Hydrogen interstitials-mediated ferromagnetism in \( \text{Mn}_x\text{Ge}_{1-x} \) magnetic semiconductors

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Abstract. Hydrogen interstitials-mediated ferromagnetism in \( \text{Mn}_x\text{Ge}_{1-x} \) magnetic semiconductors was studied by first-principles calculations. It was found that the H:1s state in Mn–H–Mn complexes can strongly hybridize with the valence states of Mn and change the spin polarization of Mn atoms. Although the doped Mn atoms tend to form the nearest-neighbor Mn atomic pairs with antiferromagnetic coupling in Mn-doped Ge without H, the asymmetrical configurations of Mn–H–Mn complexes show the ferromagnetic (FM) ground state in Mn-doped Ge with H interstitials. Therefore, Mn-doped Ge with H interstitials is predicted to be an FM semiconductor with higher Curie temperature and larger magnetization than Mn-doped Ge without H.

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1. Introduction

Diluted magnetic semiconductors (DMS) have stimulated a great deal of interest because of their potential applications in spintronics [1, 2], where electron spin becomes another degree of freedom in addition to the charge degree of freedom. Ge-based magnetic semiconductors have attracted much attention since they are compatible with the current Si-based processing technology. Park et al [3] found that epitaxial Mn$_x$Ge$_{1-x}$ shows ferromagnetism and its Curie temperature increases linearly with Mn concentration from 25 to 116 K. Li et al [4, 5] found that the Curie temperature of Mn$_{0.05}$Ge$_{0.95}$ DMS is only 12 K for the long-range ferromagnetic (FM) ordering established by the overlapping of the bound magnetic polarons. While Tsui et al [6] found that (Co, Mn)-co-doped Ge shows a Curie temperature of up to 270 K, the saturation magnetization is very small. In contrast, Bougeard et al [7] found no overall spontaneous magnetization down to 2 K in precipitate-free Mn$_{0.05}$Ge$_{0.95}$ films. From these experimental results, we concluded that the Curie temperature of most Mn$_x$Ge$_{1-x}$ DMS is much lower than room temperature and/or the average FM moment per transition metal atom is much less than the single atomic magnetic moment. All these imply that both the Curie temperature and magnetization were greatly reduced due to the antiferromagnetic (AFM) coupling of the nearest-neighbor Mn atomic pairs.

Besides the experimental studies, a lot of theoretical calculations have been performed on Ge-based DMS. First-principles calculation results revealed that the exchange interaction between Mn atoms oscillates as a function of the distance between the Mn atoms [8]. Moreover, Continenza et al [9] reported that compared with Fe and Co, Mn is the most promising transition metal dopant to make Ge suitable for spintronic applications, and the co-doping of (Mn, Co) could favor FM spin alignment. In addition, the interaction between the neighboring substitutional and interstitial Mn atoms is predicted to be AFM [10]. However, most theoretical results revealed that Mn dopants tend to cluster in the Ge host and the AFM ordering is much more stable than the FM ordering between the nearest-neighbor substitutional Mn atoms [3, 8, 11]. According to these theoretical results, it is very hard to achieve high Curie temperature ferromagnetism in Ge-based DMS. Therefore, the key problem to be resolved is to find a way to realize FM coupling between the nearest-neighbor transition metals in Ge-based DMS.

Hydrogen is usually employed to modulate the electrical character of semiconductors since its small radius makes it easy to reside in interstitial positions of crystals. Moreover, hydrogen atoms can act as a donor or acceptor depending on different electronegativity environments. According to ab initio calculations by Arantes et al [12], if an Mn-doped Ge nanowire is
saturated with H atoms at the surface, Mn atoms tend to concentrate at the surface, where the formation energy is lower than at the center of the nanowire. However, they did not give any information about the magnetic properties of the surface region. It was theoretically revealed by Sanati et al [13] that the interstitial Fe and H in Si can form the (Fe, H) pair with a deep donor and a deep acceptor level in the gap. But they did not study the exchange coupling between Fe atoms in the presence of the H interstitials, either. Although all the calculations indicate that the nearest-neighbor substitutional Mn atoms are AFM in Mn-doped Ge, we wonder whether the H interstitials can mediate a strong FM exchange interaction between neighboring Mn atoms through the formation of Mn–H–Mn complexes in Mn$_x$Ge$_{1-x}$ DMS with H interstitials.

In this paper, hydrogen interstitials-mediated ferromagnetism in Mn$_x$Ge$_{1-x}$ magnetic semiconductors was studied by first-principles calculations. It was found that the H:1s state in Mn–H–Mn complexes can strongly hybridize with the valence states of Mn and change the spin polarization of Mn dopants. As a result, Mn-doped Ge with H interstitials is predicted to be an FM semiconductor with higher Curie temperature and larger magnetization than Mn-doped Ge without H. This paper is organized as follows: in section 2, we report the calculation details. In section 3, we discuss the results regarding the total energies and the structural, electronic and magnetic properties of Mn-doped Ge without and with H interstitials. Finally, in section 4, we draw our conclusions.

2. Calculation details

The calculations were performed using the QUANTUM-ESPRESSO package [14] with generalized gradient approximation (GGA). Ultrasoft pseudopotentials [15] were used with valence configurations 3s$^2$3p$^6$3d$^8$4s$^2$ and 4s$^2$4p$^2$ for Mn and Ge, respectively. The plane wave kinetic energy cutoff was set as 40 Ryd. Atomic positions and lattice parameters were optimized until the atomic forces were smaller than $10^{-3}$ Ryd Bohr$^{-1}$ and stresses were smaller than 0.5 kbar. The Brillouin-zone integrations are performed with the special $4 \times 4 \times 4$ Monkhost–Pack $k$-points mesh [16, 17]. More accurate calculation parameters, such as 60 Ryd for the kinetic energy cutoff or a $6 \times 6 \times 6$ $k$-points grid, give negligible modifications in the electronic structures and energy differences between FM and AFM spin alignments. Therefore the calculations are believed to be reliable.

3. Calculation results and discussions

3.1. Mn-doped Ge without H

First we chose a $2 \times 2 \times 2$ $a^3$ supercell in diamond structures by using the experimental lattice constant ($a = 5.658$ Å) (the supercell contains 64 atoms) and we fully relaxed the supercell. The optimal lattice constant is $a = 5.608$ Å, which is compressed by about 0.9%. Using such a parameter, we researched different geometrical configurations of Mn-doped Ge. Previous theoretical results show that the Mn atoms prefer the substitutional sites to the interstitial sites in the Ge matrix [18]. Therefore, considering two Ge sites replaced by Mn and the symmetry of the periodic lattice, six different doping configurations were selected in an Mn$_2$Ge$_{62}$ supercell to achieve the doping concentration of 3.125%. Depending on the distance between the first Mn at the origin and the alternative sites, six geometrical configurations were named C-1 (nearest) to C-6 (farthest), respectively, as shown in figure 1.
Figure 1. Side view of the schematic Ge supercell consisting of 64 Ge atoms.

Table 1. The relative energy to the ground state, magnetic moment and energy difference between the FM and AFM couplings of various doping configurations of Mn_xGe_{1-x}.

| Configuration | Magnetic coupling | Relative energy to AFM of C-1 (meV) | Magnetic moment (µB per unit cell) | E_{AFM} − E_{FM} (meV) and ground state |
|---------------|-------------------|-------------------------------------|-----------------------------------|-----------------------------------------|
| C-1           | AFM               | 0                                   | 0.00                              | −790.7, AFM                             |
|               | FM                | 790.7                               | 6.00                              |                                         |
| C-2           | AFM               | 400.1                               | 0.39                              | 103.7, FM                               |
|               | FM                | 296.4                               | 6.00                              |                                         |
| C-3           | AFM               | 514.4                               | 0.00                              | −9.0, AFM                               |
|               | FM                | 523.4                               | 6.00                              |                                         |
| C-4           | AFM               | 556.3                               | 0.00                              | 35.1, FM                                |
|               | FM                | 521.2                               | 6.00                              |                                         |
| C-5           | AFM               | 600.6                               | 0.00                              | 223.7, FM                               |
|               | FM                | 376.9                               | 6.00                              |                                         |
| C-6           | AFM               | 551.8                               | 0.00                              | −35.9, AFM                              |
|               | FM                | 587.7                               | 6.00                              |                                         |

For the six doping configurations, the energy differences between AFM and FM states and the total magnetic moments of the Mn_xGe_{62} supercell are presented in table 1. The AFM state of C-1 is energetically favorable, and can be regarded as the ground state, while the FM state of C-1 has the highest energy. The total energy of C-2 to C-6 relative to C-1 in the ground state is also listed in table 1. The ground magnetic ordering oscillates with the Mn–Mn distances and the magnetic moment per Mn atom is $3 \mu_B$, which agrees with previous theoretical results [8, 19]. In addition, most AFM configurations have no net moment, except for ferrimagnetic-like C-2.
Therefore, the low Curie temperature of Mn$_x$Ge$_{1-x}$ DMS can be interpreted by the fact that the FM coupling only exists between non-nearest-neighbor dopants and hence it is weak.

The density of states (DOS) of Ge host, Mn$_1$Ge$_{63}$, C-1 and C-6 are shown in figure 2. For the Ge host matrix (figure 2(a)), the calculated energy gap is 0.37 eV, which is less than the experimental value of 0.67 eV due to the band gap underestimation of density functional theory calculations. The Mn$_1$Ge$_{63}$ system (figure 2(b)) shows half-metallic behavior, and the Mn:3d states are split in the tetrahedral crystal field. For the AFM states of C-1 and C-6 configurations (figures 2(c) and (e)), the total DOS is approximately symmetrical without any net magnetic moment. The DOS of C-6 in FM configurations (figure 2(f)) is analogous to that of Mn$_1$Ge$_{63}$, which indicates that the interaction between the Mn atoms is almost absent when the distance is larger than that in the C-6 configuration.

The charge distributions of C-1 in the (110) plane are shown in figures 3(a) and (b) for AFM and FM couplings, respectively. There is no visible charge transfer between Mn and Ge for both AFM and FM couplings, i.e. the bond between Mn and Ge has more covalent character. In the spin distribution pictures (figures 3(c) and (d)), the nearest Ge atoms are slightly polarized by Mn atoms, and the polarization of farther Ge atoms decreases rapidly. Interestingly, it was found that the spin polarization always undergoes a sign reversal along the Mn–Mn and Ge–Mn bonds for both AFM and FM coupling configurations. Especially for FM coupling configurations (figure 3(d)), there is a reverse polarization zone in the middle of the two Mn atoms. This implies that if an interstitial atom is added in the spin reversal zone, the FM exchange interaction between the two Mn atoms may be greatly enhanced. In fact, the following studies indicate that the H interstitials can mediate FM coupling between the nearest-neighbor Mn atoms.
3.2. Mn-doped Ge with H interstitials

Next we considered Mn-doped Ge with H interstitials. Since the key problem of Mn$_x$Ge$_{1-x}$ DMS lies in the strong AFM interaction between the nearest-neighbor Mn atoms, we mainly focus on the C-1 configuration and alter the position of the H interstitial relative to the Mn–Mn pair. We select an Mn$_2$Ge$_{30}$ supercell in body-center symmetry and introduce the hydrogen interstitial. There are three kinds of interstitial positions in the diamond structure that are favorable in energy: (i) the tetrahedral interstitial site (marked as Tetra), (ii) the hexagonal interstitial site (marked as Hexa) and (iii) the bond center (marked as BC). Considering the locations of the H interstitial relative to the Mn–Mn pair, we investigated: (i) Tetra-1 (figure 4(a)) and Hexa-1 (figure 4(c)) in which the H interstitial is close to only one Mn atom, (ii) Tetra-2 (figure 4(b)) and Hexa-2 (figure 4(d)) in which the H interstitial is close to both Mn atoms and (iii) BC of the Mn–Mn bond (figure 4(f)).

We first calculate the formation energy of hydrogen incorporation in Mn$_2$Ge$_{30}$, which is defined as $E^f = E^{\text{tot}}(\text{H}) - E^{\text{tot}}(\text{Mn}_2\text{Ge}_{30}) - \mu(\text{H}_2)/2$, where $E^{\text{tot}}(\text{H})$, $E^{\text{tot}}(\text{Mn}_2\text{Ge}_{30})$ and $\mu(\text{H}_2)/2$ are the total energy of the Mn$_2$Ge$_{30}$H supercell, the total energy of Mn$_2$Ge$_{30}$ and the hydrogen chemical potential under H-rich conditions. After the relaxation, the H interstitials tend to approach Mn atoms rather than Ge, and the formation energy is about $-0.7$ eV for different configurations, which indicates that hydrogen can be easily incorporated in Mn$_x$Ge$_{1-x}$ DMS by forming an Mn–H bond.

Table 2 lists the total energy and magnetic moments of Mn$_x$Ge$_{1-x}$ DMS with H interstitials. The Tetra-2 and Hexa-2 in the AFM state are lower in energy than the corresponding FM state, whereas for Tetra-1 and Hexa-1, the FM state becomes favorable. The total energy of the BC configuration is much higher than that of the tetrahedral and hexagonal interstitial ones, so it can be regarded as a metastable state. Meanwhile, there is negligible energy difference among the
Figure 4. Sketches of the H interstitial relative to Mn–Mn pairs before relaxation: (a) Tetra-1, (b) Tetra-2, (c) Hexa-1, (d) Hexa-2, (e) the collinear H–Mn–Mn complex of Tetra-1 and (f) BC of Mn–Mn. The small blue ball is the H interstitial.

Table 2. The total energy, magnetic moment and energy difference between the FM and AFM couplings of C-1 with H interstitials.

| Configuration | Magnetic coupling | Total energy (Ryd) | Magnetic moment ($\mu_B$ per unit cell) | $E_{AFM} - E_{FM}$ (meV) and ground state |
|---------------|------------------|--------------------|-----------------------------------------|-------------------------------------------|
| Tetra-1       | AFM              | $-920.88424$       | 0.85                                    | 190.4, FM                                 |
|               | FM               | $-920.89816$       | 7.00                                    |                                           |
| Hexa-1        | AFM              | $-920.88398$       | 0.86                                    | 193.1, FM                                 |
|               | FM               | $-920.89817$       | 7.00                                    |                                           |
| Tetra-2       | AFM              | $-920.89880$       | 0.20                                    | $-475.7$, AFM                             |
|               | FM               | $-920.86383$       | 5.00                                    |                                           |
| Hexa-2        | AFM              | $-920.89919$       | 0.08                                    | $-514.1$, AFM                             |
|               | FM               | $-920.86135$       | 5.00                                    |                                           |
| BC of Mn–Mn   | AFM              | $-920.82344$       | 0.00                                    | 292.4, FM                                 |
|               | FM               | $-920.84491$       | 7.00                                    |                                           |
Figure 5. The DOS of C-1 with H interstitials. (a, b) The Mn:3d and Mn:4s states of Mn\textsubscript{2}Ge\textsubscript{3}O; (c, d, g) the Mn:3d, Mn:4s and H:1s states of the Tetra-1 configuration; (e, f, h) the Mn:3d, Mn:4s and H:1s states of the Tetra-2 configuration, respectively. In (a–f), the solid and dotted curves represent the states of Mn dopants far from and close to the H interstitial, respectively. The vertical solid line denotes the Fermi energy, and the vertical dotted line guides the shift of states.

The polarization of Mn atoms is greatly changed by the H interstitials, which can be seen explicitly from the DOS in figure 5. A localized energy level of the H interstitial appears in the middle of the valence band (figures 5(g) and (h)) and gives rise to significant change of Mn:4s states (figures 5(d) and (f)), which indicates that the H:1s states hybridize directly with the Mn:4s states rather than Mn:3d states. For Tetra-2 (figures 5(e) and (f)), the DOS of the two Mn atoms are similar due to the symmetrical position about H. But for Tetra-1 (figures 5(c) and (d)), the influences of the H:1s state on the two Mn atoms are quite different. The polarization of an Mn atom far from the H interstitial is more significantly enhanced and induces the asymmetrical DOS of Mn:4s states. It should be noticed that after the relaxation, the original symmetry of the ground states of the four interstitial configurations. In addition, the magnetic moment of Tetra-2 and Hexa-2 in FM states is only 2.5\textmu B per Mn atom, which indicates that the H interstitial at the symmetrical position between the Mn atoms significantly suppresses the magnetization compared with that of Tetra-1 and Hexa-1.

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Figure 6. The spin density pictures in the (1\bar{1}0) plane of C-1 with the H interstitial at (a, b) Tetra-1, (c, d) Tetra-2 and (e, f) BC of Mn–Mn after relaxation. The red area represents spin up and the blue area represents spin down.

crystal field acting on H has been broken. The H interstitial approaches the Mn atom to achieve a similar structure for both the tetrahedral and hexagonal configurations. Therefore the DOS of Hexa-1 and Hexa-2 configurations is very similar to that of Tetra-1 and Tetra-2, respectively.

Figure 6 shows the spin distribution and lattice distortion around the Mn–Mn pair in the (110) plane of several configurations. For the symmetrical Mn–H–Mn complex of Tetra-2 (figures 6(c) and (d)), the AFM spin ordering (figure 6(c)) is in the ground state and the polarization distribution is nearly symmetrical. The H interstitial approaches the two Mn atoms. The three dopants bond with each other and form an approximate isosceles triangle structure (figures 6(c) and (d)). The length of the Mn–Mn bond decreases from 4.589 to 4.295 Å. Therefore, the direct AFM interaction between the two Mn atoms is still strong enough to suppress the effects of H interstitials. However, for the unsymmetrical Mn–H–Mn complex of Tetra-1 (figures 6(a) and (b)), the FM ordering is in the ground state since the H interstitial and one neighboring Ge reside in between the Mn–Mn pair and mediate the FM interaction. The Mn–Mn distance increases to 5.788 Å. The original bond is broken and the direct nearest-neighbor AFM coupling is weakened. Therefore, the FM ground state with the H interstitials is attributed to the asymmetrical electronic distributions due to the asymmetrical configuration of the Mn–H–Mn complex.

When an H atom is located at the bond center, there is a slight difference in the tetrahedral and hexagonal interstitial positions. Considering the H atom at the Mn–Mn bond center for example, the FM coupling state of Mn atoms is more energetically favorable than the AFM coupling. From the DOS picture in figure 7(c), unlike the other interstitial sites, the H:1s
states are polarized and more localized due to the strong hybridization with the Mn:3d and Mn:4s states (figures 7(a) and (b)). This configuration is similar to C-2, i.e. the two Mn atoms cannot directly couple with each other, but form Mn↑→H(Ge)↓→Mn↑ complexes, as shown in figure 6(f). Such a metastable configuration can also realize the FM spin alignment of nearest-neighbor Mn atoms.

We now do a further study on the H interstitials in C-2 to C-6 configurations where two Mn atoms are not nearest neighbors. All the configurations where the distance between two Mn atoms is relatively small (C-2, C-3 and C-4) could obtain the FM ground state by adding the H interstitial, and the effective magnetic moment is 5 \( \mu_B \) per cell. It is worthy mentioning that the asymmetrical electronic distribution introduced by H interstitials is much more universal than the symmetrical one. Therefore, if the Mn atoms are randomly distributed in the samples, most of the doped Mn atoms would form FM polarons around H. When the concentration of Mn and H dopants is high enough, local FM polarons could be merged together and long-range FM ordering and high Curie temperature could be achieved.

4. Conclusions

In summary, we have investigated hydrogen interstitials-mediated ferromagnetism in Mn\(_x\)Ge\(_{1-x}\) magnetic semiconductors by means of first-principles calculations. For Mn-doped Ge, the Mn atoms show a tendency to cluster, and the nearest-neighbor Mn atoms form AFM coupling pairs. For the asymmetrical configurations of Mn–H–Mn complexes, the H interstitial breaks the strong AFM interaction between the nearest-neighbor dopants and forms FM spin alignment. Therefore, Mn-doped Ge with H interstitials is predicted to form an FM semiconductor with higher Curie temperature and larger magnetization than Mn-doped Ge without H.

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