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Full Length Article

Electronic, magnetic properties of transition metal doped Tl_2S: First-principles study

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ABSTRACT

In this paper, the structural, electric and magnetic properties of transition metal (TM) doped monolayer Tl_2S are investigated by means of first-principles methods The results show that all the considered TM atoms are strongly bonded to the Tl vacancy site. The magnetic moment, the dilute magnetic semiconductor and metal characteristics are varied depending on the specific TM atoms. The TM doped Tl_2S (TM-Tl_2S) (from Sc to Ni) systems have fractional magnetic moments changing from 0.539 μ_B to 4.479 μ_B. However, Cu- and Zn-Tl_2S systems exit the nonmagnetic ground states. The spin polarized metallic states are achieved by Sc, Ti, V, Mn and Fe doping, while spin polarized semiconducting states are realized by Cr, Co and Ni doping. The charge transfer, the total magnetic moment and the band gap obtained with PBE method are less than the values obtained by PBE + U, which suggests that the Hubbard U plays an important role in TM-Tl_2S systems. In the case of two same types of TM atoms doped Tl_2S systems, there exist AFM in Sc-, V-, Mn-Tl_2S systems and FM only in Ti-Tl_2S system. Interestingly, the Cr-, Fe-, Co-, Ni-Tl_2S systems manifest paramagnetic. These findings may provide a new route for exploring two-dimensional diluted magnetic semiconductors experimentally and theoretically.

1. Introduction

Much attention has been paid to two-dimensional (2D) materials after graphene was first isolated during the past decade, because 2D materials show many intriguing properties which are not found in their bulk counterparts [1–7] and are considered as cornerstones of the future nanoscale electronics and spintronics [8,9]. Recently, more and more 2D materials have been produced experimentally, such as transition-metal dichalcogenides, black phosphorus, arsenene and antimonene [10–16]. In the process of developing new 2D materials, lately, a few scientists have gradually begun to show solicitude for metal chalcogenides with layered structure. It is reported that group 13 chalcogenides generally are semiconducting in nature, forming binary and ternary compounds with a chain or layered structure [17–19]. Group 13 chalcogenides have much importance in the field of both fundamental research and technical applications because of exhibiting intrinsic vacancy structure, optical, electronic, and photoelectronic properties. Very recently, thallium chalcogenides (Tl_2S) has received a great deal of attention due to Tl_2S having an unique anti-$CdCl_2$ structure, where the chalcogen atom (S) is the central atom instead of the metal atom Tl, which is also the inverse of transition-metal dichalcogenides such as MoS_2 [20–22]. Traditionally, Tl_2S, described as the rare mineral carlinite [23] with black, soft and extremely platy substance characteristics, has been synthesized [20,24]. Tl_2S nanorods were prepared via solvothermal route with the addition of KI [25]. Newly, study reported that single crystals of Tl_2S with layered structure were fabricated from pure (5N) elements in an evacuated silica tube (10−6 Torr) of 1.5 cm diameter and 20 cm length [26]. These lay a good foundation for further theoretical and experimental research to explore the nature of Tl_2S.

The extensive research on diluted magnetic semiconductors (DMSs) has set off a craze in scientific community during past years due to the DMSs giving rise to potential applications in spintronics. Initially, the study concentrates almost entirely on the transition metal doped three-dimensional (3D) semiconductors. Lately, tremendous interest was motivated in two-dimensional (2D) materials such as graphene, h-BN, black phosphorene, transition metal dichalcogenides [27–30]. The metallic character prevents the graphene putting into the practical electronic devices, because it

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is very difficult to control the charge and magnetic states though graphene has been considered as a promising host material for TM implantation. The h-BN and black phosphorene overcome the difficulty of the band gap zero and proved to be the prospective host for the DMSs, however they are chemical instability if the systems are exposed to air. Cheng et al. reported MoX_2 (X = Mn, Fe, Co, and Zn) are promising systems to explore two-dimensional DMSs [31]. Magnetism is observed for Mn, Fe, Co, Zn doping and the C_{3v} symmetry is maintained, while Jahn-Teller distortions are found in other dopants of transition metals. This inspires our passion for researching electronic and magnetic properties of the TM doped Tl_2S (TM-Tl_2S). The study on the electrochemical and electronic properties of the Tl_2S reveals that Tl_2S displays a competent performance as a hydrogen evolution reaction electrocatalyst compared to a conventional glassy carbon electrode [31]. As far as we know, there has been rarely study on the stability of Tl_2S layer structure. The magnetic and electronic characters of TM-Tl_2S remain unexplored so far. Therefore, it is necessary to perform a systematic study of TM doped Tl_2S.

In this work, we firstly verify that the Tl_2S monolayer is dynamically stable by calculating its phonon spectra. Then, we focus on exploring the electronic and magnetic properties of TM-Tl_2S systems. Our investigation may provide useful information regarding DMSs.

2. Computational details

We address all the calculations of TM-Tl_2S using the spin-polarized density functional theory (DFT) by Vienna ab initio simulation package (VASP) [32–34]. The generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) is used for an exchange functional, because GGA is very accurate to predict the magnetic states of TM atoms [28,35–37]. On the other hand, the electron correlation effect may play a role for magnetic properties of TM atoms due to the localized d orbital. Therefore, in order to get the magnetic states of TM-Tl_2S, we add the Hubbard U term to the DFT Hamiltonian and perform PBE + U calculations. The values of U are adopted as following: 4.0, 5.5, 3.3, 3.5, 3.5, 4.3, 3.3 and 6.5 eV for Sc-, Ti-, V-, Cr-, Mn-, Fe-, Co-and Ni-Tl_2S, respectively, which is verified reliably [30]. Moreover, a kinetic energy cutoff of 500 eV is selected for the plane wave expansion and high precision calculation. The Monkhorst–Pack k-point sampling $5 \times 5 \times 1$ is used for the Brillouin zone integration. A vacuum space of 20 Å is introduced to avoid interactions between images. All the structures are fully optimized with respect to the ionic positions until the forces on all atoms are less than 0.01 eV/Å. All simulations are carried out for a 4×4 supercell with 16 S atoms and 31 Tl atoms with approximately a doping concentration of 2.08%, as shown in Fig. 1(b). In order to clarify the magnetic interaction between two impurities, we also introduce two same type TM atoms in one 4×4 supercell with impurity concentration about 4.2%.

3. Results and discussion

The unit cell of monolayer Tl_2S has two Tl atoms and one S atom as shown in Fig. 1(a). The bond length of Tl—S is 2.946 Å, which matches with previous results: the Tl—S distance varies between 2.82 Å and 3.09 Å [20]. The optimized lattice constants are $a_1 = a_2 = 4.15$ Å, which agree with the cell parameters of the single crystal reported by experiments [20]. In order to theoretically verify the monolayer Tl_2S being dynamically stable, the phonon spectra are calculated as shown in Fig. 1(d). The absence of imaginary frequencies demonstrates that the monolayer Tl_2S is stable when described by the chosen potential parameters. Therefore, this lays

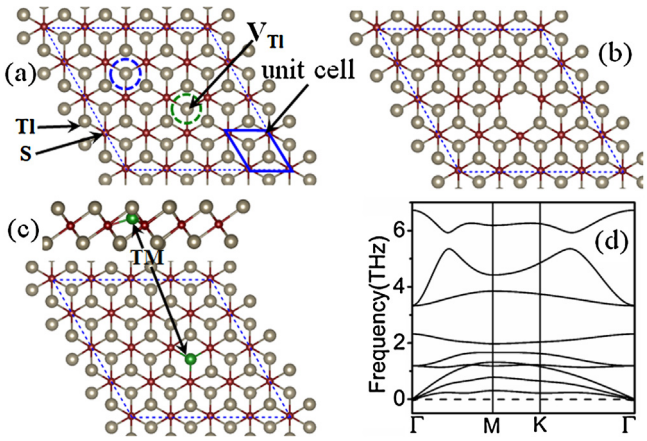

Fig 1. (a) The optimized atomic structures of unit cell and 4×4 supercell of monolayer Tl_2S, (b) V_{Tl} defect of monolayer Tl_2S, (c) single TM substitutional doped Tl_2S, (d) the phonon dispersion of monolayer Tl_2S. The green and blue dashed circle indicates the V_{Tl} site. The wine red and grey spheres represent the S and Tl atoms, respectively. The TM atom is labeled into black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

a foundation for theoretical research of monolayer Tl_2S properties and experimental synthesis of monolayer Tl_2S.

For the TM doped system realization, such as TM-MoS_2, TM-phosphorene, there are two steps as following: first creation of the vacancy (V) and then incorporation of TM dopants into the vacancy site. Therefore, our discussion begins with considering an individual Tl atom vacancy (V_{Tl}) and an individual S atom vacancy (V_S), respectively. The vacancy structures are achieved by removing one S atom or one Tl atom from a 4×4 supercell of the perfect Tl_2S sheet. The vacancy formation energy (E_{vf}) is defined as:

$$E_{vf} = E_v + E_M - E_p$$

where E_v is the total energy of the Tl_2S monolayer sheet with the V_S(V_{Tl}), E_M is the total energy of a free S (Tl) atom, E_p is the total energy of the perfect Tl_2S sheet. The calculated vacancy formation energies are 5.67 eV and 3.34 eV for a V_S and a V_{Tl}, respectively. Hence the formation of a V_{Tl} requires less energy than that of a V_S. On the contrary, in the MoS_2 system, the formation of a Mo vacancy requires more energy than that of a S vacancy [27]. In the following, we pay attention to the monolayer Tl_2S with the V_{Tl}, which is energetically easier to be produced than the V_S. Under the structure relaxation, similar to MoS_2 with the S vacancy [38], the symmetry is maintained for the monolayer Tl_2S with the V_{Tl} (See Fig. 1(c)). There are no significant displacements for the neighboring Tl and S atoms with respect to the vacancy site, which is different from the clear distortion in graphene sheet with a single C vacancy [39] and in phosphorene sheet with a single P vacancy [30]. The ground state of monolayer Tl_2S with V_{Tl} (V_S) has no magnetism, which is the same as the MoS_2 with the S vacancy [27] and the blue phosphorene sheet with a single P vacancy. While the vacancy cause a magnetic moment of 1.00 μ_B/unit cell in the black phosphorene sheet with a single P vacancy [30].

Previous research reported that pulsed laser deposition can be used to dope graphene experimentally by single transition metal atom, such as Pt, Co, and In [35]. At the same time, Co doping can be picked up at the MoS_2 edge by sulfidation of a mixture of ammonium heptamolybdate and cobalt nitrate [35]. Therefore, from a technical point of view, the same approaches may be applied to realize TM doped Tl_2S. Next, we turn to investigate the geometrical structures, stabilities, charge transfer and magnetic properties of the TM-Tl_2S systems. Various TM atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) were taken into account in this work. The typical atomic structures of TM-Tl_2S systems are shown in Fig. 1(c).