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Ab initio study of ferromagnetic semiconductor $Ge_{1-x}Mn_xTe$

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Abstract

First-principles calculations are made on the $Ge_{1-x}Mn_xTe$ diluted magnetic semiconductors with different compositions. The origin of their ferromagnetism is investigated and the carrier-induced ferromagnetism is developed for these diluted magnetic semiconductors. The Mn 3d states localized with divalent character are deep below the Fermi level, and the carriers introduced by defects are supported in our calculation. The p states of Ge also play an important role in the occurrence of ferromagnetism especially at high temperature. It is thought that $Ge_{1-x}Mn_xTe$ with a moderate composition ($x = 0.51$) of Mn atoms is a good candidate for DMS materials.

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

1. Introduction

Diluted magnetic semiconductors (DMSs) with ferromagnetism of high Curie temperature (T_c) have attracted much attention because of their good spin-polarization property, which is important for spintronic functional devices [1]. Since the initial discovery of (In, Mn)As (Munekata *et al* 1989, 1991, Ohno *et al* 1992), extensive studies have been performed for III–V-based materials [2]. In particular, $Ga_{1-x}Mn_xAs$ exhibits ferromagnetic order with relatively high Curie temperature (T_c) up to 170 K [3, 4]. Many valuable and constructive investigations have been carried out for this material. Its ferromagnetism might be ascribed to Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction [5]. Moreover, the other mechanisms, including double-exchange and super-exchange mechanisms [6, 7], are also employed to interpret the origin of the DMS's ferromagnetism. On the other hand, Fukuma *et al* have succeeded in the epitaxial growth of $Ge_{1-x}Mn_xTe$ films on $BaF_2(1\ 1\ 1)$ substrates up to $x = 0.96$ using an ionized cluster beam (ICB) technique [8]. T_c shows a maximum of 140 K at $x = 0.51$ and the

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Table 1. The structural parameters of $Ge_{1-x}Mn_xTe$ ($2 \times 2 \times 2$ supercell).

	$x = 0.25$	$x = 0.50$	$x = 0.75$
Lattice constant (Å)	11.90	11.84	11.74
$\alpha = \beta = \gamma$ (deg)	90	90	90

ferromagnetic order exists in the whole region of $x \leqslant 0.96$ [8]. The wide range of transition metal (TM) impurity solubility gives a good example for studying the influence of the TM's stoichiometric composition on ferromagnetism. In addition, spectroscopy analyses were carried out in terms of the study of electronic structure and the origin of ferromagnetism was explained for this material [9, 10]. It has been clearly shown that the magnetization depends on the carrier concentration [8, 11], but further detailed studies are still scarce, for example, what the contribution is to the carrier. Moreover, the *ab initio* studies of DMSs with a narrow gap are nearly absent. So in this paper we make a first-principles study of $Ge_{1-x}Mn_xTe$ running by the CASTEP code [12] to discuss its ferromagnetism.

2. Calculation

The calculations were made using a spin-polarized version of CASTEP whose background theory is based on DFT (density functional theory). We employed the PW91 generalized gradient approximation (GGA) to describe exchange–correlation interactions [13], and Vanderbilt-type ultrasoft pseudopotentials were used to represent the electron–ion interactions [14]. Wavefunctions were expanded in terms of plane waves with medium accuracy setting [12]. We have chosen a $2\times2\times2$ supercell containing 64 atoms in the calculation and this 64-atom supercell was built from eight-atom unit cells. The Monkhorst–Pack $2 \times 2 \times 2$ k-point grid was used in the cell [15], and the separation is set to be 0.05 $Å^{-1}$ in the calculation. It is noted that relativistic effects have an impact on the precision of calculations including a rather large atomic number Te element. However, we here make non-relativistic calculations due to only considering systematic comparisons of calculated results among $Ge_{1-x}Mn_xTe$ materials.

Three representative impurity concentrations were chosen, and set as $x = 0.25$, 0.50, 0.75 in the study, respectively. Geometry optimization was performed by using BFGS schemes [16], and experimental lattice constants of the structures were employed as an initial input geometry [8]. We only optimized internal freedom upon atoms with fixed lattice constant, that is, the internal fractional coordinate was optimized. The experimental crystal structure of $Ge_{1-x}Mn_xTe$ was similar to bulk host materials [17]. Bulk GeTe has a rhombohedrally distorted NaCl crystal structure with the lattice constant of 5.979 Å and the rhombohedral angle of 88.22°. The rhombohedral symmetry was selected below $x = 0.2$ and transformed into NaCl structure at this point for the crystal structure of $Ge_{1-x}Mn_xTe$. The three structures on which we focused are all NaCl structures and their lattice constants reduce with increasing Mn concentration. The structure of $Ge_{0.5}Mn_{0.5}Te$ is illustrated in figure 1 and the other two structures can be produced by substituting different compositions. The Mn impurities are distributed homogeneously in these crystals. Moreover, we show the structural parameters in table 1.

We performed the electronic structure calculation using the optimized geometries, and then we performed two tasks. One is a comparison between the total energy of the ferromagnetic state and that of the antiferromagnetic state. Two self-consistent solutions for the electronic structure of the DMS correspond to the two states. By the comparison of the two states, we can find which state is stable, and the total energy difference corresponds to T_c [18].

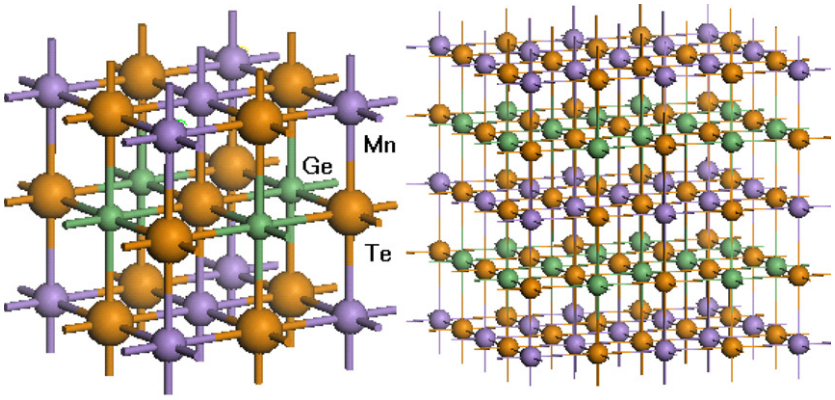

Figure 1. Unit cell (a) and 2 × 2 × 2 supercell (b) of $Ge_{0.5}Mn_{0.5}Te$.

Table 2. The energies of the ferromagnetic state (FM) and antiferromagnetic state (AFM) in $Ge_{1-x}Mn_xTe$ (2 × 2 × 2 supercell); the energy difference $\Delta E = E_{FM} - E_{AFM}$.

	$x = 0.25$	$x = 0.50$	$x = 0.75$
FM (eV)	−15 109.07	−19 481.21	−23 852.84
AFM (eV)	−15 109.98	−19 481.67	−23 855.99
ΔE (eV)	0.91	0.46	3.15

The other piece of work in our study is the analysis of DOS (density of states) with different TM impurity concentrations. In particular, 3d states of Mn atoms and the states near the Fermi level are very important. It is possible to understand the origin of ferromagnetism for $Ge_{1-x}Mn_xTe$ DMS based on DOS analysis.

3. Results and discussion

3.1. Energy comparison

In table 2 the calculated energies of the ferromagnetic state and antiferromagnetic state of the three representative impurity concentrations are presented. It is found that the differences between the ferromagnetic state and antiferromagnetic state are not obvious in the three structures. This situation is interesting. Generally, for a high T_c DMS the energy of the ferromagnetic state is lower (larger absolute value) than that of the antiferromagnetic state in the ground state, especially in the II–VI-based DMS (i.e. $Zn_{1-x}Cr_xO$, $Zn_{1-x}Co_xTe$ etc) and (III, Mn)V compounds [7, 19]. Contrarily, in $Ge_{1-x}Mn_xTe$ the energy of the antiferromagnetic state is lower. It was reported that the DMSs in which the double exchange plays the main role in the occurrence of the ferromagnetic state are likely to have a ground state of ferromagnetism, and the d states in these DMSs are often partially filled [7, 19]. However, the reverse situation of $Ge_{1-x}Mn_xTe$ indicates that the double-exchange mechanism does not work for its ferromagnetism. From an earlier experiment it is shown that the ferromagnetic state of $Ge_{1-x}Mn_xTe$ was observed at low temperature [8]. It could be ascribed to the RKKY interaction and the carriers are formed by Ge vacancies [20, 21], but in our work the situation is different. The structures we studied are perfect crystals and there are no vacancies or any other defects in them. So the calculated antiferromagnetic order in the ground state might

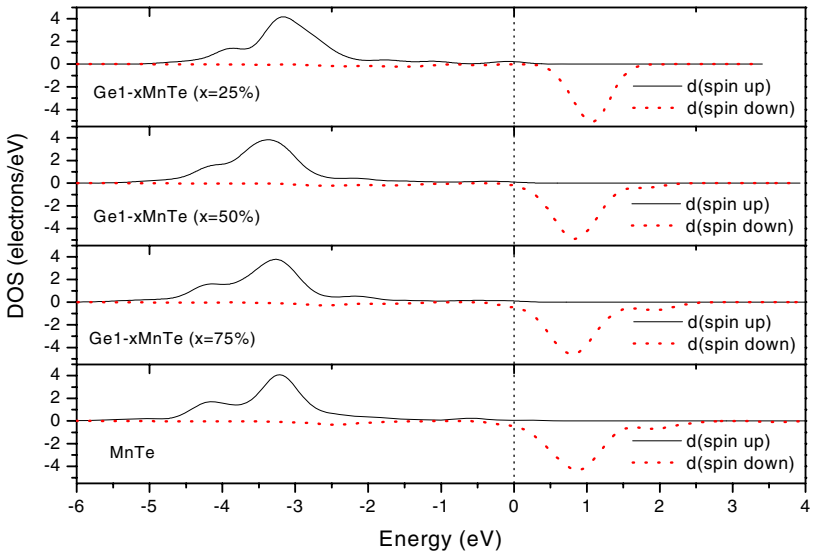

Figure 2. The d states of Mn atom in the three structures (FM) and MnTe.

be attributed to weak antiferromagnetic interaction, which is super-exchange interaction via anions between Mn ions [21]. This is also evidence for the relationship between defects and carrier-induced ferromagnetism.

Table 2 shows that the value ΔE of the second structure is the minimum among the three structures. Therefore, the stabilization of its antiferromagnetic state is the lowest one among the three impurity concentrations and it will transform to the ferromagnetic state easily. This trend shows the second structure might have the highest T_c in accord with the experiment data [8].

3.2. DOS analysis

Figure 2 displays the calculated Mn 3d states in the three structures of ferromagnetic state (FM) respectively. They have the same feature of localized Mn 3d states and all represent two main peaks. From crystal field theory [22, 23] the configuration could be understood. In an octahedral field, fivefold degenerate d states of the Mn atom are split into doubly degenerate e_g states and threefold degenerate t_{2g} states, and the energy of the t_{2g} state is lower than that of the e_g state. The two peaks of d states correspond to these two kinds of states. These configurations were verified by spectrum analysis [9, 10].

In addition, in figure 2 we compare the d states of the Mn atom in $Ge_{1-x}Mn_xTe$ with the ones in MnTe, and find that they have a resemblance. This suggests the Mn atom in $Ge_{1-x}Mn_xTe$ is in a 2+ oxidation state.

In order to explain the origin of ferromagnetism in the $Ge_{1-x}Mn_xTe$ DMS, in figure 3 we give the plots of DOS for $Ge_{1-x}Mn_xTe$ and $Ga_{1-x}Mn_xAs$ respectively, and make a comparison between them. As we know, the discussions about $Ga_{1-x}Mn_xAs$ had been made extensively [2–6]. It is well known that carrier-induced ferromagnetism plays the main role in $Ga_{1-x}Mn_xAs$ DMSs. The Mn atom acts an acceptor in GaAs-based DMSs, so that in $Ga_{1-x}Mn_xAs$, the Mn atom brings both the carriers and the localized spins. So it is very interesting to make such a comparison. From figure 3 we can find that the main part of spin up 3d states of Mn atoms in the two DMSs both fall below the Fermi level and the spin down 3d states are unoccupied above the Fermi level. However, the position of spin

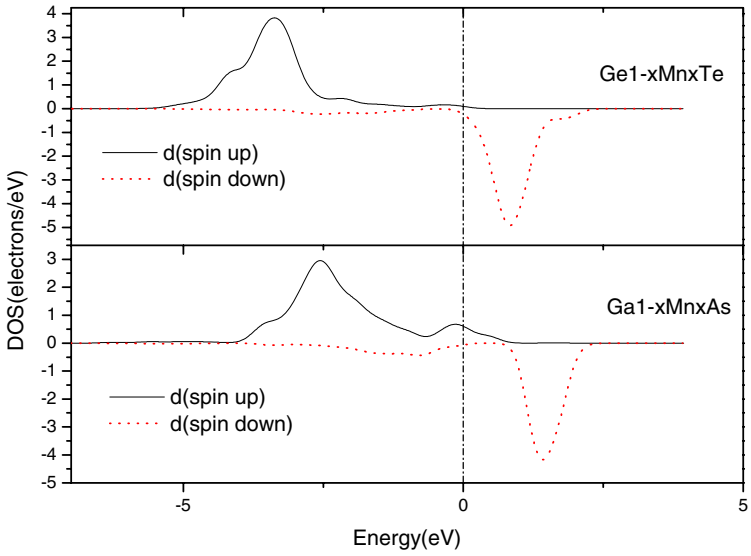

Figure 3. The d states of the Mn atom in $Ge_{1-x}Mn_xTe$ (FM) and $Ga_{1-x}Mn_xAs$.

up 3d states in $Ge_{1-x}Mn_xTe$ is deeper and they are fully filled by electrons. This finding indicates that the Mn atoms in such a system do not produce any carriers. This is different from $Ga_{1-x}Mn_xAs$ in which spin up 3d states of the Mn atom are partially occupied near the Fermi level. As mentioned above the Mn 3d states of $Ge_{1-x}Mn_xTe$ are localized with the divalent character. However, the carrier-induced ferromagnetism of the $Ge_{1-x}Mn_xTe$ DMS was found in experiment [8, 11]. From the above discussion, it is shown obviously that the origin of the carriers of $Ge_{1-x}Mn_xTe$ should be different from that of $Ga_{1-x}Mn_xAs$. It was thought that the carriers are from Ge vacancies and its concentration could be controlled by annealing [20, 21]. Additionally, the deep position of 3d states of Mn shows that the double-exchange interaction does not contribute to the ferromagnetism in $Ge_{1-x}Mn_xTe$, and it is also a good support for RKKY interaction-induced ferromagnetism.

For further study, the total density of states (TDOS) of $Ge_{0.5}Mn_{0.5}Te$ in the ferromagnetic state is shown in figure 4(a). The main parts of the TDOS are made up of p states and d states, and it indicates a full overlap between them about 2–5 eV below the Fermi level. Furthermore, from figure 4(b) we can see that the p states of Te constitute the main part of the p states below the Fermi level. Accordingly, we can say that it should be an important hybridization between the states of Mn and those of Te. This is also because the nearest-neighbouring Mn site is a Te atom. Moreover, we believe that the hybridization is an important contribution to antiferromagnetic order since MnTe is an antiferromagnet [24, 25]. The band structure of $Ge_{0.5}Mn_{0.5}Te$ in the ferromagnetic state is illustrated in figure 5 in which the bands of different spins are displayed separately. Both the spin up and spin down band structures represent metallic property with the Fermi level in the bands.

Subsequently, a series of DOS analyses for different impurity compositions are performed. We still choose the representative three structures referred to above. Their main DOS configurations of ferromagnetic state are shown in figure 6. We are concerned about the states near the Fermi level which are critical for the occurrence of carriers. From the plots we find that the three structures all represent some metallic property. This is because the impurity of Mn changes the original narrow-gap electronic structure. It is clearly observed that the differences

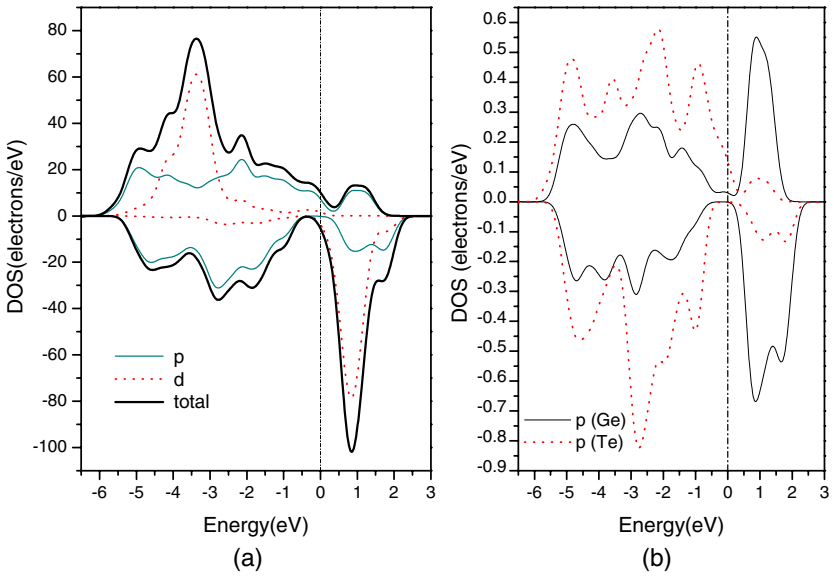

Figure 4. (a) The total density of states (TDOS) and partial density of states (PDOS) of $Ge_{0.5}Mn_{0.5}Te$ (FM); (b) the p states of the Ge atom and Te atom in $Ge_{0.5}Mn_{0.5}Te$ (FM).

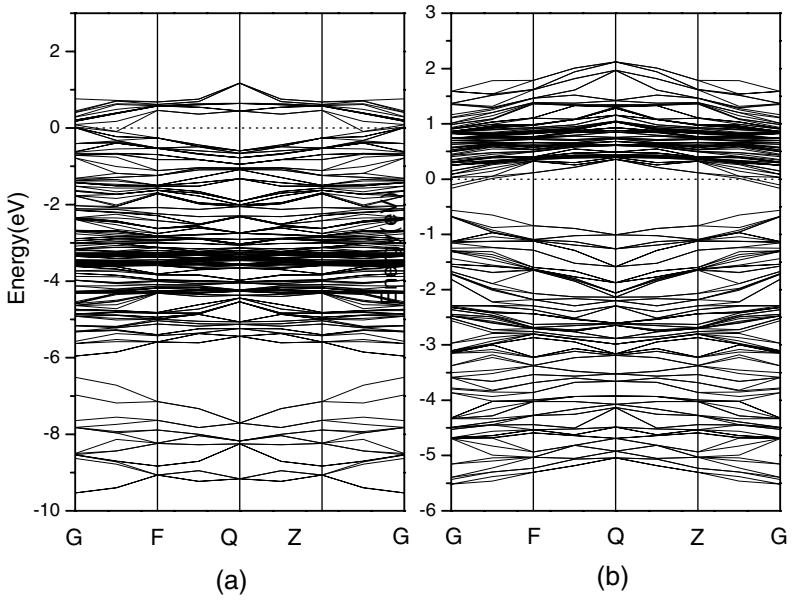

Figure 5. The band structures of spin up electrons (a) and spin down electrons (b) in $Ge_{0.5}Mn_{0.5}Te$ (FM).

among three structures occur in the states above the Fermi level. As the impurity concentration increases, the DOS of p states distributed from 0.5 to 1.5 eV decreases. This trend could be found and understood from the plots of figure 4(b) in which the main parts of p states above Fermi level consist of the Ge p states. The number of Ge atoms decreases with increasing impurity concentration.

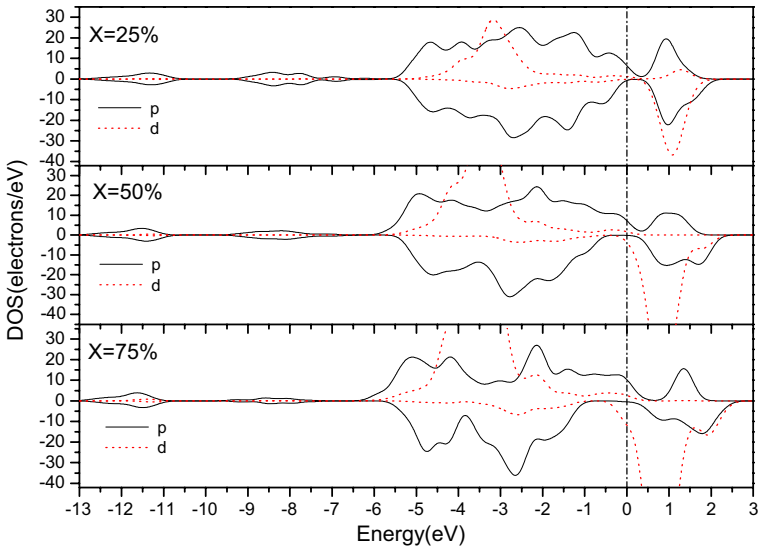

Figure 6. The d states and p states of the three structures (FM).

It was reported from the experiment that the carrier concentration increases as Ge concentration increases [8, 11]. So the Ge atom plays an important role in the occurrence of ferromagnetism. This is because Ge vacancies offer a large number of holes which are important for RKKY interaction-induced ferromagnetism. In addition, the higher the Ge concentration, the more empty p states there are just above the Fermi level. This situation gives more opportunities that the electrons could be promoted from the occupied states just below the Fermi level to the unoccupied states by thermal excitations, and this process might contribute to carrier concentration especially at high temperature.

In $Ge_{1-x}Mn_xTe$, the p states and d states constitute the main parts of DOS. The d states offer localized spins whereas the dispersing p states contribute to the carriers which are the interactive parts for localized spins. Both Mn atoms and Ge atoms make contributions to the ferromagnetic order in $Ge_{1-x}Mn_xTe$. The localized 3d states of Mn offer the spin magnetons and Ge atoms correspond to the carriers. From the theory developed by Dietl *et al*, the T_c of a ferromagnetic system could be determined in the following formula [26]:

$$T_c = C \times x \times n^{1/3}.$$

Here, x is the concentration of magnetic impurities and n is the carrier concentration. C is a constant. Accordingly, a high T_c ferromagnetic system must have contributions from high values of x and n. However, it is shown from $Ge_{1-x}Mn_xTe$ that the two atoms are competitive compositions, so the $Ge_{1-x}Mn_xTe$ with a moderate composition ($x = 0.51$) of Mn atoms will be a high T_c DMS.

4. Conclusion

In this paper, we investigate the origin of ferromagnetism in $Ge_{1-x}Mn_xTe$ DMSs using *ab initio* calculated results. The Mn 3d states of $Ge_{1-x}Mn_xTe$ are localized with divalent characters and deep in the valence band of the host materials. The carrier-induced ferromagnetism could be understood on the basis of the RKKY interaction mechanism and it is verified that the carries are formed by Ge vacancies. The hybridization between p states of Te and d states of Mn is crucial

for the antiferromagnetic interaction. From the analyses of DOS and the theory developed by Dietl *et al*, we find that both Ge atoms and Mn atoms play important roles in the occurrence of ferromagnetism with high Curie temperature. However, the Ge and Mn atoms are competitive parts in $Ge_{1-x}Mn_xTe$, and then the $Ge_{1-x}Mn_xTe$ with a moderate composition ($x = 0.51$) of Mn atoms will be a good candidate for DMS materials.

Acknowledgments

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