Magnetism in Cr-doped ZnS: density-functional theory studies

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Abstract

We investigated the magnetism and aggregation trends in cubic Zn$_{1-x}$Cr$_x$S using density-functional theory calculations. We demonstrate that all studied configurations show ground state half-metallic ferromagnetism (HMF), and Cr impurities are energetically favourable for planar clustering into delta-doping structures. The single-layer delta-doping structures of Zn$_{0.75}$Cr$_{0.25}$S and Zn$_{0.875}$Cr$_{0.125}$S show ferromagnetic stabilization energies ($\Delta E_{AF}$) of 0.551 eV and 0.561 eV per Cr–Cr pair, respectively. The half-layer delta-doping structure of Zn$_{0.875}$Cr$_{0.125}$S and the double-layer delta-doping structure of Zn$_{0.75}$Cr$_{0.25}$S show $\Delta E_{AF}$ of 0.394 eV and 0.166 eV per Cr–Cr pair, respectively. Furthermore, our studies indicate that the cubic ZnS/CrS heterostructure, one extreme situation of the delta-doping structure, also shows ground state HMF. The origin of HMF is discussed using a simple crystal field model. Finally, we anticipate the potential spintronics application of Zn$_{1-x}$Cr$_x$S.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zn chalcogenides (Zn$X$, $X = \text{S, Se, Te}$) based magnetic semiconductors (MSs) have attracted much attention recently for potential room temperature spintronics application [1–19]. Among them, ZnS based MSs are more promising for integration into the mainstream silicon technology for similar crystal structure and close lattice parameters. However, although numerous studies have demonstrated ferromagnetism with Curie temperature ($T_C$) above room temperature in Zn$X$ based MSs, the results are always controversial [13–17]. For MSs, the largest obstacle to the practical spintronics application is the intrinsic aggregation trend of magnetic impurities [20–25]. How to control the clustering of the magnetic impurities is always a hot issue with respect to MSs. Interestingly, some studies show that the magnetic clusters would endow matrix semiconductors with high $T_C$ and huge magnetic moment [23–25]. But the problem is how to pattern the magnetic clusters. The orderly patterned magnetic impurity atoms or clusters are the key to applicable MSs.

Recently, Qian et al [26] and Nazmul et al [27] introduced the delta-doping scheme into Mn doped silicon and GaAs, respectively. They found that delta doping would enhance the magnetism. Moreover, theoretical studies also predicted enhanced magnetism in delta-doping structures of (Mn, III)–V semiconductors [28]. Delta doping is a kind of heterogeneous doping with one more or less layer of impurities in a specific face of the matrix semiconductor, which can also be considered as a kind of planar clustering. A prominent advantage of delta doping is the capability to achieve higher concentration impurities, which is easy to realize via the metastable molecular beam epitaxy (MBE) synthesis. According to the Zener model [29], a higher TM impurities doping concentration suggests a higher Curie temperature ($T_C$), which is important for the practical above room temperature applications. So, we can anticipate higher $T_C$ in MSs via the delta-doping scheme.

Compared with the delicate experimental method, computational methods, in particular the parameter-free first-principles calculations, are widely used to explore the MSs.
with different doping structures from the ideal homogeneous configurations to extreme inhomogeneous ones such as delta doping. Generally, density-functional theory (DFT) within local-density approximation (LDA) or generalized-gradient approximation (GGA) tends to underestimate the band gap of the semiconductors and fails to describe the Mott insulator. A mean-field Hubbard potential approximation (U) correction of the semiconductors and fails to describe the Mott insulator. Generally, density-functional theory (DFT) within local correlations [30–32]. Correspondingly, the addition of the Hubbard term would improve the electronic structure and optical properties of these materials considerably. For Zn chalcogenides, extensive studies show that the DFT within the LDA would underestimate the band gap, while the GGA would give relatively good descriptions as the LDA + U approach [30–32]. Comparatively, the LDA + U approach would improve the description of the band gap of ZnO considerably for stronger local correlations [30–32]. Correspondingly, the addition of the Hubbard term would improve the electronic structure and magnetism of Zn chalcogenides based MSs by increasing the intermediate bandwidth and stabilizing the ferromagnetic spin order [33], but the effect is not so rudimentary [34, 35], when compared with the ZnO based MSs [36, 37].

Here, we report on magnetism in cubic Zn$_{1-x}$Cr$_x$S using the DFT calculations. We find that all studied configurations of Zn$_{1-x}$Cr$_x$S show ground state half-metallic ferromagnetism (HMF); and Cr impurities are prone to planar clustering into delta-doping structures with enhanced HMF. At the end, we discuss the origin of magnetism and anticipate the potential spintronics application of Zn$_{1-x}$Cr$_x$S.

2. Computational details

We performed spin-polarized total energy DFT calculations in the Perdew–Burke–Ernzerhof GGA [38] using the plane-wave ultrasoft pseudopotential method [39] as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [40]. To study the effect of doping configurations on magnetism, a 1 × 1 × 2 conventional supercell as shown in figure 1(a) was used for cubic Zn$_{0.75}$Cr$_{0.25}$S. Therein, N110 is a kind of single-layer delta doping in cubic ZnS (0 0 1). There, we find that Cr impurities are prone to planar clustering into the delta-doping structure. To study the aggregation trend of magnetic impurities in delta-doping configuration under lower doping concentration, a cell containing 32 atoms corresponding to Zn$_{0.875}$Cr$_{0.125}$S with lattice parameters $a = b = 7.65$ Å and $c = 10.82$ Å, as shown in figure 1(b), was used. Furthermore, a cell containing two CrS layers along the [0 0 1] direction, as shown in figure 1(c), was used to study the double-layer delta-doping structure, and a cubic ZnS/CrS superlattice containing four layers of ZnS and four layers of CrS as shown in figure 1(d) was used to simulate a kind of extreme situation of delta doping. Typically, the effect of the cutoff energies and Monkhorst–Pack grids on the ferromagnetic stabilization energy (energy difference between antiferromagnetic and ferromagnetic states, $\Delta E_{\text{AF}} = E_{\text{AFM}} - E_{\text{FM}}$) of the delta-doping structure of Zn$_{0.75}$Cr$_{0.25}$S (N110 in figure 1(a)) is checked by using different cutoff energies (350, 450 and 550 eV) and Monkhorst–Pack grids (6 × 6 × 3, 8 × 8 × 2 and 8 × 8 × 4); the result shows that the difference of $\Delta E_{\text{AF}}$ is less than 0.002 eV. To save the calculation expense, the lowest energy cutoff and Monkhorst–Pack grid are used in the calculations. For Zn$_{0.75}$Cr$_{0.25}$S in figure 1(a) and Zn$_{0.875}$Cr$_{0.125}$S in figure 1(b), the Monkhorst–Pack grids of 6 × 6 × 3 and 4 × 4 × 3 were used, respectively; for the double-layer delta-doping structure of Zn$_{0.75}$Cr$_{0.25}$S (figure 1(c)) and ZnS/CrS heterostructure (figure 1(d)), the Monkhorst–Pack grids were set 6 × 6 × 2. Both the lattice parameters and the atomic positions were fully relaxed in all calculations. Otherwise, the magnetic moments remain variable to find out the lowest energy state. Through the latter, the formation energy of Cr substitution impurities (Cr$_{Zn}$) in

Figure 1. Scheme of (a) Zn$_{0.75}$Cr$_{0.25}$S, (b) Zn$_{0.875}$Cr$_{0.125}$S, (c) double-layer delta-doping structure of Zn$_{1-x}$Cr, S and (d) ZnS/CrS heterostructure. Here, Nxyz in (a) and (b) represents configurations containing a Cr–Cr pair with one Cr at the origin and another at the Nxyz position.
moments of Zn$_{1-x}$Cr$_x$S with different doping configurations shown in figure 1. Therein $d$ is the nearest distance between Cr–Cr pair, and the total magnetic moment is the sum of all magnetic moments normalized to the unit contained one Cr atom.

Table 1. The calculated ferromagnetic stabilization energy $\Delta E_{AF}$ (eV), Cr$_{Zn}$ formation energy $E_f$ (eV), and total and Cr sites magnetic moments of Zn$_{1-x}$Cr$_x$S with different doping configurations shown in figure 1. Therein $d$ is the nearest distance between Cr–Cr pair, and the total magnetic moment is the sum of all magnetic moments normalized to the unit contained one Cr atom.

| Magnetic ground state | $d$ (Å) | $\Delta E_{AF}$ (eV) | $E_f$ (eV) | $m_{tot}$ ($\mu_B$) | $m_{Cr}$ ($\mu_B$) |
|-----------------------|---------|----------------------|-----------|---------------------|-------------------|
| (a) Zn$_{0.75}$Cr$_{0.25}$S | N112 | HMF | 5.397 | 0.060 | 1.414 | 4.00 | 4.24 |
| | N002 | HMF | 5.446 | 0.004 | 1.398 | 4.00 | 4.24 |
| | N011 | HMF | 3.679 | 0.407 | 1.197 | 4.00 | 4.26 |
| | N110 | HMF | 3.809 | 0.551 | 1.127 | 4.00 | 4.30 |
| | Double-layer delta doping | HMF | 3.833 | 0.166 | 1.014 | 4.00 | 4.32 |
| (b) Zn$_{0.875}$Cr$_{0.125}$S | N220 | HMF | 5.405 | 0.012 | 1.450 | 4.00 | 4.24 |
| | N200 | HMF | 3.806 | 0.394 | 1.324 | 4.00 | 4.26 |
| | N111 | HMF | 3.534 | 0.304 | 1.229 | 4.00 | 4.26 |
| | N222 | HMF | 7.678 | 0.113 | 1.413 | 4.00 | 4.24 |
| | Single-layer delta-doping | HMF | 3.815 | 0.561 | 1.105 | 4.00 | 4.30 |
| (c) Zn$_{0.5}$Cr$_{0.5}$S | ZnS/CrS heterostructure | HMF | 3.841 | 0.055 | 0.980 | 4.00 | 4.32 |

ZnS was calculated with the well-established formula [41, 42], which is defined as

$$ E_f[CrZn] = E[CrZn] - E[bulk] - n\mu_Cr + n\mu_{Zn}, \quad (1) $$

where $E[CrZn]$ and $E[bulk]$ are the total energies of Zn$_{1-x}$Cr$_x$S and pure ZnS reference structures (calculated with the same size supercell), respectively. Here, $\mu_{Cr}$ and $\mu_{Zn}$ are the atom chemical potentials, which represent the energy of the reservoirs with which atoms are being exchanged. The chemical potential depends on the experimental conditions under which the materials are fabricated. Here, we just considered the moderate condition:

$$ \mu_{Zn} = \mu_{Zn}(bulk) - 0.5\Delta H(ZnS), \quad (2) $$

$$ \mu_{Cr} = \mu_{Cr}(bulk) - 0.5\Delta H(CrS). \quad (3) $$

In these equations, $\Delta H(ZnS)$ and $\Delta H(CrS)$ are the heat of formation of cubic ZnS and CrS, respectively. $\mu_{Zn}(bulk)$ and $\mu_{Cr}(bulk)$ are calculated from antiferromagnetic cubic chromium (Cr) and hexagonal zinc (Zn), respectively. Generally, Cr$_{Zn}$ formation energy shows a positive value; the lower the Cr$_{Zn}$ formation energy, the easier the formation of Cr$_{Zn}$ impurities.

3. Results and discussion

The calculated ferromagnetic stabilization energy $\Delta E_{AF}$, Cr$_{Zn}$ formation energy, total and Cr sites magnetic moments of Zn$_{1-x}$Cr$_x$S with different doping configurations are given in table 1. Apparently, all calculated doping configurations show positive $\Delta E_{AF}$ (positive $\Delta E_{AF}$ means that the FM is favoured over AFM, and the larger the $\Delta E_{AF}$, the stabler the FM) and integral total magnetic moment, indicating ground state HMF. (The paramagnetic states are also calculated for Zn$_{1-x}$Cr$_x$S. The results show that the total energies of the paramagnetic states are substantially higher than the ferromagnetic and antiferromagnetic states.) In addition, many of them show robust HMF with large $\Delta E_{AF}$ close to traditional magnetic metals and alloys. For Zn$_{0.75}$Cr$_{0.25}$S shown in figure 1(a), the single-layer delta-doping (N110) and Cr dimer (N011) structures show larger $\Delta E_{AF}$ and lower Cr$_{Zn}$ formation energy than the homogeneous-doping structure (N002) and N112, indicating the clustering trend of the Cr impurities. Among them, N110 shows largest $\Delta E_{AF}$ (0.551 eV per Cr–Cr pair) and lowest Cr$_{Zn}$ formation energy (1.127 eV), which indicates that the delta-doping structure is not only the most magnetically stable but also energetically favourable. That is, Cr impurities are energetically favourable for planar clustering into the delta-doping structure. Comparatively, the delta-doping structures of cubic (Ga, Mn)As [27] and (Ga, Mn)N [43], which have been experimentally realized, show larger GaMn formation energy of 1.579 eV and 1.738 eV (under moderate conditions), respectively, when the doping concentration is 25%. Deductively, the delta-doping structure of (Zn, Cr)S is more feasible for experimental fabrication.

To explore the planar clustering trend in the delta-doping structure under lower doping concentrations, we calculated some doping structures of Zn$_{0.875}$Cr$_{0.125}$S as shown in figure 1(b). Apparently, N111 (Cr dimer) and N200 (a kind of heterogeneous half-layer delta doping) show larger $\Delta E_{AF}$ and lower Cr$_{Zn}$ formation energy than N220 (homogeneous half-layer delta doping) and N222 (homogeneous doping). Among them, N200 shows the largest $\Delta E_{AF}$ (0.394 eV per Cr–Cr pair) and N111 shows the lowest Cr$_{Zn}$ formation energy (1.229 eV).

That is, Cr impurities tend to cluster into the Cr dimer under lower doping concentrations. Comparatively, we investigated the single-layer delta-doping structure of Zn$_{0.875}$Cr$_{0.125}$S, which showed $\Delta E_{AF}$ of 0.561 eV per Cr–Cr pair and Cr$_{Zn}$ formation energy of 1.105 eV. Apparently, the single-layer delta-doping structure shows larger $\Delta E_{AF}$ and lower Cr$_{Zn}$ formation energy than the half-layer delta-doping and Cr dimer structures with the same doping concentration, and the lower concentration delta-doping structure shows larger $\Delta E_{AF}$ and lower Cr$_{Zn}$ formation energy than the higher one. Furthermore, we investigated the double-layer delta-doping structure of the Zn$_{0.75}$Cr$_{0.25}$S and ZnS/CrS heterostructure. The results indicate ground state HMF in both samples with $\Delta E_{AF}$ of
0.166 eV and 0.055 eV per Cr–Cr pair and CrZn formation energy of 1.014 eV and 0.980 eV, respectively. (Here, we define two AFM states for the ZnS/CrS heterostructure; one is defined by alternating planes of spin up/spin down in the direction [0 0 1] of cubic ZnS, another is defined by spin up and down in the same plane perpendicular to [0 0 1]. The results show that the former is more energetically favourable.) The latter shows smaller \( \Delta E_{\text{AF}} \) which is closer to the cubic CrS (0.063 eV per Cr–Cr pair). Inspection of the relations between the delta-doped CrS layers and \( \Delta E_{\text{AF}} \) and Cr Zn formation energy, we can see that both the \( \Delta E_{\text{AF}} \) and the Cr Zn formation energy show a trend to decrease as the delta-doped CrS layers increase, which decrease fast at first and get slower when the delta-doped CrS go beyond two layers. On observing the total and Cr sites magnetic moments, we can see that the doping configurations show no effect on the total magnetic moments, while little on the Cr sites magnetic moments. Generally, the more homogeneous structures show lower Cr sites magnetic moments, larger Cr–Cr distance, smaller \( \Delta E_{\text{AF}} \) and larger CrZn formation energy. The Cr dimer and the single-layer delta-doping structures show larger Cr sites magnetic moments, smaller Cr–Cr distance (compared with the Zn–Zn distance of 3.828 Å in ZnS), larger \( \Delta E_{\text{AF}} \) and smaller CrZn formation energy. The double-layer delta-doping and ZnS/CrS heterostructure show larger Cr sites magnetic moments, larger Cr–Cr distance (which is larger than the Zn–Zn distance in ZnS, but smaller than the Cr–Cr distance in cubic CrS), smaller \( \Delta E_{\text{AF}} \) and smaller CrZn formation energy. Apparently, the \( \Delta E_{\text{AF}} \) shows a clear Cr–Cr distance and structure dependence, and CrZn formation energy shows an aggregation dependence. The smaller Cr–Cr distance structures always show larger \( \Delta E_{\text{AF}} \) and intense aggregation structures show lower CrZn formation energy. In summary, all studied doping configurations of Zn\(_{1-x}\)Cr\(_x\)S show ground state HMF, and Cr impurities are prone to planar clustering into delta-doping structures with enhanced HMF.

Figure 2 shows the spin- and sites-resolved density of states (DOS) of the homogeneous-doping and single-layer delta-doping structures of Zn\(_{0.75}\)Cr\(_{0.25}\)S in their ferromagnetic states. Apparently, both samples show pronounced majority HMF around the Fermi level (\( E_F \)). The DOS curves of the homogeneous-doping structure are more regular than the delta-doping one, which should be attributed to the enhanced Jahn–Teller effect in the latter. The homogeneous-doping structure shows a S–Cr–S angle of 109.47° and a Cr–S distance of 2.385 Å (larger than the Zn–S distance of 2.344 Å in ZnS), while the single-layer delta-doping structure shows two S–Cr–S angles of 105.66° and 111.41° and a Cr–S distance of 2.389 Å. The existence of Cr impurities expands the ZnS substrate isotropically in the former, while it distorts the ZnS substrate anisotropically in the latter. Apparently, the Jahn–Teller effect is more remarkable in the delta-doping structure. For both doping structures, both Cr and S atoms contribute to the majority HMF around the \( E_F \), evidencing strong hybridization between Cr and S atoms. The DOS peaks of the impurities in the band gap of pure ZnS can be associated with the \( e^{-t_2} \) splitting expected from a simple crystal field model and the spontaneous Jahn–Teller distortion of bonding in cubic ZnS. Hordequin et al. [44] and Qian et al. [26] have investigated the relation between the electronic structure and the spin-flip transitions (electronic phase transition from half-metal to normal ferromagnet or semiconductor) temperature \( T^* \). They found that the spin-flip gap \( \delta \) is relevant for \( T^* \); the wider the \( \delta \), the higher the \( T^* \). Inspecting the DOS of the homogeneous- and delta-doping structures of Zn\(_{0.75}\)Cr\(_{0.25}\)S around \( E_F \), we can see that the latter shows a wider gap \( \delta \) than the former. So, just in view of the electronic structure, we can deduce that the delta-doping structure should possess higher \( T^* \) than the homogeneous-doping structure. Actually, besides the electronic structure, the ferromagnetic stabilization energy \( \Delta E_{\text{AF}} \) shows an impact on the spin-flip transition temperature \( T^* \) too. Basically, the larger the \( \Delta E_{\text{AF}} \), the
higher the $T^*$. From table 1, we can see that the delta-doping structures of Zn$_{1-x}$Cr$_x$S show larger $\Delta E_{AF}$ than the homogeneous-doping ones. So, just in view of $\Delta E_{AF}$, we can see that the delta-doping structure should possess higher $T^*$ than the homogeneous-doping one. In summary, the single-layer delta-doping structure shows enhanced HMF compared with the homogeneous-doping one in both electronic structure and ferromagnetic stability.

Figure 3 shows the DOS of the double-layer delta-doping structure of Zn$_{0.75}$Cr$_{0.25}$S and the ZnS/CrS heterostructure in their ferromagnetic states. Apparently, both samples show pronounced majority HMF around $E_F$. Compared with the single-layer delta-doping structure (figure 2), the DOS of the double-layer delta-doping structure of Zn$_{0.75}$Cr$_{0.25}$S and the ZnS/CrS heterostructure, in particular the impurity DOS, broaden significantly with more fingerprint peaks, which should be attributed to the enhanced Jahn–Teller effect here. Moreover, another difference would be the spin-flip gap $\delta$. For the single-layer delta-doping structure, the gap $\delta$ is defined by $E_F$ and the impurity band maximum in the majority-spin channel, while it is defined by $E_F$ and the conduction-band minimum (CBM) of the double-layer delta-doping structure of Zn$_{0.75}$Cr$_{0.25}$S and the ZnS/CrS heterostructure in the minority-spin channel.

The origin of HMF in Zn$_{1-x}$Cr$_x$S can be depicted by a simple crystal field model, where one Cr atom lies in the tetrahedral centre of four S atoms. Figure 4 schematic describes the p–d hybridization of Cr in S tetragonal (Td) field. Therein, the Cr d orbitals would experience an $e$–$t_2$ splitting, which would hybridize with the neighbour S p orbitals further and then lead to HMF. For symmetric reasons, the Cr $t_2$ orbitals hybridize with S p strongly while Cr e is weak. The energy difference between the spin-up and spin-down channel is due to the spin exchange splitting. Apparently, in Cr doped ZnS, the spin exchange splitting energy is larger than the crystal field splitting energy. That is, the crystal field splitting energy is smaller than the electron pairing energy. So, the system would follow a high-spin arrangement. To lower the total energy, the system would experience a spontaneous Jahn–Teller distortion, where only the lower degenerate energy levels are partially filled. From figure 4, we can see that the majority states around $E_F$ are mainly from the bonding p–d hybrid orbitals, and the half-metallic gap is formed by the energy difference between the minority bonding p–d hybrid orbitals and Cr e orbitals. So, any factor strengthening the p–d hybridization ($e$–$t_2$ splitting) would enhance the HMF. Delta doping is a kind of controllable distortion, which can enhance the spontaneous Jahn–Teller effect by breaking the symmetry further. Consequently, the total energy of the system is further lowered.

For Zn$_{1-x}$Cr$_x$S, the ground state magnetism is determined by the competition between the ferromagnetic double-exchange interaction and the antiferromagnetic superexchange interaction, and the former is demonstrated to be dominating [1, 9]. From table 1, it is easy to see that the nearer the Cr–Cr distance, the stabler the FM. Obviously, both the ferromagnetic and antiferromagnetic coupling in Zn$_{1-x}$Cr$_x$S are getting stronger, and the former is predominant over the latter as the Cr–Cr distance reduces. According to Sato and Katayama-Yoshida [1], the itinerant properties of the spin-polarized conduction electrons play an important role in the stabilization of the ferromagnetic state in ZnX based MSs. Apparently, compared with doping configurations containing two Cr impurities, the single-layer delta-doping structures of the cubic Zn$_{1-x}$Cr$_x$S provide a more direct (effect) channel for valence electrons (Cr $t_2$) to itinerate. Consequently, the ferromagnetic stability of the single-layer delta-doping structures is substantially enhanced. Comparatively, the double- and multi-layer delta-doping structures show decreasing $\Delta E_{AF}$ (approaching the value of cubic CrS) as the delta-doping layers get thicker. Here, the ferromagnetism can be depicted by the simple crystal field model [45].

Typically, we studied the sites-resolved magnetic moments of the single-layer delta-doping structure of...
Zn\(_{0.75}\)Cr\(_{0.25}\)S. Therein, only Cr and first-neighbour S atoms show magnetic moments of 4.30\(\mu_B\) and 0.15\(\mu_B\), respectively, while the other atoms show zero magnetic moments. Apparently, the delta-doping structure shows a two-dimensional HMF, and the magnetic coupling in Cr doped ZnS has a short-range nature.

Theoretically, we can achieve fractional- or multi-layer delta doping accurately via the metastable MBE synthesis in the laboratory by modulating the flux ratio of the precursors. Practically, ideal synthesis is hard to realize, especially mass production in a factory. There are many factors that determine the distribution of magnetic impurities during the MBE synthesis such as temperature, fluctuation of the precursors flux ratio, surface flatness of the matrix semiconductor, the post-treatment temperature and ambience and so on. That is, the magnetism in the MSs via the MBE synthesis is more dynamics determined rather than energetics. As a result, mostly, the magnetism in MSs is metastable, which depends crucially on the microscopic distributions of the clusters of magnetic impurities [23–25, 46]. Global magnetism is the collective effect of different magnetic domains. Interestingly, as discussed above, all studied doping configurations of Zn\(_{1-x}\)Cr\(_x\)S show ground state HMF. This is a valuable character, which would make the metastable MBE synthesis more technologically feasible. Moreover, ZnS not only shows small lattice mismatch with silicon but also shares a similar crystal structure. That is, Zn\(_{1-x}\)Cr\(_x\)S not only shows ground state HMF, but also has good compatibility with silicon. So, we speculate that Zn\(_{1-x}\)Cr\(_x\)S may be a more practical spintronics material integrated into the mainstream semiconductor technology.

4. Conclusions

In summary, we have investigated the magnetism and aggregation trends in Zn\(_{1-x}\)Cr\(_x\)S using DFT calculations. We find that all studied doping configurations here show ground state HMF, and Cr impurities are prone to planar clustering into the delta-doping structures with enhanced HMF. The single-layer delta-doping structure of Zn\(_{0.75}\)Cr\(_{0.25}\)S and Zn\(_{0.875}\)Cr\(_{0.125}\)S show \(\Delta E_{\text{AF}}\) of 0.551 eV and 0.561 eV per Cr–Cr pair, respectively, which are substantially higher than that of many compound semiconductor based MSs. Moreover, our studies also demonstrated ground state HMF in the half-, double- and multi-layer delta-doping structures of Zn\(_{1-x}\)Cr\(_x\)S. The magnetic coupling in Zn\(_{1-x}\)Cr\(_x\)S shows a short-range nature, and the origin of HMF is discussed using a simple crystal field model. Finally, we anticipate the potential spintronics application of Zn\(_{1-x}\)Cr\(_x\)S.

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References

[1] Sato K and Katayama-Yoshida H 2002 Phys. Status Solidi b 263
[2] Sato K and Katayama-Yoshida H 2002 Semicond. Sci. Technol. 17 367
[3] Katayama-Yoshida H and Sato K 2003 Physica B 327 337
[4] Stern R A, Schuler T M, MacLaren J M, Ederer D L, Perez-Dieste V and Himpfel F J 2004 J. Appl. Phys. 95 7468
[5] Shoren H, Ikemoto F, Yoshida K, Tanaka N and Motizuki K 2001 Physica B 10 242
[6] Fan S W, Yao K L and Liu Z L 2009 Appl. Phys. Lett. 94 152506
[7] Sarkar I, Sanyal M K, Takeyama S, Kar S, Hirayama H, Mino H, Komori F and Biswas S 2009 Phys. Rev. B 79 054410
[8] Sreekantha R D, Kang B, Yu S C, Gunasekhar K R and Sreedharra R P 2008 Appl. Phys. A: Mater. Sci. Process. 91 627
[9] McNorton R D, Schuler T M, MacLaren J M and Stern R A 2008 Phys. Rev. B 78 075209
[10] Xie W-H and Liu B-G 2004 J. Appl. Phys. 96 3559
[11] Liu Y and Liu B-G 2007 J. Phys. D: Appl. Phys. 40 6791
[12] Wang W G, Han K J, Yee K J, Ni C, Wen Q, Zhang H W, Zhang Y, Shah L and Xiao J Q 2008 Appl. Phys. Lett. 93 6791
[13] Saito H, Zayets V, Yamagata S and Ando K 2003 Phys. Rev. B 67 921506
[14] Saito H, Zayets V, Yamagata S and Ando K 2003 J. Appl. Phys. 93 6796
[15] Kang T, Sung J, Shim W, Moon H, Cho J, Jo Y, Lee W and Kim B 2009 J. Phys. Chem. C 113 5352
[16] Lakshmi P V B, Raj K S and Ramachandran K 2008 Cryst. Res. Technol. 43 155
[17] Sambasivam S, Joseph D P, Reddy D R, Reddy B K and Jayasanker C K 2008 Mater. Sci. Eng. B 150 125
[18] Radovanovic J, Milanovic V, Ikonic Z and Indjin D 2007 J. Phys. D: Appl. Phys. 40 5066

Figure 4. The scheme of the p–d hybridization in Zn\(_{1-x}\)Cr\(_x\)S.
[19] Guth M, Schmerber G, Henry Y and Dinia A 2002 J. Magn. Magn. Mater. 240 152
[20] Kaspar T C, Droubay T, Heald S M, Engelhard M H, Nachimuthu P and Chambers S A 2008 Phys. Rev. B 77 201303
[21] Collins B A, Chu Y S, He L, Zhong Y and Tsui F 2008 Phys. Rev. B 77 193301
[22] Sandratskii I. M., Bruno P and Mirbt S 2005 Phys. Rev. B 71 045210
[23] Hynninen T, Raebiger H, von Boehm J and Ayuela A 2006 Appl. Phys. Lett. 88 122501
[24] Rao B K and Jena P 2002 Phys. Rev. Lett. 89 185504
[25] Sreenivasan M G, Teo K L, Cheng X Z, Jali lMBA, L eiwT, Chong T C, Du A Y, Chan T K and Osipowicz T 2007 J. Appl. Phys. 102 053702
[26] Qian M C, Fong C Y, Liu K, Pickett W E, Pask J E and Yang L H 2006 Phys. Rev. Lett. 96 027211
[27]Nazmul A M, Amemiya T, Shuto Y, Sugahara S and Tanaka M 2005 Phys. Rev. Lett. 95 017201
[28] Fernandez-Rossier J and Shami L J 2001 Phys. Rev. B 64 235323
[29] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science 287 1019
[30] Karazhanov S Zh, Ravindran P, Kjkhus A, Fjellvag H, Grossner U and Svensson B G 2006 J. Appl. Phys. 100 043709
[31] Karazhanov S Zh, Ravindran P, Kjkhus A, Fjellvag H and Svensson B G 2007 Phys. Rev. B 75 155104
[32] Karazhanov S Zh, Ravindran P, Kjkhus A, Fjellvag H, Grossner U and Svensson B G 2006 J. Cryst. Growth 287 162
[33] Tablero C 2006 Phys. Rev. B 74 195203
[34] Miyake T, Zhang P, Cohen M L and Louie S G 2006 Phys. Rev. B 74 245213
[35] Sandratskii L M and Bruno P 2003 J. Phys.: Condens. Matter 15 L585
[36] Chanier T, Sargolzael M, Ophale I, Hayn R and Koepferik K 2006 Phys. Rev. B 73 134418
[37] Gopal P and Spaldin N A Phys. Rev. B 74 094418
[38] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[39] Vanderbilt D 1990 Phys. Rev. B 41 7892
[40] Segall M D, Lindan P L D, Probert M J, Pickard C J, Hasnip P J, Payne S M C and Clark J 2002 J. Phys.: Condens. Matter. 14 2717
[41] Zhang S B and Northrup J E 1991 Phys. Rev. Lett. 67 2339
[42] Garcia A and Northrup J E 1995 Phys. Rev. Lett. 74 1131
[43] Jeon H C, Kang T W, Kim T W, Kang J and Chang K J 2005 Appl. Phys. Lett. 87 092501
[44] Hordequin C, Ristoiu D, Ranno L and Pierre J 2000 Eur. Phys. J. B 16 287
[45] Mavropoulos Ph and Galanakis I 2007 J. Phys.: Condens. Matter 19 315221
[46] Bergqvist L, Eriksson O, Kudrnovsky J, Drchal V, Kozhavryi P and Turek I 2004 Phys. Rev. Lett. 93 137202