Structure, electronic and magnetic properties of Cr-doped \((\text{ZnS})_{12}\) clusters: A first-principles study

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We have studied the structural, electronic, and magnetic properties of \((\text{ZnS})_{12}\) clusters doped with one (monodoped) and two (bidoped) Cr atoms in terms of a first-principles method. Substitutional, exohedral, and endohedral doping are considered. The substitutional isomer is found to be most favorable in energy for monodoped clusters, while the exohedral isomers are found to be most favorable for bidoped clusters. The magnetic coupling between the Cr atoms is mainly governed by the competition between direct Cr–Cr antiferromagnetic (AFM) interaction and the ferromagnetic (FM) interaction between two Cr atoms via S atom due to strong \(p–d\) hybridization. Finally, we show that the exohedral bidoped \((\text{ZnS})_{12}\) clusters favor the FM state, which has potential applications in nanoscale quantum devices.

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1. Introduction

The discovery of ferromagnetism in Mn-doped GaAs with a Curie temperature of 110 K has created an intense interest in the study of dilute magnetic semiconductors (DMS) [1]. Studies of these systems are driven not only by the academic interest in understanding the origin of ferromagnetism but also by the potential applications. In an effort to raise Curie temperature to values above room temperature, whence DMS could become commercially visible, there has been a push towards hosts with wide band gap such as Zinc sulfide (ZnS, 3.7 eV at 300 K) [2,3]. Moreover, compared with bulk and film, cluster usually displays some unique properties due to its special geometry and the quantum confinement effect, which hold promise for advanced nanodevice applications [4–6]. With the recent emergence of nanoscience and nanotechnology, doping of clusters and nanoparticles has also attracted a great deal of attention because of their prospects in technological applications [7–10].

The pristine ZnS clusters have been extensively studied both experimentally [11–13] and theoretically [14–20]. In contrast, the doped ZnS clusters, especially those doped with transition metal (TM) elements, are less to be investigated. The effect of impurity doping on the structural stability and magnetism of the cluster is not well understood yet. Moreover, among these cage-like ZnS structures, the \((\text{ZnS})_{12}\) is the smallest cage structure with the highest possible symmetry (octahedral) [21], which can be taken as a good candidate for the investigation of Cr-doped ZnS clusters. Previous works have been performed on the \((\text{ZnO})_{12}, (\text{GaAs})_{12}, (\text{ZnTe})_{12}\), and \((\text{CdS})_{12}\) clusters doped with TM atoms [22–25]. For instance, Liu et al. have investigated the structure, electronic, and magnetic properties of Mn-doped \((\text{ZnO})_{12}\) clusters and concluded that Mn impurities have a tendency of clustering and the coupling is dominated by short-range AFM ordering [22]. Also, Yadav et al. [24] and Ghost et al. [25] have found that both the short-ranged FM and AFM coupling could exist in the Cr-doped \((\text{ZnTe})_{12}\) and \((\text{CdS})_{12}\) clusters, respectively, depending on the Cr–Cr distance and the local environment of Cr atoms.

In this Letter, we present a systematical theoretical investigation on the geometry, electronic, and magnetic properties of \((\text{ZnS})_{12}\) clusters doped with one or two Cr atoms. For the five optimized isomers of the monodoped case, the doping-induced structural changes of the clusters are very small. For the bidoped case, most importantly, we show that the exohedral bidoped \((\text{ZnS})_{12}\) clusters favor the FM state, which has potential applications in nanoscale quantum devices.

2. Theoretical method and computational details

The calculations are performed using spin-polarized density functional theory (DFT), as implemented in the DMOL package [26]. This method can perform accurate and efficient self-consistent calculations using a rapidly convergent three-dimensional numerical integration scheme. All electrons treatment and double numerical basis set including \(d\)-polarization functions (DND)
are chosen. The Direct Inversion in an Iterative Subspace (DIIS) approach is used to speed up Self-Consistent Field (SCF) convergence. We also apply thermal smearing to the orbital occupation to speed it up. For the accurate calculations, we have chosen an octupole scheme for the multipolar expansion of the charge density and Coulomb potential. The exchange-correlation interaction is treated by generalized gradient approximation (GGA) with the functional parameterized by Perdew–Burke–Ernzerhof correction (PBE) [27]. SCF calculations are done with a convergence criterion of 10^{-6} hartree on the total energy. All structures are fully optimized without any symmetry constraint with a convergence criterion of 0.002 hartree/Å for the forces and 0.005 Å for the displacement. Mulliken population analysis [28] is performed to determine the charge transfer and magnetic moment on each atomic site.

For geometry optimization of each isomer, all allowable spin multiplicities are considered. To further check the stability, frequency analysis is employed for the optimized structures. As is well known in the cluster, the orbital magnetic moment is quenched and the magnetic moment comes exclusively from the spin of the electrons [29]. Throughout this work we do not consider the relativistic effects, e.g., the spin–orbital coupling. As a result, the magnetic moments provided in this study reflect the spin-only values.

The accuracy of PBE/DND has been assessed in our previous study on ZnS nanowires [30]. Moreover, for the Cr2 dimer, at the level of PBE/DND its ground state is an AFM configuration. The molecule has a bond length of 2.19 Å, and binding energy of \(-1.25\) eV compared to the experimental values of 1.68 Å and \(-1.42\) eV, respectively [31]. It is noted that GGA generally tends to underbind yielding larger atomic distance than realistic [32]. For comparison, we further obtain the bond length 1.70 Å for Cr2 dimer in local density approximation (LDA), consistent with the experimental result and theoretical result previously calculated in LDA [33]. Nevertheless, GGA for the exchange-correlation energy improves upon the LDA description of atoms, molecules, and solids [27]. In addition, the previous studies [22, 23, 25] have indicated that the main conclusions on the structural stability, the electronic and magnetic properties of the doped semiconductor clusters are reliable at GGA/PBE level. Thus, we believe that our computational scheme is appropriate for describing the properties of the Cr atoms doped (ZnS)_{12} cluster.

As we know, the Cr atom can interact with the host cluster in three possible ways, (a) replace the atom from the host cluster (substitutional); (b) occupy the center of the cage formed by the host cluster (endoherdal); (c) absorbed on the surface of the host cluster (exohedral). We have constructed various monodoped and bidoped clusters according to the interaction between the Cr atom and the host clusters.

Commonly, the thermodynamic stability of a cluster is determined by its binding energy, which is defined as \(E_b = (E_{tot} - \sum_i E_{atom}^i) / \sum_i n_i\), where \(E_{tot}\), \(E_{atom}^i\), and \(n_i\) are the total energy of the cluster, the energy, and the number of the isolated ith atom, respectively. Furthermore, the fragmentation energy is introduced to indicate the stability of the cluster, especially for comparison between various isomers with different chemical composition. In general, for a fragmentation channel \(A \rightarrow B + C\), the fragmentation energy can be defined as \(\Delta E = E_B + E_C - E_A\), where \(E_B\), \(E_C\), and \(E_A\) are the total energies of clusters B, C, and A, respectively.

3. Results and discussion

3.1. Pristine (ZnS)_{12} clusters

We first consider the pristine (ZnS)_{12} cluster, which is found to be highly stable at a fullerenerlike structure (T_b symmetry) with eight hexagons and six isolated squares. There are two unequiv-alent Zn–S bonds: the Zn–S bond inside the four-member rings has a length of 2.351 Å, while that between the four-member rings has a length of 2.266 Å. The average Zn–S bond length of the cluster is 2.322 Å. The noticeable cavity in the structure, which corresponds to an utmost interatomic distance of 6.479 Å between Zn atoms or 7.704 Å between S atoms, provides a possibility for endohedral doping. The bonding energy of the cluster is \(-2.775\) eV/atom, which is larger than the corresponding bulk values (\(-3.079\) eV/atom for wurtzite and \(-3.081\) eV/atom for zinc-blende), showing the general expected result that the clusters are less energetically favorable than its bulk. The large HOMO–LUMO gap of 3.47 eV indicates as well as high stability character of the cluster. Our spin-polarized calculations indicate that the cluster is a closed shell system without any local atomic magnetic moment.

3.2. Monodoped (ZnS)_{12} clusters

3.2.1. Geometrical structure

The ground state structure is considered for five different kinds of monodoping structures. (a) A1: a Cr atom substitutes one Zn atom. (b) A2: a Cr atom is endohedral into the center of the cage. (c) A3: a Cr atom is initially placed at the hollow site of a Zn and two S atoms within a square surface. After geometry optimization, the Cr atom occupies original Zn position and pushes the Zn atom away. (d) A4: a Cr atom bridges over a Zn–S bond that connects two squares. (e) A5: a Cr atom bridges over a Zn–S bond of square. The fully optimized structures are shown in Fig. 1(a). Apart from the formation of new bonds due to the inclusion of a Cr atom, the other bond lengths in these clusters are more or less similar to those in the pristine (ZnS)_{12} cage. We also note that the substitutional doped isomer A1 has similar geometry with the pristine (ZnS)_{12} cluster, though the Cr–S bond is a little larger than Zn–S bond.

3.2.2. Energetic and stability

In order to explore the stability of the doped clusters, we calculated the binding energy, HOMO–LUMO gap, and the fragmentation energy. The results are presented in Table 1. For the isomers A2–A5 with the same chemical composition, the most stable isomers is A3, indicating that exohedral isomer is more favorable than endohedral one. Similar behavior was found for the Mn-doped (ZnO)_{12} and Cr-doped (CdS)_{12} cage [22, 25]. While for the Mn-doped (GaAs)_{12} cage, the endohedral isomer is more stable than exohedral one [23]. The HOMO–LUMO gaps of all doped isomers are smaller than that of the pristine (ZnS)_{12} cluster (3.47 eV) due to the newly formed hybridized states.

The fragmentation energies were calculated by two different channels. One is “Cr-doped cluster \(\rightarrow (\text{ZnS})_{12} \text{cluster} + \text{an isolated Cr atom}\)” denoted as \(\Delta E_1\). Larger positive value represents that the Cr-doped isomer is more stable. For the substitution case, the total energy of the “Cr-doped” cluster is set as sum of the total energies of A1 and Zn atom. The other is “Cr-doped cluster \(\rightarrow\) isomer A1 + an isolated Zn atom” denoted as \(\Delta E_2\). Smaller negative value represents that the corresponding Cr-doped isomer is more unstable. As listed in Table 1, the positive values of \(\Delta E_1\) for all cases imply that the pristine (ZnS)_{12} cluster can easily accommodate a Cr atom. The negative values of \(\Delta E_2\), however, suggest that the substitutional doping is more stable. For example, \(\Delta E_2\) of isomer A3 is \(-0.35\) eV. This indicated that the complex of substitution isomer A1 and an isolated Zn atom is slightly more favorable than isomer A3, which is the most stable among isomers A2–A5. It also tells us that Cr atom has preference to replace one of the Zn atoms when it is doped into the cluster.
3.2.3. Electronic and magnetic properties

Based on the optimized geometries, the magnetic properties of all doped clusters are computed and the results are presented in Table 1. Monodoped isomers show interesting magnetic properties (see Table 1). All isomers have total magnetic moments $4\mu_B$ except A2 whose total magnetic moment is $6\mu_B$. The magnetic moment is mainly contributed by the $3d$ component of Cr atom, while the $4s$ and $4p$ orbital also have certain contributions. Due to the hybridization interaction, a small magnetic moment is induced in nearest neighboring S and Zn atoms. From all the above, we can conclude that the magnetic moment of Cr-doped clusters is dependent on the local environment of the Cr atom. Similar behavior was observed for the Cr-doped (CdS)$_{12}$ clusters [25].

It is well known that the local magnetic properties of a TM impurity strongly depend on the local environment. The decreasing ordering of local magnetic moment of Cr is A5 (A4), A2, A3, and A1. The local magnetic moment decreases with increasing the number of neighboring Zn atoms around the Cr atom and decreasing Cr–S bond length. More neighboring S atoms and shorter Cr–S bond length would induce stronger quenching of local magnetic

### Table 1

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$E_b$</th>
<th>Gap</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\mu_{Zn}$</th>
<th>$\mu_s$</th>
<th>$\mu_{Cr}$</th>
<th>$Q_{Cr}$</th>
<th>$\mu_{tot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>−2.847</td>
<td>1.24</td>
<td>1.74</td>
<td>0.00</td>
<td>/</td>
<td>−0.15</td>
<td>0.50</td>
<td>0.18</td>
<td>0.11</td>
</tr>
<tr>
<td>A2</td>
<td>−2.718</td>
<td>1.20</td>
<td>1.35</td>
<td>−0.38</td>
<td>0.07</td>
<td>0.43</td>
<td>−0.06</td>
<td>0.61</td>
<td>0.11</td>
</tr>
<tr>
<td>A3</td>
<td>−2.719</td>
<td>0.74</td>
<td>1.38</td>
<td>−0.35</td>
<td>−0.15</td>
<td>−0.04</td>
<td>0.32</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>A4</td>
<td>−2.701</td>
<td>1.00</td>
<td>0.92</td>
<td>−0.81</td>
<td>−0.24</td>
<td>−0.13</td>
<td>0.30</td>
<td>0.192</td>
<td>0.02</td>
</tr>
<tr>
<td>A5</td>
<td>−2.708</td>
<td>0.94</td>
<td>1.09</td>
<td>−0.65</td>
<td>−0.24</td>
<td>−0.12</td>
<td>0.28</td>
<td>0.17</td>
<td>0.01</td>
</tr>
</tbody>
</table>

It is also observed for the Cr-doped (CdS)$_{12}$ clusters [25].
moment of Cr atom due to the enhanced hybridization between Cr and S atoms. It can be confirmed by the fact that there are 1 (1), 2, and 3 neighboring S atoms for the isomers A5 (A4), A3, and A1, respectively. We should point out that isomer A2 seems more particular, since Cr atom locates in the center of (ZnS)_{12} cage with 12 neighboring S atoms, and it has larger Cr–S distance than the other four isomers.

We further explore the effect of Cr doping on the partial density of states (PDOS) for the most stable configuration A1 and metastable isomers A2 and A3. The PDOSs of substitutional isomer A1, endohedral isomer A2, and exohedral isomer A3 are shown in Figs. 2(a), (b), and (c), respectively. Gaussian broadening has been used while plotting the PDOS curves. It is found that for all the isomers, additional peaks contributed by Cr-3d states appear in the HOMO–LUMO gap of the host cluster. It is clear to see the hybridization between the Cr-3d and the nearest neighboring S-3p for A1 and A3. While for A2, the Cr-3d state is more localized, which may account for the reason why the local magnetic moment of Cr atom is 5.50\(\mu_B\) near to the magnetic moment of an isolated Cr atom (6\(\mu_B\)).

3.3. Bidoped (ZnS)_{12} clusters

In this section, we focus on the bidoped (ZnS)_{12} clusters due to its magnetic coupling between the two Cr atoms. Bidoped isomers, including substitutional, exohedral, and endohedral doped clusters, are constructed from the monodoped (ZnS)_{12} clusters, which will be discussed in the following subsections.

3.3.1. Substitutional bidoped (ZnS)_{12} clusters

Due to high symmetry of the pristine (ZnS)_{12} cage, only five atomic configurations can be constructed for substitutional bidoped (ZnS)_{12} clusters. The fully optimized structures are shown in Fig. 1(b), labeled from B1 to B5 in order of increasing Cr–Cr distance. The geometrical structures of these clusters are similar to that of the pristine (ZnS)_{12} cluster except for certain local deformations. In Table 2, we summarized the calculated results. The total magnetic moment of the FM state is 8\(\mu_B\) for all isomers, which mainly originates from Cr-3d states. Mulliken population analysis shows that the magnetic moment of the nearest neighboring S atoms is antiparallel to that of the Cr atoms, indicating AFM coupling between them in all substitutional isomers. For comparison, the calculated binding energies based on the double numerical basis set including p-polarization functions (DNP) are also shown in Table 2. We find that the results are the same to those based on DND basis sets, indicating that the results based on DND basis sets are reliable.

For isomers B3, B4, and B5 with a large distance over 5 Å, the AFM and FM states are degenerate in energy, and have the same geometry, local charge, and magnetic moment except that the AFM state has a slightly larger HOMO–LUMO gap. The result means that magnetic coupling between the two Cr atoms is short-ranged. For isomers B1 and B2 with a small distance of two Cr atoms, the AFM state is 0.006 and 0.003 eV/atom lower in energy than the FM state. The HOMO–LUMO gap of the AFM state is again larger than that of the FM state. Among the AFM and FM states of all isomers, the AFM state of isomer B1 has the largest binding energy, as well as the largest difference against the corresponding FM state. The results indicate that direct Cr–Cr AFM interaction is dominant over the FM coupling via S atoms. By the way, the lowest energy configuration B1 is an AFM state where two Cr atoms replace two over the FM coupling via S atoms. By the way, the lowest energy configuration B1 is an AFM state where two Cr atoms replace two

3.3.2. Exohedral bidoped (ZnS)_{12} clusters

We obtain five isomers for exohedral bidoped (ZnS)_{12} clusters as shown in Fig. 1(c), labeled from C1 to C5 in order of increas-

Table 2

<table>
<thead>
<tr>
<th>Isomer</th>
<th>(d_{Cr}) (Å)</th>
<th>(E_b) (eV/atom)</th>
<th>(E_L) (eV/atom)</th>
<th>(\text{Gap}) (eV)</th>
<th>(\mu_{Cr}) ((\mu_B))</th>
<th>(\mu_{Cr}) ((\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>3.83</td>
<td>-2.914</td>
<td>-2.914</td>
<td>0.79</td>
<td>0.40</td>
<td>4.10</td>
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<tr>
<td>B2</td>
<td>3.54</td>
<td>-2.915</td>
<td>-2.915</td>
<td>0.90</td>
<td>0.40</td>
<td>4.06</td>
</tr>
<tr>
<td>B3</td>
<td>5.43</td>
<td>-2.913</td>
<td>-2.913</td>
<td>1.18</td>
<td>0.50</td>
<td>4.05</td>
</tr>
<tr>
<td>B4</td>
<td>5.70</td>
<td>-2.912</td>
<td>-2.912</td>
<td>0.99</td>
<td>0.50</td>
<td>4.05</td>
</tr>
<tr>
<td>B5</td>
<td>6.42</td>
<td>-2.912</td>
<td>-2.912</td>
<td>1.12</td>
<td>0.50</td>
<td>4.05</td>
</tr>
</tbody>
</table>
The distance of two Cr atoms ($d_{Cr}$, in Å), binding energy ($E_b$, in eV/atom), and HOMO–LUMO gap (in eV) of endohedral bidoped (ZnS)$_{12}$ clusters. The local charge ($Q_{Cr}$, in a.u.), magnetic moment ($\mu_{Cr}$, in $\mu_B$) of Cr atoms, and magnetic moment ($\mu_S$ and $\mu_{Zn}$, in $\mu_B$) of the nearest neighboring S and Zn atoms in these clusters are also shown.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>FM</th>
<th></th>
<th></th>
<th>AFM</th>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$d_{Cr}$</td>
<td>$E_b$</td>
<td>Gap</td>
<td>$Q_{Cr}$</td>
<td>$\mu_{Zn}$</td>
<td>$\mu_S$</td>
<td>$\mu_{Cr}$</td>
<td>$\mu_{tot}$</td>
</tr>
<tr>
<td>C1</td>
<td>2.85</td>
<td>−2.673</td>
<td>0.86</td>
<td>0.32</td>
<td>−0.13</td>
<td>−0.33</td>
<td>4.22</td>
<td>0.20</td>
</tr>
<tr>
<td>C2</td>
<td>5.01</td>
<td>−2.701</td>
<td>0.78</td>
<td>0.32</td>
<td>−0.13</td>
<td>−0.24</td>
<td>4.14</td>
<td>0.10</td>
</tr>
<tr>
<td>C3</td>
<td>6.38</td>
<td>−2.664</td>
<td>0.65</td>
<td>0.32</td>
<td>−0.27</td>
<td>−0.11</td>
<td>4.18</td>
<td>0.39</td>
</tr>
<tr>
<td>C4</td>
<td>8.35</td>
<td>−2.658</td>
<td>0.73</td>
<td>0.31</td>
<td>−0.28</td>
<td>−0.08</td>
<td>4.18</td>
<td>0.36</td>
</tr>
<tr>
<td>C5</td>
<td>8.52</td>
<td>−2.650</td>
<td>0.70</td>
<td>0.31</td>
<td>−0.30</td>
<td>−0.07</td>
<td>4.18</td>
<td>0.53</td>
</tr>
</tbody>
</table>

The optimized geometry of endohedral bidoped (ZnS)$_{12}$ cluster is shown in Fig. 1(d) (labeled as D). Compared with pristine (ZnS)$_{12}$ cage, the endohedral bidoped (ZnS)$_{12}$ is somewhat distorted, seems more prolate due to the encapsulation of two Cr atoms, and the average distances of Zn and S atoms become larger. The calculated results are summarized in Table 4. The Cr–Cr distance is 2.36 Å and 2.24 Å for FM and AFM state, respectively. The Cr–Cr distance is the smallest compared to all other bidoped isomers. The AFM state is 0.05 eV/atom lower than the FM state, which is the largest energy difference among all other bidoped isomers. We can conclude that the direct Cr–Cr AFM interaction is the strongest when encapsulated inside (ZnS)$_{12}$ cluster, which makes the cluster be in favor of AFM state. Similar behavior was observed for the Cr doped (CdS)$_{12}$ cage [25]. Although the binding energy is significantly reduced compared with the substitutional and exohedral bidoped cases, the AFM state has the largest HOMO–LUMO gap among all bidoped cases. The vibrational frequency is calculated for both FM and AFM states and no imaginary frequency is found for both of them, indicating that they are all stable around their local equilibrium structures. We further examine the stability of the AFM isomer by considering two fragmentation processes which include “the endohedral bidoped cluster → (ZnS)$_{12}$ + two isolated Cr atoms or a Cr$_2$ dimer.” The obtained fragmentation energies are 3.07 and 1.82 eV, respectively. This indicates that the hollow cavity of the (ZnS)$_{12}$ cage can hold the two Cr atoms steadily.

3.3.3. Endohedral bidoped (ZnS)$_{12}$ clusters

The calculated results are listed in Table 3. The total magnetic moment of the FM state of the clusters is $\mu_{tot}$, independent of their atomic configuration. Similar to the case of substitutional bidoped isomers, the magnetic moment arises mainly from the Cr-3d electron. Mulliken population analysis shows that the magnetic moments of the nearest neighboring S and Zn atoms are all antiparallel to that of the Cr atoms, indicating AFM coupling between them.

Different from the substitutional bidoped isomers which favor AFM states, we observe that the coupling is FM for C1 and C2 isomers, indicating the FM coupling via S atoms are dominant over direct Cr–Cr AFM interaction. The FM states are 0.009 and 0.011 eV/atom lower in energy than the AFM states of C1 and C2, respectively. For all other isomers, the AFM state and the corresponding FM state are degenerate. The ordering in binding energy is $C2 > C1 > C3 > C4 > C5$. The structure of isomer C2 is somewhat distorted, which leads to one of the Cr atom with three nearest neighboring S atoms, Each Cr atom has two nearest neighboring S atoms in isomer C1. The FM interaction between two Cr atoms via S atom due to strong p–d hybridization makes isomer C2 more stable than isomer C1.

In Fig. 3 we show the variation of energy difference between the FM and AFM states of substitutional and exohedral bidoped isomers ($\Delta E = E_{AFM} − E_{FM}$) with respect to the Cr–Cr separation in AFM states. The result clearly indicates that the nature of the coupling is short-ranged.

3.3.4. Comparison between the most stable isomers of various bidoped (ZnS)$_{12}$ clusters

It is interesting to compare the bidoped clusters with different doping modes. Firstly, the relative stability of the bidoped clusters should be clarified. We will focus on the most energetically favorable configurations in the substitutional, exohedral, and endohedral bidoped clusters, i.e., the AFM state of isomers B1, D, and FM state of C2. The calculated fragmentation energy is about 0.149 eV for the fragmentation channel $C2 → B1 + 2Zn$, indicating the exohedral isomer is most favorable for bidoped clusters. The vibrational properties of both C2 and B1 are calculated. From our calculations, no imaginary frequency is found for both of them, indicating that they are all stable around their local equilibrium structures. It is noted that the isomers C2 and D have the same chemical composition. As shown in Tables 3 and 4, the binding energy of isomer C2 is 0.021 eV/atom lower than that of isomer D.
This implies that isomer D would transform into other stable configurations if it deviates from its equilibrium structure too much, even though it behaves as a stable local minimum.

The PDOS of AFM and FM states of isomer B1, C2, and D are shown in Figs. 4(a)–(c) and (d)–(f). The spin-up and spin-down states are identical for the AFM states of B1 and D, consistent with its AFM nature. Although some polarized characteristics are observed near the Fermi level, there is no net magnetic moment for AFM state of C2. From Figs. 4(b) and (e), we can see that the contribution of $p$–$d$ hybridization width for FM state at Fermi level is larger compared to that of AFM state, which means that the $p$–$d$ hybridization is dominate for isomer C2.

Finally, we want to mention that the interactions among the 3$d$ electrons of Cr impurities in the GGA are only partially described, since they are strongly localized. Other scheme beyond GGA such as GGA + U would be employed to deal with local-
ized impurity levels [34]. Nevertheless, the main conclusions on the structural stability, the electronic and magnetic properties of the doped (ZnS)_{12} clusters are still reliable.

4. Conclusion

In conclusion, the structural, electronic, and magnetic properties of (ZnS)_{12} clusters doped with Cr atoms have been studied by employing a first-principles method. For the monodoped case, we find the substitutional isomer is the most energetically favorable state. The magnetic moment of the monodoped clusters is dependent on the local environment of the Cr atom. For the bidoped cases, the exohedral isomers are found to be most favorable. The magnetic coupling between the Cr atoms in bidoped configurations is mainly governed by the competition between direct Cr–Cr AFM interaction and the FM interaction between two Cr atoms via S atom due to strong p–d hybridization. Most importantly, we show that the exohedral bidoped (ZnS)_{12} clusters favor the FM state, which may have the future applications in spin-dependent magneto-optical and magneto-electrical devices.

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