$ interface is also studied taking into account the spin-orbit coupling (GGA + SO). In all calculations the Gd 5s, 5p, 6s, 5d, and 4f orbitals are treated as valence states, a $\Gamma$-centered 4 × 4 × 1 k-grid is employed, and the plane wave energy cutoff is set to 600 eV. Furthermore, the convergence criterion for the total energy is chosen to be $10^{-6}$ eV. The surface unit cell of Gd(0001) has $p(3 \times 3)$ periodicity with experimental lattice constant 10.89 Å$^2$, while the surface unit cell of monolayer MoS$_2$ has $2\sqrt{3} \times 2\sqrt{3}$ R30° periodicity with experimental lattice constant 10.98 Å$^2$. Thus, the mismatch amounts only to 0.83%. The cell volume is relaxed and the ionic positions are optimized, using the conjugated gradient method, until the Hellmann–Feynmann forces on each atom are reduced to less than 0.01 eV Å$^{-1}$. A 15 Å thick vacuum layer ensures decoupling in the slab geometry. Because of strong chemical bonding between Gd(0001) and monolayer MoS$_2$, van der Waals forces are not taken into account.
Results and Discussion

Bulk MoS$_2$ has a layered 2H structure with space group $P6_3mmc$ ($D_{3h}$ point group). The trigonal prismatic coordination of the bulk is maintained in monolayer MoS$_2$, whereas the symmetry is reduced to $P6/m2$ ($D_{3h}$ point group) due to a loss of inversion symmetry. Gd crystallizes in a hcp structure with space group $P6_3mmc$. The optimized geometries of the interfaces between two- and six-layer Gd and monolayer MoS$_2$ are shown in Fig. 1. The results for the interface between four-layer Gd and monolayer MoS$_2$ turn out to be very similar to those of the six-layer system and thus are not further discussed in the following. According to Fig. 1(e), three S and Mo atoms in each layer sit above the hexagonal (H) hollow sites and nine S and Mo atoms are located above face-centered (F) hollow sites. The optimized lattice constants of Gd and MoS$_2$ are 3.65 and 3.18 Å, respectively, whereas for both the two- and six-layer Gd/MoS$_2$ interfaces we obtain 11.03 Å (3.68 and 3.18 Å for Gd and MoS$_2$). This means that there is almost no strain. In order to quantify the interaction strength between Gd and MoS$_2$, we calculate the binding energy $E_B = E_I - E_M - E_{Gd}$, where $E_I$, $E_M$, and $E_{Gd}$ represent the total energies of the Gd/MoS$_2$ interface, monolayer MoS$_2$, and the Gd slab, respectively. We obtain per surface Gd atom values of $-0.62$ and $-0.64$ eV for the two- and six-layer Gd/MoS$_2$ interfaces, reflecting substantial bonding. The distance between the S$_{I,H}$ and Mo$_{H}$ atoms is larger, namely, 3.17 and 4.69 Å (3.14 and 4.67 Å).

Figure 1 | (a, c) Side view of the charge density difference due to the interaction at the two- and six-layer Gd/MoS$_2$ interfaces. The cyan and yellow isosurfaces ($\pm 0.003$ e/Å$^3$) represent accumulation and depletion of electrons, respectively. (b, d) Side view of the spin density difference for the two- and six-layer Gd/MoS$_2$ interfaces. The isosurface value is 0.002 e/Å$^3$. Red color indicates cuts through the isosurface. (e) Top view of the optimized two-layer Gd/MoS$_2$ interface.

Figure 2 | DOS of (a) the Mo and S atoms in pristine monolayer MoS$_2$ and (b) the Gd atoms in bulk Gd.
The density of states (DOS) of pristine monolayer MoS\textsubscript{2} is addressed in Fig. 2(a). The crystal-field splitting of the Mo 4\textit{d} states in the trigonal prismatic environment of the S atoms is visible. Hybridization between the Mo 4\textit{d}\textsubscript{\textit{3}z\textsuperscript{2}r\textsuperscript{2}, d\textsubscript{xy}, d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}}} and S 3\textit{p} states at the conduction and valence band edges is consistent with previous results\textsuperscript{26}. Figures 3 and 4 give the DOSs obtained for the two- and six-layer Gd/MoS\textsubscript{2} interfaces. The majority spin Mo F states at the Fermi energy (\(E_F\)) display high 4\textit{d}\textsubscript{\textit{3}z\textsuperscript{2}r\textsuperscript{2}, d\textsubscript{xy}, d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}}} DOSs with \(d\textsubscript{yz}\) and \(d\textsubscript{xz}\) admixtures, while the minority spin DOSs are small. The majority spin Mo H DOS at \(E_F\) is slightly larger than the minority spin DOS (mainly \(d\textsuperscript{\textit{3}z\textsuperscript{2}r\textsuperscript{2}}\), \(d\textsubscript{xy}\), \(d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}}\), and \(d\textsubscript{yz}\), \(d\textsubscript{xz}\) states). Furthermore, the broader peaks in Fig. 3(a) as compared to Fig. 3(b) reflect more dispersive bands in the two-layer Gd/MoS\textsubscript{2} interface. To illustrate the charge transfer, we show the charge density difference between the Gd/MoS\textsubscript{2} interfaces and the sum of the isolated Gd and MoS\textsubscript{2} subsystems in Figs. 1(a) and (c). Charge accumulates at the Mo atoms and in the Gd-S bond region. The Mo excess electrons populate majority spin states, resulting in enhanced Mo 4\textit{d} magnetic

Figure 3 | DOS of the Mo atoms at the F and H sites for the two- and six-layer Gd/MoS\textsubscript{2} interfaces.

Figure 4 | DOS of the S atoms at the F and H sites for the two- and six-layer Gd/MoS\textsubscript{2} interfaces.
moments. Figure 4 demonstrates that for S II the $p_z$ DOS is larger than the $p_x$ and $p_y$ DOSs, similar to pristine monolayer MoS$_2$, at the valence band edge, while for S I mainly the $p_x$ and $p_y$ orbitals contribute. This means that the Gd-S II interaction is weak (large distance). Due to hybridization with the Gd 5$d$ states (details later), some S $p$ states show up at $E_F$, especially majority spin states, which leads to a tiny S magnetic moment (0.01 $\mu_B$). It is worth noting that, due to the nonmagnetic nature of MoS$_2$, we have set the initial magnetic moments of S and Mo to zero in all calculations. The spatial extension of the spin density in MoS$_2$ induced by the contact to Gd is shown in Figs. 1(b) and (d). It mainly extends into the Mo region and is small for S (large change of the Mo DOS). We find that the Mo magnetic moments order ferromagnetically. The shorter MoF-Gd distance as compared to the MoH-Gd distance enhances the interaction so that Mo$_F$ has a larger magnetic moment of about 0.12 and 0.15 $\mu_B$ (Mo$_H$: 0.07 and 0.10 $\mu_B$) in the two- and six-layer Gd/MoS$_2$ interfaces, respectively.

Figure 5 | Band structure of (a) pristine monolayer MoS$_2$ and (b, c) the two- and six-layer MoS$_2$ interfaces. $E_F = 0$ eV. The red lines correspond to the bands of monolayer MoS$_2$.

Figure 6 | DOS (sum of both spin channels) of the Mo atoms at the F and H sites for the two-layer Gd/MoS$_2$ interface: Comparison between the GGA and GGA+SOC methods. $E_F = 0$ eV.
Figure 5(a) shows a band gap of 1.6 eV for pristine monolayer MoS$_2$, consistent with previous GGA calculations$^{27}$. In the combined systems, although the bands of MoS$_2$ hybridize with those of Gd, they can still be identified, see the red color in Figs. 5(b) and (c). We find $E_F$ 0.34 and 0.51 eV, respectively, above the conduction band edge for the majority and minority spin bands, making MoS$_2$ display a metallic character. Figs. 6(a) and (b) show the DOS for Mo$_{2d}$ and Mo$_{3d}$ in the two-layer Gd/MoS$_2$ interface as obtained by GGA+SOC in comparison to simple GGA. We find that the SOC has almost no influence, except for a slight reduction of the $d_{z^2}$–$p$ DOS.

The distance between nearest neighbor atoms is 3.60 Å in bulk Gd, while the distances of nearest neighbor atoms in the interface and surface Gd layers, see Figs. 1(a, e) and (c), respectively, are smaller. The very short distance between layers V and VI in the six-layer Gd/MoS$_2$ interface points to a substantial surface relaxation. On the other hand, the distances in the subsurface, see Fig. 1(c), are larger than the bulk value. This variation is consistent with a contraction of the surface layer by 0.085–0.115 Å ($\sim$3–4%) and an expansion of the subsurface layer by 0.050–0.075 Å ($\sim$1.5–2.5%) as measured by low-energy electron diffraction$^{28,29}$.

In bulk Gd the unoccupied $f$ states are located 3.6 eV above $E_F$ and the occupied $f$ states 8.8 eV below $E_F$, see Fig. 2(b), reflecting an exchange spin splitting of 12.4 eV. This value agrees with results of the full potential linear augmented plane wave method$^{30}$ and is close to the experimental value of 12 eV$^{31}$. The fact that the Gd magnetic moment (7.43 $\mu_B$) exceeds 7 $\mu_B$ suggests an induced polarization of other orbitals. We find magnetic moments of 0.02, 0.03 and 0.40 $\mu_B$ for the Gd $s$, $p$, and $d$ states, which can be explained by the s-f exchange model$^{32}$. The total Gd magnetic moments are enhanced in the surface Gd layers by 0.9% and 1.9% for the two- and six-layer Gd/MoS$_2$ interfaces, respectively, and reduced by 0.9% and 0.5% in the interface Gd layers. The magnetic moments of the different layers given in Table 1 show no effect for the $f$ states; all changes are carried by the $d$ states. The Gd $d$ DOS in Fig. 7, in contrast to the bulk, shows majority spin states from $-0.5$ to 0.4 eV (from $-0.2$ to 0.2 eV) for the two-layer (six-layer) Gd/MoS$_2$ interface for the surface$^{33–35}$ (more pronounced) and interface Gd atoms. Moreover, a strong hybridization between the Gd $d$, Mo $d$ and $p$ states appears near $E_F$ (see Figs. 3, 4 and 7). The majority and minority spin Gd $d$ DOSs at $E_F$ are different because of an enhancement in the surface and a reduction in the interface Gd layers. In the other Gd layers the Gd magnetic moments are close to the bulk value of 7.43 $\mu_B$. The Gd $f$ DOSs of layers I and II, respectively, show downward shifts of 0.2 and 0.3 eV for the majority spin states and of 0.3 and 0.4 eV for the minority spin states, relative to the bulk Gd $f$ states, where the different amplitude is due to the interaction with MoS$_2$ in layer I. The same is found for the I and VI layers in the six-layer Gd/MoS$_2$ interface, which is consistent with inverse photoemission spectroscopy$^{37}$, while for the II, III, IV, and V layers the shifts are very small. Gd core-level shifts can be attributed to the different chemical environments of the surface and interface atoms, thus being small in other layers.

### Table 1 | Gd 5d and 4f magnetic moments ($\mu_B$) in each layer of the two- and six-layer Gd/MoS$_2$ interfaces, as compared to bulk Gd

| System | Layer | $d$ | $f$ |
|--------|-------|----|----|
| Bulk   |       | 0.4| 7.0|
| Two-layer | I     | 0.3| 7.0|
|        | II    | 0.5| 7.0|
| Six-layer | I     | 0.4| 7.0|
|         | II    | 0.4| 7.0|
|         | III   | 0.4| 7.0|
|         | IV    | 0.4| 7.0|
|         | V     | 0.4| 7.0|
|         | VI    | 0.5| 7.0|

**Conclusion**

We have investigated the geometry, electronic structure, and magnetism at the interface between Gd(0001) and monolayer MoS$_2$. Strong chemical bonds are formed and seriously modify the electronic states of MoS$_2$, especially at $E_F$. Interaction with the Gd $d$ states shifts $E_F$ into the conduction band and makes MoS$_2$ metallic. Large magnetic moments appear on the Mo atoms. Moreover, distinct surface/interface Gd $d$ states are formed at $E_F$ and a clear downward shift of the Gd $f$ states is observed for both the surface and interface, whereas the Gd magnetic moments are enhanced at the surface but reduced at the interface.

![Figure 7](image-url) | DOS of the Gd atoms in the different atomic layers of the two- and six-layer Gd/MoS$_2$ interfaces. $E_F = 0$ eV.
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Author contributions
X.Z. and W.M. designed the outline of the manuscript and wrote the main text. U.S. gave many good suggestions and contributed detailed discussions and revisions. X.W. and Y.C. contributed detailed discussions and revisions. All authors reviewed the manuscript.

Additional information
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