Magnetic properties of carbon doped CdS: A first-principles and Monte Carlo study

Hui Pan and Yuan Ping Feng[*]

Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore

Qin Yun Wu and Zhi Gao Huang

Department of Physics, Fujian Normal University, Fuzhou 350007, People's Republic of China

Jianyi Lin

Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, Singapore 627833, Singapore
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Carbon doping of CdS is studied using first-principles calculations and Monte Carlo simulation. Our calculations predict ferromagnetism in C doped CdS, resulting from carbon substitution of sulfur. A single carbon substitution of sulfur favors a spin-polarized state with a magnetic moment of $1.22\mu_B$. Ferromagnetic coupling is generally observed between these magnetic moments. A transition temperature of 270 K is predicted through Monte Carlo simulation. The ferromagnetism of C doped CdS can be explained by the hole-mediated double exchange mechanism.

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I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have attracted intense interest because it brings the possibility of devices which combine information processing and storage functionalities in one material.[1,2] Control of spin state of carriers may be realized by injecting spin-polarized current into semiconductors, which can be useful for carrying out quantum bit operations required for quantum computing.[3] To date, most of the attention on DMSs has been focused on doping semiconductors, such as GaAs, GaN, and InAs, with magnetic elements, such as Mn.[4] The Curie temperatures of such systems are typically below room temperature. Recently, it was demonstrated that ZnO can be a high-Curie-temperature magnetic semiconductor when doped with Sc, Ti, V, Fe, or Co.[5] However, clustering of the magnetic elements and of secondary phases are obstacles for applications of these materials. Furthermore, for II-VI semiconductors, the valence of the cation matches that of the common magnetic ions which makes it difficult to dope such materials to create *p*- and *n*-type devices. Therefore, it may be useful to go beyond magnetic elements and to consider unconventional doping elements. Cd-based II-VI semiconductor compounds and alloys have attracted considerable interest due to their applications in photovoltaic devices.[6] Among these, CdS is of considerable importance in optoelectronic applications because of its band gap energy (2.58 eV), which happens to be in the visible range. CdS is also widely used as an *n*-type window material in thin-film solar cell devices. Magnetic CdS can be achieved by doping with metallic elements, such as Mn, Fe, and Co.[7–9] However, it is not clear that the magnetism was occurring in the doped semiconductor or in the clumps of the magnetic metal.

Recently, DMSs obtained by doping with nonmagnetic elements has attracted attention. It has been demonstrated that room temperature ferromagnetism can be obtained in ZnO by doping with carbon.[10] Even though it remains a challenge to integrate these materials into devices, the ferromag-

netism in such systems motivated us to consider C doping of CdS as a possible way of producing magnetic semiconductors which may find applications in spintronics, spin-field effect transistors, spin-light emitting diodes, and optical switches operating in the terahertz range. In this work, we explore possible magnetic property of carbon doped CdS by using first-principles calculation and Monte Carlo simulation.

II. CALCULATION DETAILS

First-principles method based on the spin-polarized density functional theory and the generalized gradient approximation (GGA), as implemented in the VASP program, was used in our theoretical investigation of carbon doping of CdS.[11] In the total energy calculations, the ionic potentials were described by the ultrasoft nonlocal pseudopotential proposed by Vanderbilt.[12] Exchange-correlation functional parametrized by Perdew and Zunger was used.[13] Because CdS is stable in the wurzite structure,[14] our system was modeled with a periodic supercell of $12.55 \times 12.55 \times 13.52$ Å^3 with 18 formula units of wurzite CdS (see Fig. 1), which is sufficient to avoid interaction of C atom with its images in neighboring supercells. An energy cutoff of 300 eV was used for the plane wave expansion of the electronic wave function. Special *k* points were generated with a $3 \times 3 \times 3$ grid based on Monkhorst-Pack scheme.[15] Good convergence was obtained with these parameters. The total energy was converged to 2.0×10^{-5} eV/atom, while the Hellman-Feynman force was smaller than 5.0×10^{-2} eV/Å in the optimized structure.

III. RESULTS AND DISCUSSION

The periodic unit cell of wurtzite CdS was optimized first. The lattice constants of the optimized structure ($a=4.18$ Å, $c=6.76$ Å) within GGA are in good agreement with the experimental values ($a=4.14$ Å, $c=6.71$ Å).[16] The calculated
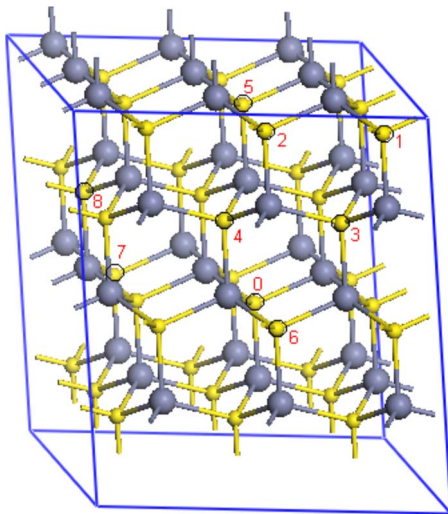
FIG. 1. (Color online) The supercell structure used in the calculation. Small (yellow) balls indicate S and larger (gray) balls represent Cd. C dopant substitutes S at positions indicated by 0–8.

band gap of 1.17 eV within GGA is consistent with the results of other similar studies.[17] When a sulfur atom is replaced by a C atom in the periodic supercell, the relaxed C-Cd bond length (2.267 Å) is less than that of a S-Cd (2.565 Å) bond, and the local structure around the C dopant is slightly suppressed with the Cd atoms drawn closer to the C atom up on geometry optimization.

As an indication of the stability of the carbon dopant, the defect formation energy (E_f) is estimated from

$$E_f = E_t + n(E_S - E_C) - E_b, \qquad (1)$$

where E_t is the total energy of the supercell with n S atoms replaced by C atoms and E_b is the corresponding energy of bulk CdS. E_C and E_S are the energies of an isolated carbon atom and a sulfur atom, respectively. The calculated formation energy for a single substitution of S by C is 1.2 eV. The moderate formation energy indicates that C doped CdS can be easily realized experimentally.

Figure 2 shows the calculated band structure of CdS with one sulfur atom substituted by a carbon atom (CdS-C_S, position 0 in Fig. 1). The band structure of the spin-up states shows a semiconducting behavior with a gap of 1.11 eV within GGA. An interesting feature of the band structure is
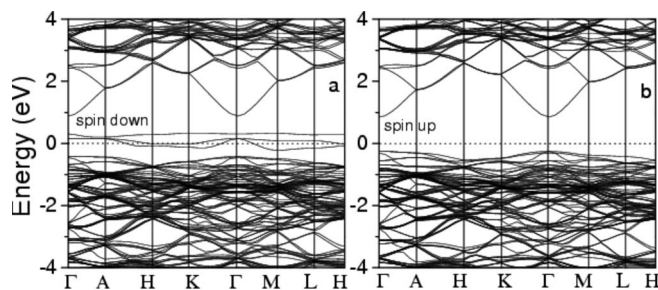

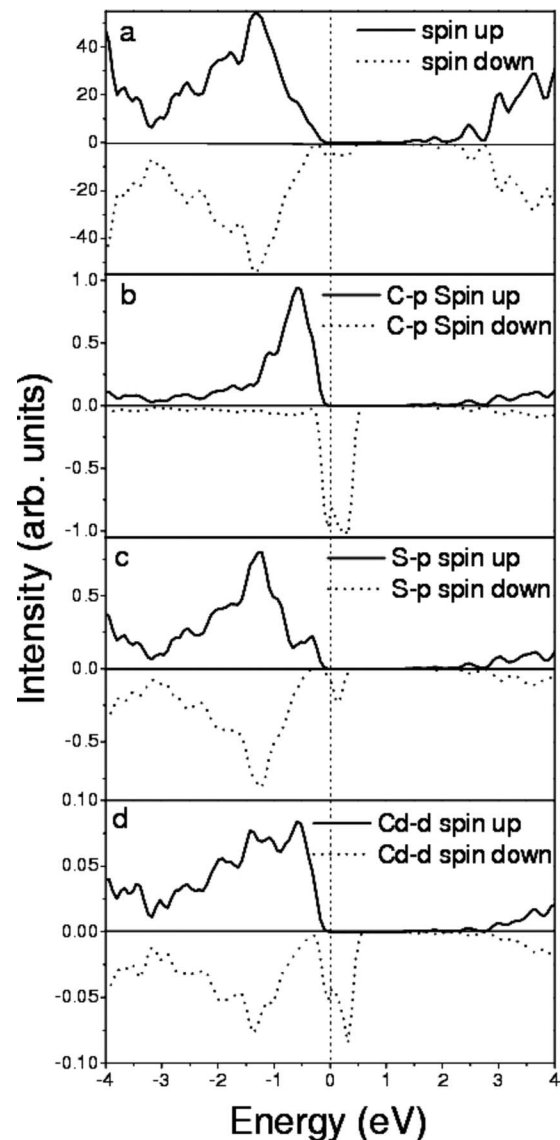FIG. 2. Calculated band structure of CdS-C_S. The Fermi level is indicated by the dotted line.

FIG. 3. Calculated density of states of CdS-C_S. (a) TDOS, (b) LDOS of carbon, (c) LDOS of sulfur, and (d) LDOS of cadmium. The Fermi level is indicated by the dotted vertical line.

the occurrence of impurity bands (C-induced bands) in the spin-down bands over the whole Brillouin zone [Fig. 2(a)], while a gap remains in the spin-up bands [Fig. 2(b)]. These bands are separated from the valence bands and located within the band gap in the spin-down band structure [Fig. 2(a)]. More importantly, the Fermi level is within the impurity bands. Therefore, charge carriers within the impurity bands are sufficiently mobile. Figure 3 shows the total density of states (TDOS) of the CdS-C_S system and the local density of states (LDOS) of the carbon dopant and the neighboring Cd and S atoms. The substitution of S by C does not lead to the spin polarization of the conduction band but results in a significant spin polarization of the valence band [Fig. 3(a)]. Strong coupling between the p orbitals of C and S atoms and the d orbitals of Cd atoms near the Fermi level can be seen [Figs. 3(b) and 3(c)]. The d orbitals of Cd are hybridized with the p orbitals of C. The spin-up bands are fully occupied, while the spin-down bands are empty, result-
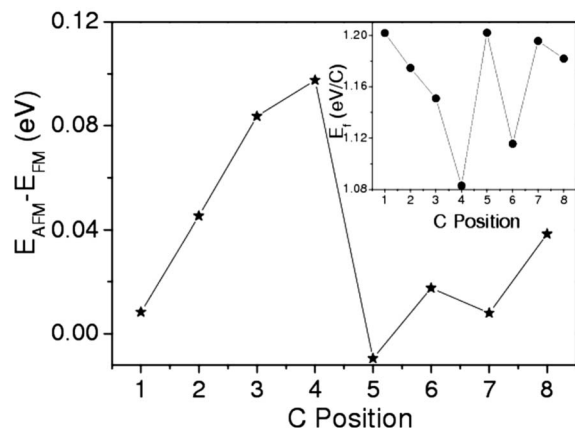
FIG. 4. The energy difference between the antiferromagnetic and ferromagnetic states of CdS-2C$_S$ for various configurations. The inset shows the formation energy (E_f) for various configurations.

FIG. 5. The simulated magnetization (M) and susceptibility χ as a function of temperature for C doped CdS.

ing in a magnetic moment of $1.22\mu_B$ per carbon dopant. The magnetic moment is mainly contributed by the carbon p orbitals. The neighboring Cd and S atoms are also spin polarized and the moments, $0.52\mu_B$ for Cd atoms and $0.56\mu_B$ for S atoms, respectively, are positive (i.e., parallel to the moment of carbon).

To further investigate the coupling between the magnetic moments and determine the Curie temperature (T_C), we incorporated two carbon atoms, each substituting a sulfur atom, in the supercell (CdS-2C$_S$). Various possible and independent configurations of the two carbon atoms, as shown in Fig. 1, were considered. In each case, one carbon atom occupies position 0, and the other substitutes a sulfur atom at one of the other positions (1–8). The formation energy was calculated from Eq. (1) with $n=2$ and the results are shown in the inset of Fig. 4. Among all these configurations considered, configuration 0–4 has the lowest formation energy per carbon dopant. As seen in Fig. 1, positions 0 and 4 are the closest sulfur sites. Its low formation energy indicates the possibility of achieving high concentration of carbon doping in CdS. At the same time, the configuration 0–4 has the largest difference between the antiferromagnetic (AFM) and ferromagnetic (FM) states, as shown in Fig. 4, which is expected to lead to a strong ferromagnetism in C doped CdS. The energy of the FM state is also lower by 10–100 meV than that of the AFM state in the other configurations, except configuration 0–5 where the energy of the FM state is slightly higher (by about 8 meV) than that of the AFM state. However, the formation energy of this configuration is the highest among all considered configurations, indicating that this configuration has a low probability to occur. Therefore, it can be concluded that ferromagnetism can be realized by C substitution of S in C$_S$S.

Monte Carlo (MC) simulation was carried out to determine the transition temperature. The details of the MC procedure were given in Ref. 18. The Hamiltonian of the system is described by
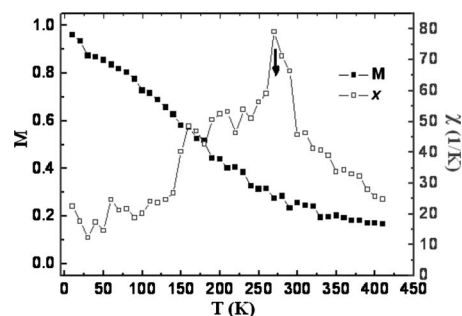
$$E = -\sum_{(ij)} J_{ij}\vec{S}_i \cdot \vec{S}_j - K\sum_i (\vec{S}_i \cdot \vec{u}_i)^2 - H\sum_i S_i^z, \qquad (2)$$

where J_{ij} is the exchange coupling constant. The thermodynamic magnetization per atom and the susceptibility are calculated by $M(T) = \langle [(\sum_i S_i^x)^2 + (\sum_i S_i^y)^2 + (\sum_i S_i^z)^2]^{1/2} \rangle / N$ and $\chi = N(\langle m^2 \rangle - \langle m \rangle^2)/T$, respectively. N is the number of the magnetic C atoms in C doped CdS. In the simulation, $M(T)$ is no dimension by letting $|\vec{S}_i|=1$. The exchange coupling constant [Eq. (1) in Ref. 18] is taken to be $\Delta E = E_{FM} - E_{AFM}$. Figure 5 shows the simulated magnetization (M) and susceptibility (χ) as a function of temperature for CdS with 5.55% carbon doping. It shows a clear ferromagnetic feature. T_C is estimated to be 270 K which is marked by a sharp susceptibility peak.

The origin of ferromagnetism in DMSs has been intensively discussed over the past years. Several models, including the phenomenological Zener/Ruderman-Kittel-Kasuya-Yoshida, superexchange, double exchange, p-d hybridization exchange, and magnetic polarons, have been proposed to explain the ferromagnetism of semiconductors doped with magnetic elements which have $3d$ or $4f$ orbitals.[19–23] Results of our first-principles calculations seem to suggest that the ferromagnetism in C doped CdS can be explained based on the carrier-mediated mechanism. The carriers, i.e., holes, were introduced by the carbon substitution of sulfur (Fig. 2). A significant part of the holes comes from the p states of carbon (Fig. 3). For the hole-mediated ferromagnetism, there are two distinct mechanisms that determine the stabilization of ferromagnetism.[24] The difference between them is related to the position of the impurity levels with respect to the valence band edge. If the impurity states are in the band gap, ferromagnetism can be explained by the double exchange interaction. That is, given the incomplete filling of bands, when the exchange splitting is bigger than the bandwidth, the band energy of the ferromagnetic state is lower than that of the antiferromagnetic state if a sufficient (usually rather small) number of holes (or electrons) exist.[20] If the filled impurity states are below the valence band edge, ferromagnetism can be explained by the Zener model,[25] which is related to the coupling between the impurity levels and the host valence states. In both cases, it is necessary to have holes, either free or localized, to stabilize the ferromagnetism. As seen in the band structure of CdS-C$_S$ (Fig. 2), the

impurity bands are located within the band gap and separated from the valence bands, and the Fermi level falls in the gap of the spin-up band structure but within the impurity bands of the spin-down electrons. The ferromagnetic state is thus half metallic. The exchange splitting is bigger than the valence band [Figs. 2 and 3(c)], and there are a considerable number of holes. We can therefore conclude that carrier-mediated double exchange is responsible for the observed ferromagnetism in C doped CdS.

IV. CONCLUSIONS

In summary, we have demonstrated that ferromagnetism can be realized in CdS with carbon doping via substitution of sulfur. The magnetic moments of C and its neighboring S and Cd atoms are parallel. Ferromagnetic CdS with a high carbon concentration is possible because the formation energy is the lowest when two carbons substitute two S atoms at the closest separation and the corresponding FM state is energetically favored by about 100 meV than the AFM state. MC simulation predicted that the Curie temperature is 270 K at a carbon concentration of 5.55%. Based on the fact that the impurity bands are located within the band gap and the Fermi level crosses the impurity bands, the ferromagnetism in C doped CdS can be attributed to the hole-mediated double exchange interaction.

*Corresponding author: phyfyp@nus.edu.sg

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