



Communication

Insight into the origin of magnetism in Iron-doped cadmium sulfide thin films from first principles calculations



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ABSTRACT

We report a theoretical study of electronic structures and magnetic properties of Fe-doped CdS (10–10) thin films using first principle calculations within the density functional theory. It is shown that Fe atoms occupying Cd sites prefer to reside on the surface and couple antiferromagnetically. However, our results show the existence of competition between ferromagnetic and antiferromagnetic coupling because of the smaller total energy difference. Moreover, our density of states shows the existence of a simultaneous hybridization between the Fe *d* and S *p* states near the Fermi level.

The development of new spintronic materials with high Curie temperatures remains priority of many scientists [1,2]. As a particular magnetic material, dilute magnetic semiconductors (DMSs) have received a much attention due to combine of magnetic and semiconductor properties, hence high potential for spintronic materials [3–7]. Moreover, the importance of ferromagnetic semiconductors has increased due to their potential as spin-polarized carrier sources and the relative ease of their integration into spintronic devices [8,9]. Nowadays, experimental and theoretical studies have been achieved to show ferromagnetic properties into the host semiconductor (e.g., GaAs, ZnTe, CdS) materials doped with transition metal impurities (e.g., V, Cr, Mn, Fe, Co or Ni). Following the prediction of Dietl *et al.* [10] based on the Zener mean-field model that the transition metals doped wide band gap semiconductors should result in a Curie temperature exceeding room temperature. Recently, the success of the research in graphene [11] has led to growing in developing and designing other single-layer 2-dimensional spintronics materials as boron nitride (BN), silicene, and transition metal dichalcogenides (TMDCs) [12,13]. More recently, another new family of DMS's based on the I–II–V semiconductor LiZnAs has been discovered, including compounds such as the “111”-type Li(Zn,Mn)As [14], “122”-type (Ba,K)(Zn,Mn)₂As₂ [15], and (Ba_{1-x}K_x)(Zn_{1-y}Mn_y)₂As₂ (*T_C* = 185 K, 180 K) [16,17].

Since the original report of ferromagnetism in Mn-doped GaAs above 100 K [18], alternative materials such as III–V [19,20], oxides [9,21–24] and II–VI [25,26] also have proven to exhibit room temperature ferromagnetism. Moreover, II–VI based DMSs have been investigated extensively due to possibility of optimizing the lattice constant and band gap parameters by varying the composition of the

material. Among the potential II–V DMS, CdS (owing to the wide band gap of 2.42 eV [27]) is a potential host material for DMS under doping with 3d transition metal impurities. Recently, many studies of CdS have been realized in photo-catalysis, solar cells, gas sensors, biological sensors, and magneto-optical devices [28–30]. These studies demonstrated that doping efficiency can optimize the optical properties and magnetic properties. As a result, CdS-based thin films have been synthesized recently, including Fe and Ni-doped nanocrystalline films, which are ferromagnetic at room temperature [27,31–33]. In a recent study El-Hagary and Soltan [32] reported that the nanocrystalline Fe-doped CdS thin films samples have been found to show ferromagnetic between room temperature and low temperature (5 K) with a Curie temperature at or above room temperature. Previous *ab-initio* calculations [34] on bulk Fe-doped CdS found half-metallic ferromagnetism character. In order to investigate the mechanism of ferromagnetism in Fe-doped CdS thin films, we have explored in the present work the electronic and magnetic properties of Fe doped CdS thin films by using first principles calculations. We have determined the preferential site of Fe, the relative stability of ferromagnetic and antiferromagnetic configurations and magnetic moment.

Our calculations were carried out by using the projected augmented wave (PAW) method [35] within density functional theory as implemented in the Vienna Ab initio Simulation code [36]. The generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof [37] functional was used to treat the exchange–correlation interaction between electrons. The energy cut-off of 500 eV for the plane wave was used. We applied the rotationally invariant version of the GGA+*U* method developed by Liechtenstein *et al.* [38]. The on-site Coulomb interaction, *U*, and on-site exchange interaction, *J*, were applied to the

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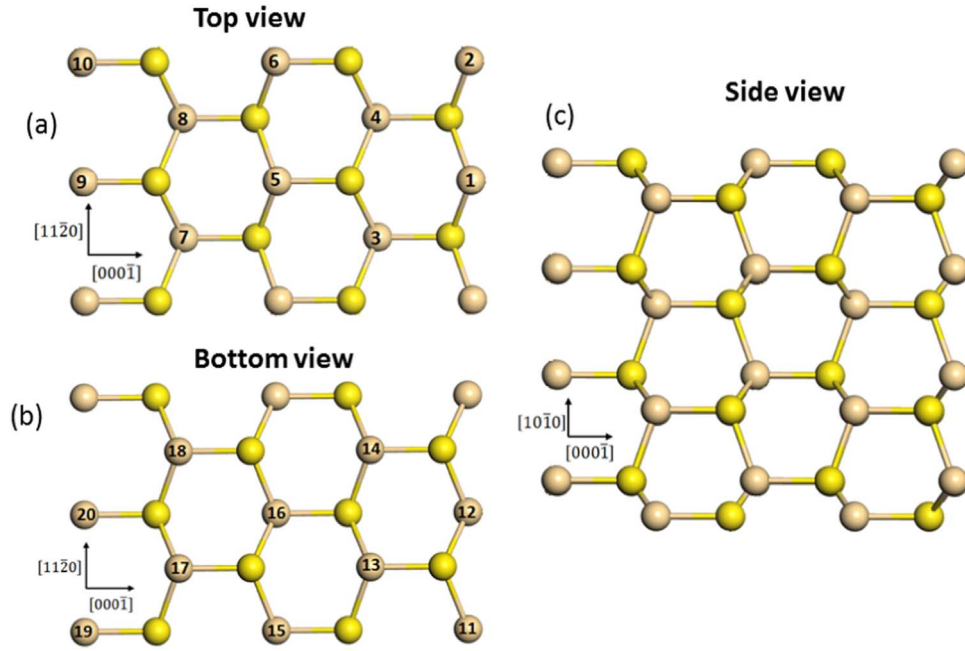


Fig. 1. (Color online) (a) Top view, (b) bottom view and (c) side view of eight layer slab model for CdS (10-10) surface. The silver balls (bluish-gray metallic) are Cd atoms and the yellow (lemon) are S atoms.

d orbitals of Fe (3 eV and 1 eV, respectively), as suggested in Ref. 39. All atoms in the unit cell were fully relaxed until the force on each atom is less than 0.005 eV/Å. All Brillouin zone integrations were performed according to Monkhorst-Pack scheme [40]. Meshes of $6 \times 4 \times 1$ and $8 \times 6 \times 2$ points were found to be enough for the geometry relaxation and electronic structure calculations, respectively.

We build the CdS thin film from the optimized wurtzite bulk stable CdS structure with lattice constants $a=4.204$ Å and $c=6.842$ Å which are overestimated by 2.1% and 1.72%, compared to the experimental values $a=4.119$ Å and $c=6.7264$ Å [33], respectively. The CdS thin film was modeled by a (1×2) eight-layer slab supercell in [10] orientation, as shown in Fig. 1. Our CdS thin film model contains 32 Cd atoms and 32 S atoms. The top and bottom surface layers are separated from other slabs by a vacuum region of 10 Å thickness to avoid the interaction between layers induced by the periodic boundary condition. Our supercell takes into consideration surface effects which are neglected in bulk calculations [41,42]. Note that in our model, the top and bottom of the slab are equivalent by symmetry since the substitution of Cd by Fe atoms is done on both sides of the slab. To examine the energetically preferable positions of Fe dopants, we calculated the total energy of substitutional Fe on the surface and subsurface layers. The surface site is 1.96 eV in energy lower than that the subsurface site, indicating that the surface is preferable for substitution.

To investigate the properties of Fe-doped CdS thin films, we started by calculating the magnetic interaction between two Fe atoms and the preferable positions of the dopants atoms. For this aim, we substituted two Cd atoms by Fe atoms on the top and bottom of the CdS slab. This yields a dopant concentration of 12.5% for Fe doped CdS thin films. The geometry optimization and total-energy calculations were carried out corresponding to both ferromagnetic (FM) and antiferromagnetic (AFM) spin alignments to find the lowest energy configuration, and hence the preferred geometrical and magnetic states. In the present work, seven distinct replacing configurations are considered, as shown in Fig. 1.

In configuration I, two Cd atoms are replaced by Fe at nearest-neighbor sites (Nos 5 and 6) at top and (Nos 17 and 18) at bottom on the surface layer (with distance of 4.137 Å). In configuration II, two cations sites are substituted by Fe on sites (Nos 2 and 6) at top and

(Nos 14 and 18) at bottom on the surface layer with a large distance of 6.714 Å. Configuration III represents the replacement of Cd atoms with Fe atoms at sites (Nos 1 and 6) and (Nos 13 and 18) on the surface layer with a large distance of 7.887 Å. Configuration IV is obtained by replacing one Cd atom on the surface layers and the other on the subsurface with Fe atoms i.e. (Nos 6 and 8) at top and (Nos 18 and 20) at bottom with distance 4.120 Å. Configuration V corresponds to the replacement of one cation site on the surface layer and the other on the subsurface with Fe atoms at sites (Nos 3 and 6) and (Nos 15 and 18) (see Fig. 1) with a large distance 7.166 Å. Configuration VI corresponds to substitution at two nearest-neighbor Cd atoms on the subsurface layer with Fe atoms on sites (Nos 3 and 4) at top and (Nos 15 and 16) at bottom of the slab of distance 4.137 Å. Finally, in configuration VII two Cd atoms are replaced by Fe on the subsurface layer with a large distance of 7.887 Å with labels (Nos 4 and 7) at top layer and (Nos 16 and 19) at bottom layer.

Our total energy calculations in Table 1 show that configuration II is the ground state with lowest energy than the other configurations with the AFM ground state (The FM state is 0.001 eV higher in energy). This indicates that the Fe atoms show surface site preference and prefer to be close to each other. We find that the FM state for configurations II and III with Fe atoms substituting at various surface sites, is higher in energy than their corresponding AFM states. Furthermore, when the distance between Fe impurities on the surface layer increases, the energy differences decrease. This involves that the AFM state is slightly preferred than the FM state. In the case of

Table 1

The calculated energy difference (ΔE) between AFM and FM states, the relative energy ($\Delta \epsilon$) and the optimized nearest Fe1-Fe2 distances as well as the preferred coupling mode for each of the configuration.

Configurations	ΔE (eV)	$\Delta \epsilon$	$d_{\text{Fe1-Fe2}}$	Coupling
I	-0.001	0.401	4.137	AFM
II	-0.001	0.000	6.714	AFM
III	-0.006	0.010	7.887	AFM
IV	0.007	0.092	4.120	FM
V	-0.132	0.265	7.166	AFM
VI	-0.064	0.273	4.137	AFM
VII	-0.085	0.141	7.887	AFM

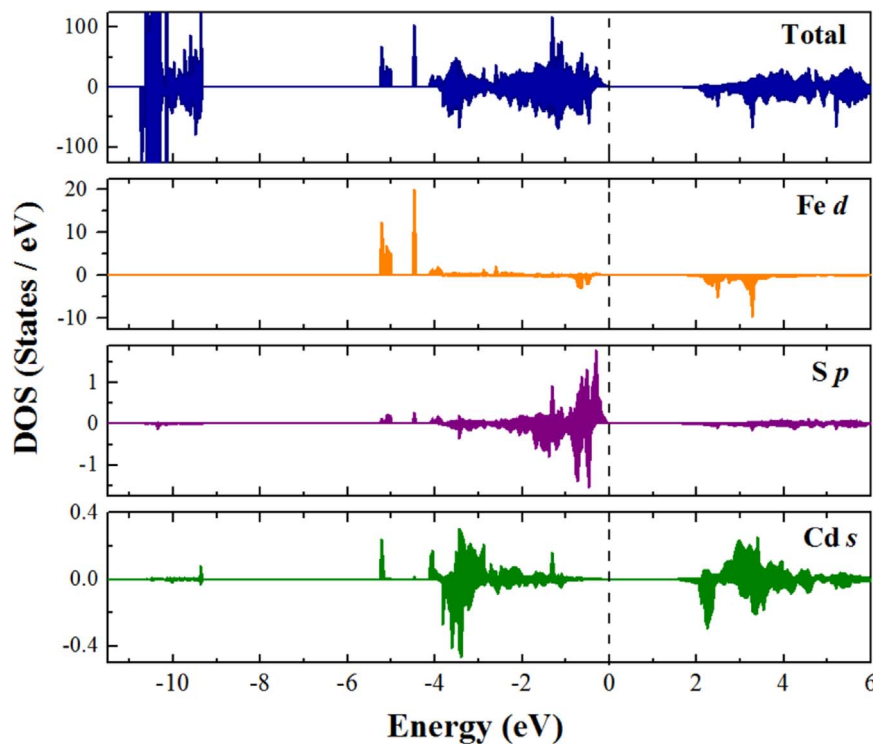


Fig. 2. (Color online) Total spin-polarized density of states for Fe-doped CdS thin films. Spin up and spin down DOS are shown as positive and negative, respectively. The vertical solid line denotes the Fermi level.

configuration IV, the FM state is 0.007 eV lower in energy than the AFM state indicating that the FM coupling is energetically favored over AFM. Our results reported in Table 1, show that there is a competition between FM and AFM coupling because of the smaller energy difference for configurations I, II, III and IV. The configurations VI and VII in which Fe atoms are substituted on the subsurface layers prefer AFM coupling. It was found that their relative energies are higher than those of configuration I.

Furthermore, our results show that configuration II, where the two Fe atoms were substituted on the surface layer, is the ground state, indicating also that Fe prefers to be on the surface. Our geometric optimization shows that the Cd–O bond length along the [0001] and [1–100] directions changed from the initial 2.53 Å and 2.52 Å, to 2.55 Å and 2.45 Å, respectively. The Fe–O bond length decreases from 2.53 Å and 2.52 Å, to 2.30 Å and 2.22 Å, respectively. In contrast, the bond length between Fe–Fe is slightly increased from 6.71 to 6.77 Å. Note that the magnetic moments are mainly localized on the surface Fe atoms, with a local magnetic moment of $3.50 \mu_B$ which is similar to the magnetic moment distribution in Fe doped ZnO [43]. Note also that the S neighbors of Fe atoms on the surface and subsurface layers show smaller magnetic moments of $0.024 \mu_B$ and $0.040 \mu_B$, respectively, while Cd atom carries a weak magnetic moment of $0.014 \mu_B$.

To deeply elucidate the electronic structures of Fe-doped CdS and address the origin its ferromagnetism, we calculated the total and partial density of states (DOS) using GGA+*U* approximation, as shown in Fig. 2. The DOS of the majority spins and minority electrons of Fe-doped CdS thin films exhibit an asymmetric near the Fermi level, indicating ferromagnetic behavior (see Fig. 2). However, the partial DOS shows Fe-induced states in the lower part of the valence band and at the bottom of the conduction band. Though the majority states of Fe states are located at –6 to –2 eV from the top of the valence band, while unoccupied minority states of Fe peaks are merged into the minimum conduction band. It is interesting to note that the Fe doping maintains the insulating nature of CdS. Furthermore, the top of the valence band of CdS thin films is mainly built up from S 3p and Fe 3d states and the conduction band (CB) is mainly from Cd 5 s states. In addition, due to

the decomposition of the DOS shown in Fig. 2, the substitutional Fe impurities dominate the upper region of the valence-band and overlap with its nearest neighboring S 3p states. It is clear that the p–d hybridization mechanism is responsible for the predicted ferromagnetism.

We have investigated the electronic structure and magnetism of Fe-doped CdS thin films using ab initio calculations. It was found that a single dopant atom preferred to occupy the surface site. Furthermore, the magnetic ground state is antiferromagnetic coupling when two cations sites were substituted by Fe on the surface layer sites. In addition, Fe-induced state contains a large contribution of Fe d states together with small components of S 2p states, demonstrating the occurrence of the S 3p–Fe 3d hybridization. This hybridization between Fe 3d and S 3p orbitals has led to small magnetic moments on the sulfur atoms. Our results endorse that Fe-doped CdS thin films might be promising for efficiently realizing nanoscale magnetic device.

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