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Orienting spins in dually doped monolayer MoS₂: From one-sided to double-sided doping[†]

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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Electron spins of the doped monolayer MoS₂ were aligned by placing two magnetic impurities at sulfur vacancies, both on the same side and different sides of the slab. Origins of the calculated magnetisms are beyond most conventional physical models, yet interactions of single-molecule magnets are tentatively proposed.

Electron spins are of key importance for magnetism, one of the fundamental properties of matter. Proper doping of magnetic impurities may lead to long-range interaction among ions, and introduce ferromagnetism in the matrix. Hence, dilute magnetic semiconductors (DMSs) were predicted through a simple Zener model in the semiconductive ZnO, taking into account features of the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction.¹ In the metallic matrix, the Kondo effect² describes the coupling of the localized magnetic moments, arising from the screening of impurity spins, with their host or magnetic adatoms below a characteristic temperature. The interplay between the RKKY interactions and Kondo effect was realized in iron dimers buried under Cu(100) surface.³ Recently, the Kondo effect was also revealed on a graphene monolayer, the representative two-dimensional (2D) crystal with semi-metallic features.⁴ In fact, as an inorganic relative of graphene, the monolayer molybdenum disulfide (m-MoS₂) has shown distinct optical^{5,6} and semiconducting properties.⁷ For this reason, investigations of the 2D crystals have further been extended from the organic graphene^{8,9} to the inorganic layered crystals (ILCs).¹⁰

Thanks to non-zero bandgaps and rich forms of compounds and composites, the ILCs have been considered as promising semiconducting hosts in doping strategies. In an analogue to the ZnO-based DMS designs,^{11,12} introducing proper dopants has been considered as an effective way to reach intrinsic DMSs¹³. However, due to stable in-layer covalent bonds, direct substitution of central metal atoms in ILCs is typically not feasible via ion bombardment,

without deterioration of the inorganic complexes.^{14,15} Introducing transition metal (TM) impurities during chemical synthesis can hardly circumvent producing intrinsic defects.¹⁶ Alternatives were suggested e.g. by replacing both Mo and neighboring S atoms with the FeX₆ (X = S, C, N, O, F) clusters¹⁷ or encapsulating the ILC slab with proper composite layers^{18,19}. Adsorption of TM clusters on ideal ILCs has also been reported as a doping protocol.^{20,21} Indeed, large amount of defects, especially sulphur vacancies (V_S) are widely distributed in m-MoS₂, leaving room for materials manipulation.^{22,23} Latest experimental results further proved that the V_S did not deteriorate the layered nature of MoS₂ flakes deposited on carbon coated grids,²⁴ in agreement with theoretical results.²⁰ Magnetism can actually be implanted into ILCs with a single dopant, by filling these vacancies with proper 3d TMs.²⁵ So far, TM atoms or their aggregated forms have only been laid on one side of the ILCs, and dopant types have been limited only one element at any one dose. Similar to coins, the ILCs have two sides where many possible varieties of dopant combinations can be implanted. In contrast to the prototypic, thoroughly studied graphene, long-range interactions of the dopants, as well as interactions through the ILC matrix have not been explicated up to now. Thus, understanding dually-doped ILC systems may yield novel findings in electronic coupling and correlation schemes beyond DMS manipulations.

Fig.1 Doping configurations of the studied transition metal (TM) dopant atom pair at different doping sites of monolayer MoS₂. The cyan, yellow and red balls represent the Mo, S and transition metal dopant atoms, respectively. TM₀ represents always the site of the first TM atom and TM_{1–5} correspond to the different sites of the other one. Dashed circles are used to emphasize the double-sided doping configurations.

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[†]Electronic Supplementary Information (ESI) available: pin densities and total density of states for the doubly-doped systems, spin band structures for the Cr homo-doped and hetero-doped MoS₂ systems, total and partial density of states for hetero-doped MoS₂ systems, partial density of states of dopants, and Hubbard computational details. See DOI: 10.1039/x0xx00000x

Here, we carried out a first-principles study to investigate the magnetic properties of m-MoS₂ that is doubly-doped by two TM dopants, placed either on the same side or different sides of the monolayer. Fig. 1 shows a (5×5) supercell of MoS₂ with double TM adatom configurations. The first TM impurity, TM_a, was fixed at the center of the supercell, positioned as $i=0$ in the doping configuration depicted in Fig. 1. The sites j for the second doping atom, TM_b, are labeled as site 1 directly beneath position 0, and 2 on the same side and in the nearest-neighbor position to 0. To study the geometry-induced magnetism, we further experimented with the V_S sites on the opposite side, and label them as 3, 4, 5, following the increasing distance from position 1. These systems are named as TM_a(i)TM_b(j)-MoS₂ and TM_a(i)-MoS₂-TM_b(j) for the two cases where TM_a and TM_b are implanted on the same side, and on the opposite sides of the layer, respectively. In total, 11 distinct systems were studied, including 5 configurations of Cr homo-element doping and 6 cases of hetero-element doping, where Cr, Co and V dopants have been combined.

All calculations were performed on the PWscf code of the Quantum Espresso package²⁶ at the spin-polarized density functional (DFT) level. For the exchange and correlation energy, the Perdew-Burke-Ernzerhof (PBE)²⁷ generalized-gradient approximation (GGA) was used. Ultrasoft pseudopotentials²⁸ were applied to describe the electron-ion interactions. The Kohn-Sham orbitals were expanded on a plane-wave basis-set with cut-off of kinetic energy at 50 Ry and electron density representation of 500 Ry. In structure optimizations, the effects of van der Waals interactions were included by employing Grimme's semiempirical DFT-D2²⁹ corrections. The electronic and ionic energy gradients were converged to 1×10^{-6} eV and 5×10^{-3} eV/Å, respectively. Gamma-centered Monkhorst-Pack grid with $2 \times 2 \times 1$ Brillouin zone (BZ) sampling was sufficient for the structural relaxation. A vacuum region of 20 Å was selected in the z-direction to exclude mirror interactions.

Table 1 PBE-U calculated coupling values $J = E_{AFM} - E_{FM}$ (in meV), distances D (heights, in Å) of the two TM dopants from the MO layer, total magnetic moments M of the whole supercell (in μ_B), and bandgap value (eV) and type (ID=indirect, D=direct) for the doubly substituted monolayer-MoS₂ systems at uniform concentration $\theta = 2/75$.

Systems	J (meV)	Distance i (Å)	Distance j (Å)	M (μ_B)	Bandgap (eV)/Type
Cr(0)-MoS ₂ -Cr(1)	-17	2.09	2.09	0	0.55/D
Cr(0)Cr(2)-MoS ₂	124	1.81	1.86	8	0.4/ID
Cr(0)-MoS ₂ -Cr(3)	190	2.06	1.94	8	0.2/D
Cr(0)-MoS ₂ -Cr(4)	44	1.96	2.09	8	0.4/D
Cr(0)-MoS ₂ -Cr(5)	4	1.92	1.97	8	0.35/D
Cr(0)-MoS ₂ -Co(1)	350	2.04	1.73	5	0.05/D
Cr(0)Co(2)-MoS ₂	225	1.89	1.50	5	0.35/D
V(0)-MoS ₂ -Co(1)	-441	1.68	1.77	0	0.45/D
V(0)-MoS ₂ -Co(3)	-183	1.73	1.70	0	0.60/D
V(0)-MoS ₂ -Co(4)	-3	1.72	1.61	0	0.45/D
V(0)-MoS ₂ -Co(5)	-32	1.68	1.61	0	0.45/D

The electronic structure properties were computed with a $10 \times 10 \times 1$ BZ. To account for the correlation energy of the strongly localized 3d orbitals of the dopants, the Hubbard U -corrected PBE-GGA was used through a method based on the rotationally invariant DFT+ U formalism.³⁰ The system-dependent effective local Coulomb interaction parameters U_{eff} (tabulated in Table S1 of the Electronic Supplementary Information, ESI) for the TMs, were adopted by the

linear response approach.³¹ The DFT+ U method was also crosschecked with the highly accurate, *ab initio* multiconfigurational CASPT2 method³² to evaluate the effect of the Hubbard correction to the pure GGA. The present results are consistent with those given by Ref.³³ (see Table S2 in the ESI).

Fig. 2 Spin densities of (a) Cr(0)-MoS₂-Cr(1), (b) Cr(0)Cr(2)-MoS₂, and (c) Cr(0)-MoS₂-Cr(3) systems for antiferromagnetic (left) and ferromagnetic (right) configurations. Majority (minority) spin density component is shown in red (blue) with the isosurface value of 0.005 (-0.005) e/Å³.

Fig. 2 illustrates the spread of spin-resolved densities, in both antiferromagnetic and ferromagnetic (AFM/FM) states, for three of the eleven studied doubly-doped systems Cr(0)MoS₂-Cr(1) and Cr(0)-MoS₂-Cr(3), doped on both sides, together with the one-sidedly-doped Cr(0)Cr(2)-MoS₂. Corresponding density plots for the other studied systems are exemplified in Fig. S1 in ESI. These two figures show that, in all cases, the TM-dopant atoms are highly spin-polarized, having same spin-polarization directions, and that the polarization is only spread significantly over the nearest Mo atoms.

The magnetic states of the systems are justified by $J = E_{AFM} - E_{FM}$, the difference between the DFT total energies of the AFM and FM states. The system is AFM when $J < 0$ or FM with positive J values. Table 1 assembles the calculated systems and, in addition to the aforementioned results, their bandgap types and values, total magnetic moments, and distances of the TM ions from the central plane, D_i or D_j . Generally, magnetism in the doubly Cr-doped systems is very different from the antiferromagnetism in the ground state of the Cr₂ dimer.^{34,35} All Cr homo-doped systems, with the exception of the totally geometrically symmetric Cr(0)-MoS₂-Cr(1), are FM in their ground states. Their total magnetic moments are 8 μ_B , which is equal to twice the 4 μ_B of the single substitutional Cr dopant atom.²⁵

The highest coupling value among pure Cr-doped systems is 190 meV in the Cr(0)-MoS₂-Cr(3). Single-sidedly doped Cr(0)Cr(2)-MoS₂ has the second-highest coupling value (124 meV). Obviously, in the former double-sidedly-doped system, the distance between the Cr dopants is longer than in the latter case. This example differs from the general RKKY theorem where smaller distance between dopants corresponds to higher exchange energy.³⁶ Furthermore, exchange energies in the present arrangement are relatively larger than in similar systems with one-sided doping. For instance, Shu et al.³⁷ obtained a 20 meV coupling value for the latter type of system, where Fe atoms reside in the nearest V_S on the same side of the MoS₂ layer. Here, the increasing distance between the Cr atoms, from the Cr(0)-MoS₂-Cr(3) onward, causes a rapid decrease of the coupling

values. For Cr(0)-MoS₂-Cr(4) and Cr(0)-MoS₂-Cr(5), the exchange energy equal 44 meV and 4 meV, respectively. Surprisingly, the Cr(0)-MoS₂-Cr(1) system appears to be AFM with the J value of -17 meV. This is totally different from all the other cases where introducing two high-spin dopants results in even higher-spin FM systems.

The unexpected antiferromagnetic Cr(0)-MoS₂-Cr(1) system inspires additional studies of magnetic interactions in double-sidedly-doped systems. Later, we firstly change TM_b to a less magnetically robust dopant of Co, and then both TM_a and TM_b species. The parameters for the CrCo hetero-doped systems are collected in Tab.1. In the Cr(0)-MoS₂-Co(1) and Cr(0)Co(2)-MoS₂ systems, the total magnetic moments are equal to the sum of the values of the singly-doped Cr(0)-MoS₂ and Co-MoS₂ systems,²⁵ regardless of the doping sides. Double-sidedly-doped systems with the TM₁=V (configuration 4s²3d³) and TM₂=Co (4s²3d⁷) were then investigated. Both bare dopants have 3 unpaired electrons in the 3d orbitals, but are different in the number of paired electrons. All four V-Co doubly-doped systems are AFM. The exchange energy decreases with the dopant separation, implying smaller matrix overlap. However, larger J value was found in the V(0)-MoS₂-Co(j) (j =5) system than the one of j =4. Such a trend again agrees with the CrCr-doped case where more symmetric system tends to be AFM. It is noteworthy that, either with V or Co, the singly-doped ILC systems have a FM ground state with a magnetic moment of 1 μ_B .

Electronic structures are investigated to understand coupling mechanism of the co-doped systems. The spin band structures were plotted in Fig. 3 for 3 CrCr homo-doped systems, and 2 Cr hetero-doped systems. Corresponding total density of states were shown in Fig.S2, and band structures for other systems in Fig.S3-S4 at ESI. Partial density of states (PDOS) for the homo-doped, hetero-doped systems were computed and depicted in Fig.S5 and S6 respectively, while PDOS for dopants and nearest Mo atoms in Fig.S7. Fig. 3 reveals that crossing of the impurity states/bands takes place in (or near) the Fermi level. According to the PDOS analysis for the doubly Cr-doped systems (Fig.S5) it is mainly the spin-polarized Cr-3d states that are responsible for the magnetism, as it was in the case of Fe₃FeS.³⁷ Here in all the eleven systems, the Mo-4d states are partially spin-polarized in the vicinity of the Fermi level but, in the lower energy range, those states are strongly hybridized with the S-3p states, inherited from the stable 2D MoS₂ network.

For the systems with the "beneath" pattern of TM dopants, PDOS of the d electrons for the dopants and three nearest Mo atoms, take care of the most part of the Fermi-level spin polarization of the MoS₂ layer (Fig.S7). The distribution of spin polarizations in both up and down directions is similar for the nearest three Mo atoms in Cr(0)-MoS₂-Cr(1), and hence, the PDOS values of spin-up and spin-down polarizations are exactly equivalent, keeping the aforementioned AFM state (Fig. S7(a)). In contrast, the FM state of Cr(0)-MoS₂-Co(1) is apparently due to the fact that the three nearest Mo atoms have similar down-spin polarization, arising from Cr, at the Fermi level (Fig. S7(b)). Here, Co does not contribute to the spin densities at/next to the Fermi level. In the V(0)-MoS₂-Co(1) system, the strong AFM nature arises from cancellation of the opposite spin polarizations of the nearest Mo atoms (Fig. S7(c)).

The present doping route serves a materials design strategy, where magnetism and band types can be operated simultaneously. Inherited from the m-MoS₂, most of the present doped systems possess a direct bandgap as shown in Fig. 3. The only system that possesses an indirect gap, Cr(0)Cr(2)-MoS₂ (in Fig. 3(b)), features a quasiparticle band structure where emerging electronic transitions can be prompted by the existence of phonons.³⁸ Introducing double dopants into the system lowers the bandgaps as viewed in Fig. 3 and

Table 1. Noteworthy, the CrCo hetero-doped case (Fig. 3(d,e)) features a band opening from semimetallic Cr(0)-MoS₂-Co(1) to the value of the gap equal to 0.35 eV in Cr(0)Co(2)-MoS₂. In the case of antiferromagnetically coupled CoV hetero-doped systems, the gap increases from 0.45 eV to a value of 0.6 eV in V(0)-MoS₂-Co(3). Similar to the CrCr homo-doped systems, the bands around Fermi level in the hetero-doped systems also arise from the hybridization between the TM and the host. Additionally, the proposed materials design route is also practical. *In-* and *ex-* situ controls of the defects have been realized down to atomic level²³, while the free-standing MoS₂ layers have also been found stable under external voltages³⁹. Furthermore, low energy ion implantation has already been proved as efficient route to precisely introduce external dopants in the monolayer MoS₂⁴⁰. Benefiting from these latest progresses, double-sided doping is very feasible to be realized on a free-standing but defective MoS₂ monolayer.

Fig. 3 Spin band structures of (a) Cr(0)-MoS₂-Cr(1), (b) Cr(0)Cr(2)-MoS₂, (c) Cr(0)-MoS₂-Cr(3), (d) Cr(0)-MoS₂-Co(1), and (e) Cr(0)Co(2)-MoS₂. In (f), the band structure of spin-unpolarized MoS₂ is given as a reference. Red (blue) bands correspond to spin-up (spin-down) states.

The spin interactions of doubly-doped ILC systems are beyond explanations furnished by conventional interpretations of magnetic mechanisms in DMS systems.⁴¹ Magnetic exchange schemes or their interplays⁴² are not valid here due to distances or absence of a non-metal atom between the dopants. Magnetic interactions through the electron sea of the host are vetoed in present semiconducting systems, invalidating explanations from Kondo effect. The interactions do not follow the RKKY theorem neither in the coupling energy distance variation nor the magnetic moments. Here we notice that the final magnetic states of the doped systems are influenced by the geometric arrangement of the dopants, and the magnetism of the singly-doped systems. For this reason, we tentatively propose an explanation based on single-molecular magnets (SMM)⁴³ and their magnetic couplings with the environment. In general, after being placed at the V_s, each dopant constitutes a SMM locally. This magnet has the 'north' and 'south' poles defined by the symmetry of the ILC

plane.⁴⁴ It also has the possibility of acting as a normal magnet, to magnetize other matter, or being a ferromagnet, becoming magnetized itself. The stability of the magnet is ensured thanks to the hosting capability of the ILC. In the cases where two strong SMMs are not placed in a zig-zag configuration, the SMMs act individually, leaving the magnetic moment of the total system equal to double the individual ones. However, when the two strong SMMs are placed directly opposite to each other, the spin-up and spin-down states are overlapping spatially, as if two magnets were placed back-to-back with the N(S)-pole of one next to the N(S)-pole of the other, leaving the total magnetic moment at zero. The host slab is more distorted due to the repelling forces induced in this case, as seen from the Cr distances to the central plane in Cr(0)-MoS₂-Cr(1). When a strong SMM is placed next to a ferrimagnet (Cr(0)-MoS₂-Co(1)), the latter will be magnetized and align with the polaron direction. When two ferrimagnets are placed nearby (V(0)-MoS₂-Co(1)), the states again cancel each other, making the full system AFM. The SMM also interacts with the substrates, forming different magnetic states. In the V-Co co-doped systems, the singly-doped MoS₂-Co(*j*) (*j*=3,4,5) acts as the ferrimagnetic but non-metallic substrate, while the V-SMM as a magnetic dopant. Interactions at molecule-magnetic surface interface results in the antiferromagnetism of the system, in an analogy to the latest results where the TM-complex SMM may be antiferromagnetically coupled to the ferrimagnetic surface.⁴⁵

In conclusion, through first-principles predictions, we have presented a manipulation strategy of electron spins in doped MoS₂ monolayer, by placing two magnetic impurities at sulfur vacancies. Very different from the single-dopant doping routes, the present work shows a possibility to create also antiferromagnetic and ferrimagnetic states, by novel double-sided doping, on the low-dimensional host. Based on the computational results, interactions of single-molecule magnets were tentatively proposed to explain the obtained results. However, analytical explanations remain elusive. Taking the large variety of the 3d TM combinations and geometric placements, the present work is hoped to debut a material design route to meet urgent materials functionalities, and a computational framework to be enriched successively. We also hope that the work will inspire theoretical investigation at microscopic level, as well as experimental realizations in orienting electron spins by precisely engineering sulfur vacancies²³ on free standing monolayers.²⁴

The Academy of Finland is acknowledged: Nos. 285666 (PL) and 296292 (JVa). The work is also supported by Oulu University Strategic Funding, EU Regional Development Fund and Council of Oulu Region. Computations were partially performed at CSC Finland.

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Single- and double-sided doped monolayer MoS₂ show electron spin alignments with their origins beyond explanations of exist models.