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p-electron magnetism in CdS doped with main group elements

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Abstract

On the basis of ab initio supercell calculations employing density functional theory (DFT) and post-DFT methods, we investigate the behavior of main group element impurities (B, C, N, Al, Si, P, Ga, Ge) in wurtzite (w) and zincblende (zb) CdS lattices. It is found that the impurities prefer the sulfur position and most of them, depending on the concentration, exhibit magnetic order. We find that for small concentrations (64zb and 72w supercells) a half-metallic behavior is found. For a 16-atom supercell for both the zb- and w-structure partly also unsaturated magnetic moments occur. The field dependence of the magnetic moments in these materials may lead to new technological applications of these magnetic semiconductors as tunable spin injection materials.

(Some figures may appear in colour only in the online journal)

1. Introduction

Pan et al [1] proposed carbon-doped magnetic wurtzite CdS as a possible material for spintronics application. Their proposal was motivated by the need for half-metallic ferromagnets in spintronic devices [2], which are seen as key ingredients. Magnetically ordered p-electron elements have been described by Sieberer et al [3] in stoichiometric zincblende CaAs and other I/II–V compounds, where magnetic order is carried by the anion p-electrons without any direct involvement of d-electrons as in the magnetic transition metals and their compounds. These materials can be regarded as parent compounds for the understanding of other systems, where the magnetic polarization again appears at a main group element, which however is an impurity replacing another p-electron element. Another type of p-electron polarization is defect triggered p-electron magnetism, which occurs in irradiated pyrolytic graphite containing defects [4–6] or CaB$_6$ doped with La [7]. During the past decade an enormous amount of work has been invested to study dilute magnetic semiconductors (DMS). The prospect to exploit both the charge and the electron spin as information carriers would combine information processing and storage at the same time [8–10].

In this paper we calculate the magnetic and electronic properties of main group element impurities (B, C, N, Al, Si, P, Ga, Ge) in CdS. Our calculations are performed for supercells of the wurtzite (w) and zincblende (zb) modification of CdS for cell sizes 72(w) and 64(zb) and 16(zb)/(w) atoms. The main group element replaces a sulfur atom leading to nominal impurity concentrations of 2.7, 3.125, and 12.5 atom% impurity. Ma et al [11] performed a study where they considered an impurity concentration of 3.125 of some of these dopants on zincblende CdS. The findings of this study are, however, limited by the generalized gradient approximation, which underestimates the bandgap of this material and may lead to spurious ferromagnetism caused by false occupancies [12]. In order to minimize this problem, our calculations are carried out using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional [13–15], which improves the description of semiconductors and their defect states [16–18] by mixing in a small amount of the Hartree–Fock exchange to the DFT exchange. Heyd et al have shown that the HSE functional improves the bandgap of CdS [19] over previous LDA and GGA studies. For the large cell sizes it is found that errors due to the underlying periodicity are reasonably small, so that interactions between the impurity atoms can be ruled out. For the 16-atom cell, however, the impurity atoms do interact and the respective bands appear to be broadened, leading to a non-fully polarized state.
2. Crystal structure

Wurtzite CdS is a prototypical II/VI semiconductor with an experimental direct bandgap of 2.42 eV. At a pressure of 2.7 GPa the wurtzite structure becomes transformed into the zincblende structure and the bandgap is reduced to about 1.5 eV. We perform our simulation for the two closely related structures; wurtzite and zincblende.

(i) The hexagonal wurtzite (w) structure (P63mc, Nr. 186) is the ground state modification of CdS. If one assumes the ideal c/a ratio of $\sqrt{8/3}$ and an internal $u$-parameter of 3/8 for the anion site and 0 for the cation site at the (2b) Wyckoff position one obtains the same coordination numbers as for the zincblende structure.

(ii) The zincblende (z) structure (F43m, Nr. 216) is the cubic analog of the wurtzite and consists of two interpenetrating fcc lattices, one of them shifted by a vector $[1, 1, 1]$, resulting in a two-component analog of the diamond structure. Each atom of one kind is situated in an ideal tetrahedron made up of atoms of the other kind. As most semiconductors crystallize in this structure, it is of great technological importance.

3. Computational method

The system was modeled in the hexagonal wurtzite structure (the ground state of CdS) as well as in the cubic zincblende structure. To simulate different impurity concentrations, two supercells with the following dimensions were constructed in structure. To simulate different impurity concentrations, two supercells with the following dimensions were constructed in structure. To simulate different impurity concentrations, two supercells with the following dimensions were constructed in structure. To simulate different impurity concentrations, two supercells with the following dimensions were constructed in structure. To simulate different impurity concentrations, two supercells with the following dimensions were constructed in structure.

$$a = 5.83 \quad a = 5.94$$

$$a = 4.16; c = 6.76 \quad a = 4.20; c = 6.85$$

Table 1. Calculated lattice parameters for CdS. The experimental values for the zincblende configuration are taken from [30] and the values for the wurtzite configuration from [31].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Experimental lattice parameters (Å)</th>
<th>GGA-PBE lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zincblende CdS</td>
<td>$a = 5.83$</td>
<td>$a = 5.94$</td>
</tr>
<tr>
<td>Wurtzite CdS</td>
<td>$a = 4.16; c = 6.76$</td>
<td>$a = 4.20; c = 6.85$</td>
</tr>
</tbody>
</table>

Table 2. Comparison between the bandgaps calculated with GGA-PBE and HSE.

<table>
<thead>
<tr>
<th>Structure</th>
<th>GGA-PBE (eV)</th>
<th>HSE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zincblende CdS</td>
<td>1.05</td>
<td>2.09</td>
</tr>
<tr>
<td>Wurtzite CdS</td>
<td>1.11</td>
<td>2.16</td>
</tr>
</tbody>
</table>

smaller than $1 \times 10^{-2}$ eV Å$^{-1}$. The relaxed structures were used as input for post-DFT calculations using the HSE hybrid functional.

4. Structure relaxations and magnetic ordering

We first performed a series of calculations on pure CdS in order to obtain the parameters that will be used as a reference to compare and evaluate the structural changes induced by the impurities. The theory used for each of these steps is analogous to the one used for the corresponding step on the doped systems, i.e. we relaxed the structures using the GGA-PBE approximation and use the resulting structure as input for a post-DFT calculation using the HSE functional. The calculated lattice parameters (table 1) are in good agreement with the experimental values. The bandgaps calculated with the HSE functional show a considerable improvement over the GGA results (table 2), and are consistent with the ones reported by Heyd et al [19].

To study the concentration dependence of the magnetic properties of the impurities on the zincblende structure we perform calculations for two different supercells containing 16, and 64 atoms. In the 16-atom supercell (figure 1) the impurities are only separated from each other by a single S atom. Consequently the impurities are not decoupled from each other and their interaction leads to a relatively large width of the impurity bands. The use of supercells raises the question whether the artificial long-range order introduced influences the results. To this end we performed...
Figure 2. 16-atom zincblende cell. Magnetic moments are given in Bohr magnetons. \( \Delta NN \) is the change in distance between the impurity and the NN Cd atom after relaxation. \( \Delta NNN \) is the change in distance between the impurity and the NNN S atom after relaxation. \( \Delta V \) is the volume change of the unit cell after relaxation. All structural changes due to relaxation are related to the theoretical equilibrium CdS structure.

A test calculation for a 64-atom supercell doped with four carbon atoms at random positions. The results are in excellent agreement with the smaller 16-atom cell with a single impurity, both concerning the magnetic moment and the electronic structure. In the systems studied here three major interactions exists:

(i) interaction between the impurities;
(ii) interaction between the impurity and the nearest neighbor (NN);
(iii) interaction between the impurity and the next nearest neighbor (NNN).

All three can produce a broadening of the impurity bands which suppresses the formation of a magnetic moment (figure 2). A detailed analysis of the interactions in carrier-mediated magnetic systems has been given by Dalpian and Wei [32]. For the second period substitutions, only the carbon-doped system presents a saturated magnetic moment, which can be explained in terms of the Stoner model. When two holes are introduced in this system, the Fermi energy in the non-magnetic state lies in a peak of the density of states which is large enough to fulfill the Stoner criterion so that the p-bands of carbon split magnetically and produce a magnetic moment of 2 \( \mu_B \). This also explains the saturated magnetic moment obtained with the other impurities which also introduce two holes (Si and Ga). The boron-doped system exhibits an unsaturated magnetic moment because the extent of this impurity wavefunction is larger than the carbon one and, thus, the interaction between the impurities in the boron-doped system is stronger, causing a partial suppression of the magnetic moment. The same happens in the aluminum- and gallium-doped systems, however, the extent of the impurity wavefunction in these cases is even larger and, therefore, the magnetic moment vanishes. The unrelaxed nitrogen-doped system presents a magnetic moment of 1 \( \mu_B \), which vanishes as the system is relaxed, because the interaction between the nitrogen atom and its nearest neighbor is the strongest among all the studied impurities. This, however, does not occur for the phosphorus-doped system, which remains magnetic.

The crystal form of the ground state of CdS is the wurtzite structure, which is less symmetric than the zincblende. For this reason, computational simulations involving this configuration are more demanding, hence, it is desirable to determine the influence of the crystal structure on these systems. To this end, we repeated the calculations replacing the zincblende supercell with a 16-atom supercell in the wurtzite configuration (figure 3), where one sulfur atom was replaced by the corresponding impurity to obtain the same impurity concentration as in the zincblende case. The results of this calculations resemble the corresponding ones in the zincblende structures (figure 4), with the exception of the silicon- and germanium-doped systems, because there is a lower density of states at the Fermi energy of the non-magnetic state after introducing two holes. Carbon, however, remains magnetic because the atomic spin polarization of p-orbitals is the strongest for light atoms from the second row of the periodic table [33].

To simulate a lower impurity concentration in zincblende CdS, we construct a 64-atom supercell (figure 5) and replace one sulfur atom by one main group impurity. In these calculations, a detailed analysis of the interactions in carrier-mediated magnetic systems has been given by Dalpian and Wei [32]. For the second period substitutions, only the carbon-doped system presents a saturated magnetic moment, which can be explained in terms of the Stoner model. When two holes are introduced in this system, the Fermi energy in the non-magnetic state lies in a peak of the density of states which is large enough to fulfill the Stoner criterion so that the p-bands of carbon split magnetically and produce a magnetic moment of 2 \( \mu_B \). This also explains the saturated magnetic moment obtained with the other impurities which also introduce two holes (Si and Ga). The boron-doped system exhibits an unsaturated magnetic moment because the extent of this impurity wavefunction is larger than the carbon one and, thus, the interaction between the impurities in the boron-doped system is stronger, causing a partial suppression of the magnetic moment. The same happens in the aluminum- and gallium-doped systems, however, the extent of the impurity wavefunction in these cases is even larger and, therefore, the magnetic moment vanishes. The unrelaxed nitrogen-doped system presents a magnetic moment of 1 \( \mu_B \), which vanishes as the system is relaxed, because the interaction between the nitrogen atom and its nearest neighbor is the strongest among all the studied impurities. This, however, does not occur for the phosphorus-doped system, which remains magnetic.

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systems the distance between impurities increases and, by the same token, the strength of the impurity–impurity interaction diminishes; consequently, saturated magnetic moments are predicted for all systems but nitrogen (figure 6), where the interaction between the impurity and its nearest neighbor is still large enough to suppress magnetic ordering.

In order to determine the difference between the magnetic moments predicted in the zincblende and the wurtzite lattices in the low impurity concentration regime, it is necessary to construct a supercell in the wurtzite configuration, which is comparable to the 64-atom zincblende supercell not only in the impurity concentration that it reproduces, but also in how the impurities are distributed. Based on this criteria, a 72-atom supercell (figure 7) was employed to carry out the calculations, as it is the best compromise between these two requirements. Our results show that there is no difference in the magnetic moments predicted in the low concentration regime between this crystal configuration and the zincblende (figure 8) and that the small variation in the NN and NNN distances is not relevant enough to affect the magnetic ordering.

5. Defect formation energies

A measure of how easy it is to incorporate a particular defect into a material is the defect formation energy (DFE). It is important to estimate this quantity in calculations that involve DMSs since it provides a guideline for the experiment or subsequent calculations and plays a relevant role in the choice of the most useful materials for technological applications. The DFE is influenced by the conditions under which the material is prepared, by the so-called growth conditions. The formation energy of a impurity X in charge state $q$ is defined as

$$E_f[X^q] = E_{tot}[X^q] - E_{tot}[\text{bulk}] + n(\mu_S - \mu_{\text{Cd}}) + q(E_F + E_v + \Delta V)$$ (1)

where $E_{tot}[X]$ is the total energy of the supercell with one sulfur atom replaced by the impurity X ($X = B, C, N, Al, Si, P, Ga, Ge$), $E_{tot}[\text{bulk}]$ is the total energy for the corresponding supercell containing only bulk CdS without impurities. $n$ indicates the number of sulfur atoms that have been replaced.
by dopant atoms from the supercell, $\mu_S$ and $\mu_{\text{Cd}}$ are the corresponding chemical potentials. Elemental sulfur lacks a well-defined ground state structure; it has one of the largest number of allotropes among the elements, and for this reason, the chemical potentials were calculated with respect to the free atom, as it represents a well-defined reference to compare the defect formation energies among the different systems.

$E_F$ is the Fermi level, referenced to the valence-band maximum in the bulk. Due to the choice of this reference, one needs to explicitly put in the energy of the bulk valence-band maximum, $E_v$, in the expressions for formation energies of charged states. It is also necessary to add a correction term $\Delta V$, to align the reference potential in the defect supercell with that in the bulk. Since we are dealing with charge neutral dopants, the last term in (1) is zero.

Our results suggest that most of the systems can be realized experimentally since we found moderate DFE values among them (tables 3 and 4). It is also possible to observe that the crystal structure does not have a strong influence on these values, since the variation between the zincblende and the wurtzite system is not significant. The aluminum- and gallium-doped systems are the only ones that present a relative high DFE and may not be easily synthesized, which may be a consequence of the large change in volume of the CdS lattice that they induce, as was noted in section 4.

### 6. Post-DFT results

It is well known that the local density approximation (LDA) and relatives such as the generalized gradient approximation (GGA) underestimate the bandgap in nonmetals. Consequently, the impurity states resonate with the conduction band of the host, producing a delocalized orbital which favors long-range interactions, promising (spurious) high-$T_C$ ferromagnetism. In order to overcome this problem, we carried out a series of calculations using the HSE hybrid functional which not only improves the description of the bandgap, but also avoids the failure to localize holes that is present in LDA calculations. Although hybrid functionals represent an improvement over LDA/GGA calculations, they are computationally more demanding due to the need to calculate the non-local Fock exchange integrals, which is a factor that becomes relevant in the calculations that involve less symmetric structures, such as wurtzite. The results of the previous sections show, however, that the predicted magnetic moments on the systems here studied are not strongly affected by the crystal configuration and, thus, we perform our simulations on the more symmetric zincblende structure.

In contrast with the GGA-PBE results, our HSE calculations predict saturated magnetic moments not only for the carbon-doped system, but also for boron-, silicon-, phosphorus- and germanium-doped systems with higher impurity concentration (table 5). We also found non-saturated magnetic moments for the nitrogen-, aluminum- and gallium-doped systems instead of the vanishing moments predicted by GGA-PBE. Nevertheless, in qualitative terms these results follow the previously observed trend and can be understood in the same way, by considering the strength of the impurity–impurity interaction which depends on the extent of the impurity wavefunctions and their corresponding overlap as well as the number of holes introduced and the value of the density of states at the Fermi energy. This clearly explains the non-saturated magnetic moments in the higher impurity concentration systems doped with Al and Ga. The interaction between the impurity and its nearest neighbor is less significant in HSE calculations in comparison to GGA-PBE, and for this reason the nitrogen-doped system exhibits a non-saturated magnetic moment. The magnetic moments predicted in the systems with a lower impurity concentration are the same as the corresponding ones predicted by the GGA-PBE calculations, with the exception of nitrogen, for the same reason stated above.

Most of the systems that show saturated magnetic moments are found to be half-metals (figure 9). Coupling between the impurity and sulfur p-orbitals and cadmium d-orbitals produces states that sit at the Fermi energy in the spin-down channel and extend over the whole Brillouin zone, while a gap remains in the spin-up channel. A special case of technological interest is observed in the lower concentration boron- and aluminum-doped systems (figures 10 and 11), where the valence band is polarized and the impurity-induced states in the spin-down channel are pushed beyond the Fermi energy level, resulting in a magnetic insulating behavior, which is rather new in p-electron DMS.

### Table 3. Defect formation energies (DFE) for the doped CdS zincblende systems.

<table>
<thead>
<tr>
<th>Supercell size</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Ga</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 atoms</td>
<td>2.44</td>
<td>1.59</td>
<td>2.01</td>
<td>4.75</td>
<td>2.46</td>
<td>2.01</td>
<td>4.02</td>
<td>2.91</td>
</tr>
<tr>
<td>64 atoms</td>
<td>2.5</td>
<td>1.77</td>
<td>2.02</td>
<td>5.03</td>
<td>2.74</td>
<td>2.15</td>
<td>4.33</td>
<td>3.19</td>
</tr>
</tbody>
</table>

### Table 4. Defect formation energies (DFE) for the doped CdS wurtzite systems.

<table>
<thead>
<tr>
<th>Supercell size</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Ga</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 atoms</td>
<td>2.53</td>
<td>1.61</td>
<td>1.95</td>
<td>4.84</td>
<td>2.55</td>
<td>2.05</td>
<td>4.13</td>
<td>2.97</td>
</tr>
<tr>
<td>72 atoms</td>
<td>2.52</td>
<td>1.72</td>
<td>2.03</td>
<td>5.08</td>
<td>2.72</td>
<td>2.14</td>
<td>4.37</td>
<td>3.18</td>
</tr>
</tbody>
</table>

### Table 5. Magnetic moments calculated with the HSE06 hybrid functional for the doped zincblende CdS systems.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>16-atom supercell</th>
<th>64-atom supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnetic moment ($\mu_B$)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>C</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>N</td>
<td>0.75</td>
<td>0.81</td>
</tr>
<tr>
<td>Al</td>
<td>1.25</td>
<td>3.00</td>
</tr>
<tr>
<td>Si</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>P</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ga</td>
<td>1.47</td>
<td>3.00</td>
</tr>
<tr>
<td>Ge</td>
<td>2.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>
Figure 9. Total density of states (top panel), and partial density of states (both in eV$^{-1}$/spin) for the 16-atom carbon-doped zincblende supercell calculated using the HSE06 functional.

Figure 10. Total density of states of the 64-atom boron-doped zincblende CdS supercell calculated using the HSE06 functional.

7. Conclusions

In this study we have shown that hybrid functional calculations predict half-metallic magnetic state with saturated magnetic moments when CdS is doped with B, C, Si, P and Ge in low and high impurity concentration systems (nominal impurity concentrations of 2.7 and 12.5 atom% impurity). These materials are of interest in the field of spintronics not only because they exhibit moderate defect formation energies but also because in these systems, the saturated magnetic moments are produced without direct intervention of d-electrons, and they are stabilized by the holes introduced through doping. We found magnetic insulating behavior in boron- and aluminum-doped CdS in the low concentration schemes, which is a rather new phenomena in p-electron magnets. The computational and theoretical approach used in this investigation avoids the most common pitfalls [12] that have produced false positive results in previous investigations.

Acknowledgments

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References


[34] Van de Walle C G and Neugebauer J 2004 *J. Appl. Phys.* **95** 3851