

Density-functional study on the magnetic properties of Re atom adsorbed by MoS₂ single layer

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Abstract. We have investigated the magnetic properties of Re atom adsorbed by single layer MoS₂ by first-principle calculation. Our results reveal that the cohesive energy of the adsorbed Re is 1.7 eV and the total moment of the adsorbed system is $3.0 \mu_B$. The magnetic anisotropy reaches 19.0 meV and the easy axis is perpendicular to the surface of MoS₂ layer. The giant anisotropy mainly comes from the strong spin-orbital coupling of 5d orbital of Re, which hybridizes with 2p orbital of S.

1 Introduction

Low-dimensional materials have attracted much attention for their fascinating electric and magnetic properties. Previously, researchers believe that the strict single atom layer can not exist in real world due to the large thermal fluctuation in low-dimensional materials. However, this opinion has changed since the single layer graphene has been discovered and fabricated. Recently, metal-dichalcogenide MoS₂ has attracted much attention due to their semiconducting properties. It has been widely used in lubricants, electrodes and catalyzers. Similar to graphene, the single layer MoS₂ can be exfoliated from the bulk material.[1] The bulk MoS₂ is the semiconductor with indirect energy gap of 1.29 eV, while the single layer is the semiconductor with direct energy gap of 1.8 eV. The single layer MoS₂ has been used to fabricate the heterostructure of thin films, which have important application in optoelectronics and spintronics devices.[2] Pristine MoS₂ is nonmagnetic and by doping or adsorbing the magnetic atoms, the magnetism can arise in the doped system. The magnetism of doped MoS₂ has been investigated widely. However, the adsorption of transition metal atoms for MoS₂ has rarely been studied.

In this article, we have investigated the magnetic properties of Re atom adsorbed by single layer MoS₂ by first-principle calculation. The cohesive energy, density of states and energy band of the adsorbed system are calculated. We studied the effect of adsorption on the magnetic and electronic properties of the adsorbed system. Moreover, spin-orbital coupling is also included in our calculation and the magnetic anisotropy is calculated.

Methods

The lattice of MoS₂ belongs to hexagonal system and the space group symmetry is P63/mmc. The distance between nearest Mo layers is 6.4 Å. The force of Van Der Waals type dominates between the layers and sliding is much easy to occur between layers. We build the single layer supercell with size of 3×3×1 from the unit cell of MoS₂. Totally, 9 Mo atoms and 18 S atoms exist in the supercell. A slab of vacuum with thickness of 10 Å was added to the layer to prevent the overlaps of atomic waves from the image layer. Re atom initially was relaxed from the position shifted above the surface of MoS₂ with 3.0 Å until it was adsorbed by three sulfur atoms. The relaxed structure was shown in Fig. 1.

We calculate the magnetic properties of the adsorbed system by projected augmented wave method, as implemented into VASP computing code. The energy cut off of plane waves is set to 400 eV. The conjugate-gradient algorithm is used to relax the atoms to equilibrium positions with the force criterion 0.01 eV/Å. Generalized gradient approximation of Perdew-Burke-Ernzerhof form is used for

the exchange-correlation potential. [3] Spin-orbital coupling was included via second variational method with scalar-relativistic basis.[4] A $7 \times 7 \times 1$ k-mesh is used for the Brillouin sampling.

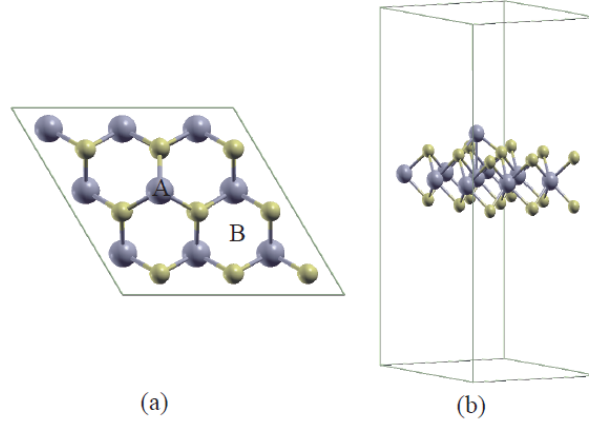


Fig. 1: (a) Top view of MoS_2 layer adsorbed by Re. Possible sites of adsorption are labeled by A and B. (b) Side view of the adsorbed system. Re atom locates on the surface of sulfur layer. The yellow spheres represent sulfur atoms. Mo layer lies between the sulfur layers.

Calculation results

In the same layer, the sulfur atoms are arranged into the triangular lattice. Each Mo atom lies exactly below the center of three sulfur atoms. Therefore, there are two different positions for the adsorption of Re, as shown in Fig. 1(a). There is one Mo atom lies below the position of A while it is hollow for the position of B. Our calculations reveal that the system has lower energy when Re is adsorbed to the site A. The adsorption on A site is about 1.18 eV lower in energy than the adsorption on B site. Therefore, we deduce that Re atom prefers to occupy the A site. Due to the adsorption, the three nearest S atoms lift about 0.1 Å compared to the other S atoms. The bond length of Re-S is 2.22 Å, which is significantly less than the bond length of Mo-S. To indicate the magnitude of adsorption, we define the cohesive energy as $E_c = E(\text{Re}) + E(\text{MoS}_2) - E(\text{Re@MoS}_2)$, where $E(\text{Re})$ and $E(\text{MoS}_2)$ are the energy of isolated Re atom and pristine MoS_2 layer. Our results reveal that the cohesive energy reaches 1.70 eV, which is larger than the cohesive energy of graphene adsorbed by magnetic atoms.

To study the electronic structure of the adsorption system, we calculate the density of states (DOS) and show them in Fig. 2. Due to the adsorption, local states are introduced into the energy gap. The local states mainly comes from the 5d states of Re. Because of the p - d hybridization between S and Re, additional states are introduced to the energy gap. Compared to the 5d states of Re, the 4d states of Mo mainly lie below the Fermi level. Also, the spin splitting mainly occurs to the 5d states of Re. For the majority states, two peaks emerge near the Fermi level, which is caused by crystal field. Our results reveal that Re has the local moment of $1.40 \mu_B$ while the nearest S atoms have the moment of $0.02 \mu_B$. The nearest Mo atom becomes also spin-polarized and has the moment of $0.45 \mu_B$. The total moment of the system is $3.0 \mu_B$. Bader charge analysis indicates that totally 1.1 charge transfers to the MoS_2 layer.

We also calculate the spin-orbital coupling (SOC) of the adsorbed system. Essentially, SOC originates from the relativistic effect. The energy of SOC can be expressed as $E_{soc} = -\langle \psi | \xi \hat{s} \cdot \hat{L} | \psi \rangle$, where ξ is the parameter of SOC and $\xi \propto Z^4$. When heavy atoms are introduced and the system has much high DOS near the Fermi level, the SOC effect is remarkable. SOC can be affected by the spin orientation. Thus we define the magnetic anisotropy as $\Delta E = E_{soc}(\parallel) - E_{soc}(\perp)$, where $E_{soc}(\parallel)$ and $E_{soc}(\perp)$ are the energy of system with atom spin lying in and out of the plane respectively. Our results reveal that the magnetic anisotropy of Re atom is 19.0 meV and the easy axis is out of the MoS_2 plane.

This value is significantly larger than the anisotropy of 9.0 meV for single atom Co grown in Pt surface.[5]

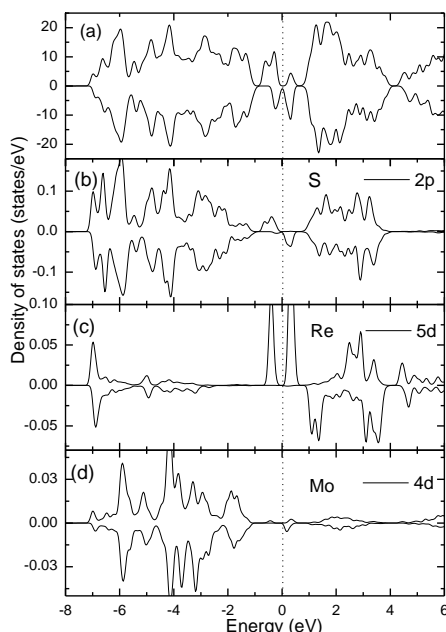


Fig. 2: (a) Total density of states. (b) 2p states of S. (c) 5d states of Re. (d) 4d states of Mo.

Conclusions

We have investigated the magnetic properties of MoS₂ single layer adsorbed by Re atom. The cohesive energy is 1.70 eV and the total moment is $3.0 \mu_B$. The adsorbed Re atom introduce local states in the energy gap. Our results reveal that the magnetic anisotropy is about 19.0 meV and the easy magnetic axis is out of the MoS₂ plane.

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