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Electronic Structure and High Magnetic Properties of (Cr, Co)-codoped 4H-SiC Studied by First-Principle Calculations

Mengyu Zhang ¹, Jingtao Huang ², Xiao Liu ^{3,*}, Long Lin ^{2,4} and Hualong Tao ⁵¹ Yellow River Conservancy Technical Institute, Kaifeng 475004, China; zmy3660@163.com² Henan Key Laboratory of Materials on Deep-Earth Engineering, School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China; 211706020022@home.hpu.edu.cn (J.H.); linlong@hpu.edu.cn (L.L.)³ School of Energy Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China⁴ School of Mathematics and Informatics, Henan Polytechnic University, Jiaozuo 454000, China⁵ Liaoning Key Materials Laboratory for Railway, School of Materials Science and Engineering, Dalian Jiaotong University, Dalian 116028, China; Taohualong01@163.com

* Correspondence: liuxiao666_hpu@163.com

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Abstract: The electronic structure and magnetic properties of 3d transition metal (Cr, Co)-codoped 4H-SiC were studied by density functional theory within GGA methods. The results show that all doped magnetic atoms have high magnetic properties in both Cr-doped and Co-doped 4H-SiC, resulting in the net magnetic moments of 3.03, 3.02 μ_B for $\text{Si}_{35}\text{CrC}_{36}$ and $\text{Si}_{35}\text{CoC}_{36}$. The electronic density of states reaches the peak at Fermi level, which is beneficial to the electronic transitions, indicating that Cr-doped 4H-SiC is a semi-metallic material. In addition, the magnetic properties of (Cr, Co)-codoped 4H-SiC were also calculated. The results show that the (Cr, Co)-codoped 4H-SiC system has more stable ferromagnetic properties with ΔE_{FM} of -244.3 meV, and we estimated T_C of about 470.8 K for the (Cr, Co)-codoped 4H-SiC system. The (Cr, Co)-codoped 4H-SiC can be ferromagnetic through some mechanism based on hybridization between local Cr:3d, Co:3d and C:2p states. These interesting discoveries will help promote the use of excellent SiC-based nanomaterials in spintronics and multi-function nanodevices in the near future.

Keywords: dilute magnetic semiconductor; 3d transition metal; magnetism; 4H-SiC; density functional theory

1. Introduction

Dilute magnetic semiconductors (DMSs) have stimulated extensive attention because of their important applications in spintronics [1–6]. In recent years, there have been many ways to prepare DMSs by doping transition metals (TM) atoms in semiconductors host [7–9]. SiC is a promising wide bandgap DMS host that has broad application prospects in high-temperature, high-power, high-frequency and high-thermal conductivity devices [10–13]. The coherent manipulation at the millisecond level of isolated electron spins within the double-vacancy defects of silicon carbide has also appeared in recent literature studies [14–16]. This research laid the foundation for the application of silicon carbide in the fields of quantum communication, nano-scale nuclear magnetic resonance, intracellular magnetic, electrical, and thermal field imaging. Compared with other polytypes, 4H-SiC is an ideal DMS material because of its high electron mobility, electron saturation and drift speed. Because of its excellent properties, 4H-SiC has been widely studied by theoretical and experimental researchers [17–19].

In the design of actual electronic equipment, defects and impurities are the most commonly used means to regulate electrical, magnetic, optical and other properties. As far as experiments are concerned, Song et al. [20] studied the magnetic properties of 6H-SiC doped with Mn atoms. They found that both the doping concentration of Mn and the defects affected ferromagnetism. Wang et al. [21] synthesized Mn-doped SiC thin films and studied the structure and magnetic properties of Mn-doped SiC. Huang et al. [22] tested the magnetic properties of Cr-doped 6H-SiC single crystal and observed the ferromagnetic properties of the sample at low temperature. The Curie apparent temperature is 69.8 K. In addition, the electronic structure and magnetic properties of the transition metal-doped with SiC were studied. Ma et al. [23] studied the magnetic properties of TM (TM = Cr, Mn, Fe) atom doped 6H-SiC. The results show that Cr- and Mn-doped 6H-SiC are semi-metallic ferromagnetic, Co- and Ni-doped 6H-SiC have almost no magnetic properties, and Fe-doped 6H-SiC is paramagnetic. Alazri et al. [24] studied the magnetism of 6H-SiC doped with Mn atom. They found that Mn atoms have magnetic moments for the substitution of Si and C. Bouziane et al. [25] studied the magnetism of 3C-SiC doped with Mn atom. The results showed that replacing Si with Mn can enhance the magnetic properties. Luo et al. [26] investigated the magnetism of different non-magnetic metal dopants on the 2D-SiC monolayer. The results show that, with the increase of Mg–Mg distance, the interaction between the two Mg dopants tends to be magnetic coupling over a long distance, and the coupling comes from *p-d* exchange.

With the DMSs, the coupling between local magnetic moments is an indispensable factor for inducing long-period spin ordering. For DMSs doped with a transition metal, the local magnetic moment is mainly provided by transition metal elements. The debate on ferromagnetic theory is primarily focused on the determination of local magnetic moment coupling media. It is shown that if the impurities have a limited local magnetic moment, it is possible to generate magnetism in the matrix material. Some related modeling work [27,28] using first principles not only extends the scope of DFT methods for silicon-based systems containing transition metal atoms, but also demonstrates the feasibility of predictions made at the level of similar theoretical approaches. As far as we know, theoretical studies on the magnetic properties of SiC-base wide band-gap semiconductors doped with Cr and Co atoms are relatively rare. Using the first principle, the mechanism of local magnetic moment and ferromagnetic properties in (Cr, Co) co-doped 4H-SiC was studied in this paper.

2. Model and Computational Method

The $3 \times 3 \times 1$ supercell model of 4H-SiC with 72 atoms was shown in Figure 1. The large supercells used in the calculations allow us to simulate the distribution of various dopants and their magnetic configurations. As shown in Figure 1, the Cr dopant is fixed at the position marked 0, the Si atom labeled 1–12 is the position substituted by the doped Co atom, and the silicon vacancy is labeled V_{Si} . Site 0 is selected as the position where the Cr atom is mono-doped and the Co atom is mono-doped. This work is carried out by using the first-principles calculation package Cambridge Sequential Total Energy Package (CASTEP) [29] based on the spin density functional theory (DFT) [30–32], and the Kohn-Sham equations were solved using the Perdew–Burke–Ernerhof GGA approximation [33]. We have considered both DFT+U and DFT calculations in the system for all configurations of (Cr, Co)-codoped 4H-SiC, where the U value were selected as 3.0 and 2.5 for Cr and Co atoms [34,35]. The convergence criteria for the geometric structures, stability, electronic and magnetic properties of 4H-SiC are as below, plane-wave energy cut-off is 400 eV, the Brillouin-zone integrations are performed with the special $2 \times 2 \times 2$ Monkhost and Pack k-points mesh.

Figure 1. A $3 \times 3 \times 1$ supercell model of 4H-SiC with 72 atoms. The Cr dopants is fixed at the position labeled 0, the Si atoms labeled by 1–12 are the sites to be replaced by the doped Co atoms. The silicon vacancy is labeled V_{Si} .

3. Results and Discussion

3.1. Cr and Co-doped 4H-SiC

We first considered a single Cr-doped 4H-SiC system, as shown in Figure 1, with a doping concentration of 2.78 at.%. The hybrid state of Cr and Si after replacing a Si atom with a Cr atom in $3 \times 3 \times 1$ supercells was calculated. The results show that the maximum magnetic moment is $3.03 \mu_B$ due to the presence of Cr impurities in the Si site. Cr atoms play an important role in the generation of magnetic moments.

Hence one Cr contributes $2.79 \mu_B$ to the moment. The total and partial density of states (DOS) of Cr-doped 4H-SiC system were calculated, as shown in Figure 2, compared to the intrinsic 4H-SiC system [36], we found that the total DOS after doping are asymmetrical. This is also an important reason why the system displays magnetism. It also can be seen from Figure 2a that the total DOS indicates that the Cr-doped 4H-SiC system is half metallic (i.e., spin-up (-down) states are available (not available) at the Fermi level, E_F). From Figure 2 we can see that the spin-down state is essentially idle, which is the same trend as most DMSs. To further investigate the electronic structure of Cr-doped 4H-SiC system, we present the spin-dependent partial DOS of the Cr, Si and C atoms for the $Si_{35}CrC_{36}$, which is listed in Figure 2b–d. It can be seen from Figure 2 that the total DOS near the Fermi level is mainly composed of the Cr:3d states and the C:2p states. There is a great exchange split between the majority spin bands and the minority spin bands of Cr:3d states.

Figure 2. (a–d) The total and partial density of states (DOS) of Cr-doped 4H-SiC. The Fermi level is set to 0 eV.

Due to the local magnetic moment is the basis of ferromagnetic formation [37,38], next, we choose Co atoms instead of Si atoms to see if there is local magnetic effect. We chose site 0 as the research object, as shown in Figure 1. The doping concentration of Co-doped 4H-SiC is 2.78 at.%. As a result, the total magnetic moment of Co-doped 4H-SiC system is $3.02 \mu_B$ and the Co atom plays a major role. Here, a Co atom provides a magnetic moment of $2.14 \mu_B$. Next, we calculated the total DOS and partial DOS of the Co-doped 4H-SiC system, as shown in Figure 3. We can see from Figure 3a that the total DOS are asymmetrical, which may be the origin of the magnetic properties. Further, we have given the spin-related partial DOS of Co, Si and C atoms of $\text{Si}_{35}\text{CoC}_{36}$ listed in Figure 3b–d. The results show that the spin up and spin down of the total DOS are asymmetric, indicating that the Co-doped 4H-SiC system has magnetic properties. It is found that the Co:3d state has a significant contribution near the Fermi level. For the Co-doped 4H-SiC systems, as shown in Figure 3b–d, the Co:3d states and the C:2p states have strong hybridization near the Fermi level. It is worth noting that majority and minority spin have significant asymmetry in total DOS, which comes from the Co:3d states. This indicates that the Co:3d states have a large effect on the induction of magnetic moment. The change of the energy gap with different doping atoms can be explained by partial DOS analysis.

3.2. (Cr, Co)-codoped 4H-SiC

In the following calculations, we considered the magnetic properties of (Cr, Co)-codoped 4H-SiC. The ferromagnetic stability of Cr and Co atoms in (Cr, Co)-codoped 4H-SiC was investigated by replacing Si at different positions with Co, and the relationship between Cr and Co sites and magnetic properties was found. As shown in Figure 1, we calculated 12 configurations of (Cr, Co)-codoped 4H-SiC. The 12 configurations of the lattice parameters, Cr-Co distance (d (Cr-Co)) before

(Non-spin-polarization, NSP) and after (Spin-polarization, SP) relaxation, magnetization energy (ΔE_{FM}) and the magnetic moment (M) of total, Cr and Co atoms are summarized in Table 1. The magnetization energy ($\Delta E_{FM} = E_{FM} - E_{AFM}$) is used to evaluate the relative stability of ferromagnetism (FM) and anti-ferromagnetism (AFM) states, where E_{FM} and E_{AFM} are the total energies for ferromagnetism and anti-ferromagnetism ordering, respectively. If ΔE_{FM} is negative, it means that the system was ferromagnetic, and if ΔE_{FM} is positive, it means that the system was anti-ferromagnetic.

Figure 3. (a–d) The total and partial DOS of Co-doped 4H-SiC. The Fermi level is set to 0 eV.

By optimizing the spacing of Cr and Co atoms before and after optimization, it is found that the variation of the spacing between Cr and Co atoms is about 0.05 Å, which shows that the geometry of (Cr, Co)-codoped 4H-SiC does not change much, indicating the rationality of the cell. The results show that the doped super-cells established by us are correct and the calculated structural data is reliable. The results also show that the calculation results are very accurate for the total DOS and partial DOS analysis. Our results show that magnetic atoms tend to be ferromagnetic coupled, as shown in Table 1, the most stable configuration of ferromagnetism is the (0, 10) configuration with $\Delta E_{FM} = -244.3$ meV. In the experiment, the influence of the structure for the compound and magnetic doping SiC film was studied by Sun et al. [39], and they found that when the annealing temperature rose to 1200 °C, the doping atom Co formed the compound complete CoSi, and the magnetic film results showed that all films exhibit intrinsic ferromagnetism at 300 K. In order to evaluate the intensity of FM magnetic coupling, the T_C is roughly estimated by the mean-field approximation method of total energy difference $\Delta E_{FM} = E_{FM} - E_{AFM}$, and calculated by the following formula [40,41]:

$$T_C = 2\Delta E_{FM} / 3k_B x \quad (1)$$

where the k_B is the Boltzmann constant and x is the sum of doping atoms ($x = 2$). By using the Equation (1), we estimated T_C of about 470.8 K for the (Cr, Co)-codoped 4H-SiC system. It can

be expected that above room temperature ferromagnetism can be obtained for (Cr, Co)-codoped 4H-SiC-based DMSs. In the next calculation, we chose (Cr, Co)-codoped 4H-SiC the most stable ferromagnetic configuration (0, 10) as the research object, as shown in Figure 1. The total magnetic moment of (Cr, Co)-codoped 4H-SiC system in (0, 10) configuration is $6.02 \mu_B$, which is on account of Co impurity at Si site. The Cr and Co atoms play an important role in the generation of the total magnetic moment, and the Cr and Co atoms contribute $2.16 \mu_B$ and $3.00 \mu_B$ to the moment. To further investigate the magnetic origin, we calculated the total DOS and partial DOS for (0, 10) configuration of (Cr, Co)-codoped 4H-SiC system, as shown in Figure 4. The total integer magnetic moment is consistent with the semi-metallic property shown by the total DOS (see Figure 4), which is consistent with the total magnetic moment obtained from the spin-resolved of total DOS. The (Cr, Co)-codoped 4H-SiC can be ferromagnetic through some mechanism based on hybridization between local Cr:3d, Co:3d and C:2p states.

Figure 4. (a–e) Total and partial density of states of (0, 10) configuration (Cr, Co)-codoped 4H-SiC. The Fermi level is set to 0 eV.

In order to consider the effect of adding U on the system, we further considered the effect of adding U on the system magnetism. As we expected, when we consider the calculation results of all ferromagnetic configurations with U, we find that the most stable ferromagnetic state (0, 10) configuration changes little with $\Delta E_{FM} - 222.3$ meV. The spin population of atoms can also be visually displayed by the way of atom coloring. To understand the magnetic property, the spin density of states is calculated to further investigate the interaction of (0, 10) configuration of (Cr, Co) co-doped 4H-SiC, which is shown in Figure 5. The value is set to 0.05 e^3 . It turns out that the spin-up moments (blue isosurface) locate mainly on TM (TM= Cr, Co) atoms, while the spin-down moments (yellow isosurface) locate mainly on the surrounding C atoms or even not display. The total magnetic moment arises mainly from TM (TM= Cr, Co) atoms, while the contribution of the three nearest-neighbor C atoms with a shorter TM-C bonds. For (Cr, Co)-codoped 4H-SiC system, the magnetic moment is mainly dominated by Cr:3d states and Co:3d states. The hybridization between C:2p, Cr:3d and Co:3d states is observed in Figure 5. It is obvious from Figure 5 that the coupling between C:2p, Cr:3d and Co:3d states is the main reason for the strong ferromagnetism of (Cr, Co)-codoped 4H-SiC system.

Table 1. Calculation results of 12 configurations for (Cr, Co)-codoped 4H-SiC, lattice parameters, Cr–Co distance (d (Cr–Co)) before (NSP) and after (SP) relaxation, magnetization energy (ΔE_{FM}) and the magnetic moment (M) of total, Cr and Co atoms, respectively.

Configuration (a,b)	a	b	c	d (Cr–Co) (NSP)	(Å) (SP)	ΔE_{FM} (meV)	Total	M (μ_B) Cr	Co	Coupling
(0,1)	9.28	9.28	10.14	3.082	3.028	−223.3	5.98	2.16	2.98	FM
(0,2)	9.27	9.28	10.12	5.338	5.355	614.0	6.04	2.35	2.61	AFM
(0,3)	9.27	9.27	10.12	6.163	6.241	668.6	6.01	2.39	2.59	AFM
(0,4)	9.27	9.28	10.12	8.153	8.204	615.4	6.02	2.41	2.58	AFM
(0,5)	9.28	9.28	10.12	4.360	4.363	236.2	5.99	2.36	2.61	AFM
(0,6)	9.28	9.27	10.13	5.339	5.348	258.9	6.03	2.34	2.62	AFM
(0,7)	9.29	9.29	10.14	6.892	6.959	−84.0	6.03	2.17	2.99	FM
(0,8)	9.28	9.29	10.13	8.155	8.205	−179.2	5.96	2.13	2.97	FM
(0,9)	9.29	9.28	10.14	5.344	5.346	−204.9	6.03	2.12	3.01	FM
(0,10)	9.28	9.29	10.13	6.169	6.198	−244.3	6.02	2.16	3.00	FM
(0,11)	9.30	9.29	10.14	6.896	6.927	9.6	6.01	2.16	3.00	AFM
(0,12)	9.28	9.29	10.13	8.158	8.189	−227.7	6.01	2.13	3.00	FM

Figure 5. Spin density distribution of (Cr, Co)-codoped 4H-SiC in ferromagnetism coupling. The blue and cyan yellow display positive and negative spin charge density. The isovalue is set to $0.05 \text{ e}/^3$.

3.3. (Cr, Co, V_{Si})-codoped 4H-SiC

Studies on silicon vacancy and carbon vacancy have been reported in previous literature [42], and we define V_{Si} and V_C indicate the formation of silicon vacancy and carbon vacancy. From their computational results, it is found that the formation energy of V_{Si} is slightly less than that of V_C , which makes it easier to remove a Si atom than C atom in 4H-SiC system, and there's a pattern in other SiC systems [43,44]. So it is interesting to investigate the impact of V_{Si} on the electronic structures and magnetic properties. In the following calculation, we calculated (Cr, Co, V_{Si})-codoped 4H-SiC system based on the (0, 10) configuration, as seen in Figure 1. As a result, ΔE_{FM} of (Cr, Co, V_{Si})-codoped 4H-SiC system is -58.7 meV , which indicates that the magnetism of the system is weakened after the introduction of V_{Si} , while the whole system shows ferromagnetism.

In order to further understand the cause of magnetic changes, here taking the change of the magnetism of (0, 10) configuration for (Cr, Co, V_{Si})-codoped 4H-SiC system as an example. We also investigated the total and partial DOS of (Cr, Co, V_{Si})-codoped 4H-SiC for comparison. As seen in Figure 6, Figure 6a is the total DOS of (Cr, Co, V_{Si})-codoped 4H-SiC, and Figure 6b–e are partial DOS of Cr, Co, Si and C atoms. The lower impurity state near Fermi level mainly comes from hybridization of Cr:3*d* and C:2*p* states with some contributions of Co:3*d* and C:2*p* states. To further clarify the characteristic of the magnetism in (Cr, Co, V_{Si})-codoped 4H-SiC, the visualized spin density distributions are displayed in Figure 7, with a 0.05 $e/3$ iso-surface. The results show that the ferromagnetic coupling of (Cr, Co, V_{Si})-codoped 4H-SiC system is obviously weaker than that without V_{Si} . Our results are consistent with those of Lin et al. [42] In addition, Lin et al. also studied the effect of the presence of carbon vacancies on the ferromagnetism of 4H-SiC system, and they found that the ferromagnetism of the system would be enhanced due to the presence of carbon vacancies. Therefore, silicon vacancy should be avoided as much as possible in the actual production.

Figure 6. (a–e) Total and partial density of states of (0, 10) configuration (Cr, Co, V_{Si})-codoped 4H-SiC. The Fermi level is set to 0 eV.

In the end, we make a conclusion that V_{Si} doped 4H-SiC is not a suitable candidate for exploring the origin of magnetism due to the inappropriate ΔE_{FM} . Therefore, the introduction of similar defects should be avoided in future scientific research work.

Figure 7. Spin density distribution of (Cr, Co, V_{Si})-codoped 4H-SiC in ferromagnetism coupling. The blue and cyan yellow display positive and negative spin charge density. The isovalue is set to $0.05 \text{ e}/^3$.

4. Conclusions

In a word, we have done first-principles calculations to study structure, electron and magnetism of Cr- and Co-mondoped, (Cr, Co)- and (Cr, Co, V_{Si})-codoped 4H-SiC system with different configurations. This work demonstrates the magnetic behavior of 4H-SiC with the help of total spin-polarized energies, magnetic moment, total DOS and partial DOS. In Cr-doped case, the magnetism with maximum magnetic moment of $3.03 \mu_B$ on account of Cr impurity at Si site, and the doping Cr contributes $2.79 \mu_B$ to the moment. In the Co-doped case, the total magnetic moment of the Co-doped 4H-SiC system is $3.02 \mu_B$, and the Co atom contributes $2.14 \mu_B$. The ferromagnetism of the most stable ferromagnetism configuration changes little between GGA and GGA+U. The results show that (Cr, Co)-codoped 4H-SiC is semi-metallic properties. Our calculation results show that the magnetic moments are large and reach up to $6.02 \mu_B$ with $\Delta E_{FM} - 244.3 \text{ meV}$ in (Cr, Co)-codoped 4H-SiC systems, and we estimated T_C of about 470.8 K for the (Cr, Co)-codoped 4H-SiC system. Therefore, the (Cr, Co)-codoped 4H-SiC is a very promising magnetic material for spintronic devices.

The research results also show that the introduction of silicon-vacancy weakens the magnetism of the system, while the introduction of carbon vacancy enhances the magnetism of the system. Our calculation results have a guiding effect on the application of a dilute magnetic semiconductor. In all, (Cr, Co)-codoped 4H-SiC may be a good candidate in the electronic and magnetic fields.

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