Experimental and theoretical investigations on ferromagnetic nature of Mn-doped dilute magnetic semiconductors

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Abstract. X-ray absorption fine structure (XAFS) and first-principles calculations are effectively combined to establish correlations of fabrications, atomic and electronic structures as well as ferromagnetism for the Mn-doped dilute magnetic semiconductors (DMS), and to shed light on the magnetism origin for a variety of ZnO-, GaN-, and Si-based DMSs. The results of Mn:ZnO and (Mn,N):ZnO thin films reveal that either the existence of Zn vacancy or N substitution of O sites can stabilize the ferromagnetic interactions between neighboring Mn-Mn pairs, and enhance the magnetic moment per Mn. In a 2.5 at.% Mn-doped GaN film, a part of substantial Mn ions is found to locate at the interstitial sites near the substitutional Mn ions, forming Mn-Mn dimers that possess unique electronic and magnetic properties. Similar phenomena have also been found in the Mn-doped Si system in which the interstitial Mn atoms intend to assemble together via an intervening substitutional Mn ion. We have proposed a pathway to understand the microscopic origin of ferromagnetism in the DMS materials from the viewpoint of experimental determination and theoretical calculations.

1. Introduction
Since the discovery of (Ga,Mn)As dilute magnetic semiconductor (DMS) and the achievement on the coherence of optically injected spin-polarized carriers over nanosecond time scales [1, 2], a comprehensive research interest has been devoted to the experimental and theoretical studies of Mn-doped III-V, II-VI, and IV DMSs. This is attributed to that the DMS spintronic device possessing the properties of electron’s charge and spin make it capable of realizing the nonvolatility, the low electric power consumption, and the increased integration densities in future technological applications [3-5]. For the practical device application, the ideal ferromagnetic semiconductors should have Curie temperature ($T_C$) above room temperature (RT) and be easy to dop the $p$-type and $n$-type impurities. A number of studies have suggested that the substitutional GaN- and ZnO-based DMSs are favored to form ferromagnetic phases [6-9]. At the same time, group-IV DMSs have also received the remarkable attention both in experiment and theory in the recent years due to its full compatibility with mainstream silicon technology [10, 11]. However, numerous contradicting experimental results on the magnetic order in DMS have been reported, and the origin of ferromagnetism is still under debate. For GaN-based DMSs, recently, Chitta et al. [12], Jeon et al. [13], and Thaler et al. [14] have reported $p$-type and $n$-type ferromagnetic (Ga,Mn)N DMS thin films with $T_C$ above 350 K. Practically, it is expected that ferromagnetism indeed arises from the Mn ions properly incorporated into the host...
semiconductors in spintronic devices, but it is quite possible that the ferromagnetism of the (Ga,Mn)N DMSs may come from the energetically favorable Mn compounds and/or clusters. Similarly, for ZnO-based DMSs, numerous experimental investigations have shown that Mn-substituted ZnO samples fabricated by different methods exhibit distinct magnetic properties. For example, Fukumura et al. [15] found a spin-glass behavior; Tiwari et al. [16] observed paramagnetism; Jung et al. [17] observed ferromagnetism with $T_C$ of 45 K; Sharma et al. [18] observed ferromagnetism with $T_C$ of 425 K. Theoretically, Dalpian et al. [19] have predicted that the substitutional site Mn can stably exist in the Si matrix, and suggested that it might be possible to grow Mn$_x$Si$_{1-x}$ samples with a high enough concentration of substitutional Mn. It is also found that the structural defects in the samples could play an important role in the occurrence and stability of ferromagnetism [20]. To interpret the origin of the magnetic properties, a number of magnetic interaction mechanisms have been proposed, including direct superexchange, indirect superexchange, and carrier-mediated exchange. Nowadays, the local structure and microscopic origins of the high-$T_C$ ferromagnetism in ZnO-, GaN, and Si-based DMSs are still under debate. The development of such an understanding has emerged as one of the most important challenges in the magnetism of DMSs.

In this work, x-ray absorption fine structure (XAFS) and the first-principles calculations are effectively combined to establish correlations of local atomic and electronic structures as well as ferromagnetism of dilute magnetic semiconductors, and to shed light on the magnetism origin for a variety of Mn-doped ZnO-, GaN-, and Si-based DMSs. Based on the results, we have proposed a pathway to understand the microscopic origin of ferromagnetism in the DMS materials from the viewpoint of experiment and theory. This work is organized as follows: section 2 introduces a synopsis of DMS theory. We show the results for GaN-, ZnO-, and Si-based DMSs in sections 3, 4, and 5. Section 6 is a summary.

2. A synopsis of DMS theory
In DMSs a portion of atoms is randomly substituted by transition-metal (TM) elements, giving rise to localized magnetic moments in the semiconductor matrix. The presence of magnetic ions affects the free carrier behaviour through the $sp-d$ exchange interaction between the localized magnetic moments and the spins of the itinerant carriers [21]. The important characteristic of a ferromagnetic material is the spontaneous magnetization below the Curie temperature. As shown in Figure 1 in ferromagnetic materials [22], the $d$ band is divided into spin-up and spin-down sub-bands, and the up and down states are displaced in energy with respect to one another, so that the spin-up band is filled first, and the spin-down states contain the remaining, if any, electrons. The difference in the number of spin-up and spin-down electrons gives rise to the observed spontaneous magnetic moment [9, 23]. In order to gain insight into the processes involved, a brief tutorial of the recently proposed mechanisms for ferromagnetism in DMS materials, such as Zener model, carrier-mediated exchange, double exchange, and magnetic polarons, is presented in this section.

In the Zener model, the direct interaction between $d$ shells of the adjacent Mn atoms leads to an antiferromagnetic (AFM) configuration of the $d$ shell spins because the Mn-$d$ shell is half-filled. On the other hand, the indirect coupling of spins through the conduction electrons tends to align the spins of the incomplete $d$ shells in a ferromagnetic manner. It is only when this dominates over the direct superexchange coupling between adjacent $d$ shells that ferromagnetism is possible. Accordingly, the mean-field approach assumes that ferromagnetism occurs through interactions between the local moments of the Mn atoms mediated by free holes in the material. The spin-spin coupling is also assumed to be a long-range interaction, allowing the use of a mean-field approximation. The mean-field model calculates the effective spin-density due to the Mn ion distribution. The direct Mn-Mn interactions are antiferromagnetic so that the Curie temperature, for a given material with a specific Mn concentration and hole density (derived from Mn acceptors and/or intentional shallow level acceptor doping), is determined by a competition between the ferromagnetic and antiferromagnetic interactions [9, 23-25]. Based on this model, it was predicted that TM-doped $p$-type GaN and ZnO are the most promising candidates for
ferromagnetic DMS with high Curie temperature. However, these predications are made on the incorporation of some 5% transition-metal element and hole concentrations of above $10^{20}$ cm$^{-3}$.

Sato and Katayama-Yoshida [26] performed first-principles ab initio calculations of the electronic structures of TM-doped ZnO and proposed the double exchange mechanism for the carrier-induced ferromagnetism. The double exchange mechanism has been successfully used to explain the ferromagnetism observed in (In,Mn)As [27, 28]. In the double exchange mechanism originally proposed by Zener magnetic ions in different charge states couple with each other by virtual hopping of the ‘extra’ electron from one ion to the other. In the DMS material, if neighboring TM magnetic moments are in the same direction, the TM-$d$ band is widened by the hybridization between the up-spin states. Therefore, in the ferromagnetic configuration the band energy can be lowered by introducing carriers in the $d$ band. In these cases, the $3d$ electron in the partially occupied $3d$-orbitals of the TM is allowed to hop to the $3d$-orbitals of the neighboring TM, if neighboring TM ions have parallel magnetic moments. As a result, the $d$-electron lowers its kinetic energy by hopping in the ferromagnetic state. This is the so-called double exchange mechanism.

In addition to the models mentioned above, ferromagnetism in DMS has been accounted for by the formation of bound magnetic polaron (BMP) [29]. The bound magnetic polarons are formed by the alignment of the spins of many transition-metal ions with that of much lower number of weakly bound carriers such as excitons within a polaron radius. The basic idea is schematically illustrated in Fig. 2. The localized holes of the polarons act on the transition-metal impurities surrounding them, thus producing an effective magnetic field and aligning all spins. As temperature decreases the interaction distance (boundary) grows. Neighboring magnetic polarons overlap and interact via magnetic impurities forming correlated clusters of polarons. One observes a ferromagnetic transition when the size of such clusters is equal to the size of the sample. This model is inherently attractive for low carrier density systems such as many of the electronic oxides.

![Figure 1. A schematic representation of the density of electronic states available to electrons in a normal metal and in a ferromagnetic metal.](image1)

![Figure 2. Representation of bound magnetic polarons.](image2)

3. ZnO-related DMSs

3.1. Mn-doped ZnO

In this subsection, the XAFS technique and first-principles calculations were used to study the local structure and ferromagnetism origin of Mn-doped ZnO thin films [30]. The Zn$_{0.97}$Mn$_{0.03}$O thin film was grown on Si(100) substrate at 450 °C. Diethyl-zinc, tertiary-butanol and liquid (CO)$_3$CH$_2$C$_5$H$_4$Mn were used as the zinc, oxygen, and manganese precursors, respectively. The thicknesses of the film sample are about 300 nm. The crystalline structure of the sample was determined by XRD, showing the single phase of wurtzite type structure. The magnetization was measured using superconducting
quantum interference device (SQUID) at room temperature in a magnetic field up to 4 kOe. Figure 3 shows the magnetic-field dependence of magnetization ($M$ vs $H$) for the Zn$_{0.97}$Mn$_{0.03}$O thin film. A well-defined hysteresis loop can be observed at 300 K, demonstrating the room-temperature ferromagnetic behavior.

The Mn $K$-edge XANES spectrum of Zn$_{0.97}$Mn$_{0.03}$O is displayed in Fig. 4 along with the reference crystalline MnO, MnO$_2$, and Mn$_3$O$_4$. The existence of MnO, MnO$_2$, and Mn$_3$O$_4$ in Zn$_{0.97}$Mn$_{0.03}$O sample can be easily excluded, since their XANES features are quite different from those of Zn$_{0.97}$Mn$_{0.03}$O. It is well known that some native defects in ZnO, such as O vacancy, Zn vacancy and Zn interstitials are easily generated in the Mn-doped ZnO films. To study the influence of these defects on the XANES features, the XANES calculations by using FEFF8.2 code for some other representative Mn-doped ZnO model clusters, such as the substitutional Mn (Mn$_{Zn}$) plus O vacancy (V$_O$), Mn$_{Zn}$ plus Zn vacancy (V$_{Zn}$), and Mn$_{Zn}$ plus interstitial Zn (Zn$_i$), were performed. The calculated XANES spectra for these models together with the experimental ones of Zn$_{0.97}$Mn$_{0.03}$O are shown in Fig. 5. It is evident that the main features of the experimental spectra of the Zn$_{0.97}$Mn$_{0.03}$O thin film at the Mn and O $K$ edges can only be reproduced by the calculated spectra for the model structure of Mn$_{Zn}$+V$_{Zn}$. This suggests the existence of numerous Zn vacancies in this sample. For the model structure of Mn$_{Zn}$ without any native defects, the O $K$-edge calculated spectrum presents a strong preedge peak D related to the transition of O 1s electron to the unoccupied Mn 3d and O 2p hybridized states. When V$_{Zn}$ is present along with Mn$_{Zn}$, peak D is only visible as a weak shoulder Fig. 6. The $a_1$ state is overlapped with the valence band (VB) and nearly occupied. Therefore, the O 1s electron can hardly transit to this defect state, giving rise to a weak shoulder peak in the rising edge of the O $K$-edge XANES.

![Figure 3. Hysteresis loops for Zn$_{0.97}$Mn$_{0.03}$O. The inset in Fig. 3 is a magnified plot near zero field for better clarity.](image)

![Figure 4. Mn $K$-edge XANES spectra of the Zn$_{0.97}$Mn$_{0.03}$O sample, Mn metal, MnO, MnO$_2$, and Mn$_3$O$_4$. The inset displays EXAFS fitting results of the sample at Mn and Zn $K$-edge.](image)

In order to further understand the magnetic properties induced by the Zn vacancy, the calculations of the electronic structure and magnetic interactions between Mn ions in the model structure of Mn$_{Zn}$ plus Zn vacancy were performed based on density functional theory. From our calculations, the total energy difference ($\Delta E_{\text{AFM-FM}}$) of the ferromagnetic relative to the antiferromagnetic configuration is 22 meV, indicating the stability of FM state against the AFM state for Mn$_{Zn}$ plus Zn vacancy. The obtained DOSs are shown in Fig. 6, and those of Zn vacancies in ZnO are also plotted for comparison. For the Mn-doped ZnO with a Zn vacancy, the acceptor band shows a large spin-split, with the spin-up part $a_1$ overlapping with the VB. The Mn 3$d^3$ states cross the Fermi level in the defect state $a_1$. Therefore, the hybridization between the Mn 3$d^3$ and defect state $a_1$ facilitates the electron transfer from Mn 3$d^3$ states to the acceptor, thus increases the acceptor density in the vicinity of the Mn ions. According to the BMP model, the charge transfer between Mn 3$d$ and Zn vacancy induced $a_1$ state is favorable to enhance the Curie temperature $T_C$. Based on the XANES and the first-principles results, we therefore consider that the Zn vacancy favors to induce the room-temperature ferromagnetism in the Zn$_{0.97}$Mn$_{0.03}$O thin film.
3.2. (Mn,N)-codoped ZnO

Codoping is suggested as an alternatively effective approach to modify the structural and electronic properties of DMSs recently. In this subsection, the structural and magnetic properties of (Mn,N)-codoped ZnO thin films were studied [31]. The Zn$_{0.96}$Mn$_{0.04}$O and Zn$_{0.96}$Mn$_{0.04}$O:N films were synthesized by using inductively coupled plasma enhanced chemical vapor deposition (ICP-CVD) method [32]. The magnetizations were measured with SQUID at 300 K under magnetic fields up to 6 kOe. It is clear that both samples demonstrate the room temperature ferromagnetic behavior as indicated by the hysteresis loops [Fig. 7]. However, the N doping in Zn$_{0.96}$Mn$_{0.04}$O film significantly increases saturation magnetic moment ($M_S$) from $0.3\mu_B$/Mn atom to $1.4\mu_B$/Mn.

As shown in Fig. 8, the Mn K-edge XANES spectra of the Zn$_{0.96}$Mn$_{0.04}$O and Zn$_{0.96}$Mn$_{0.04}$O:N thin films have quite similar XANES features with three characteristic peaks: A (6534 eV), B (6547 eV), and C (6556 eV). The theoretical spectrum for ZnO with substitutional Mn calculated by FEFF8.2 code is depicted simultaneously in Fig. 8 for reference. It is clear that the calculated spectrum also presents three peaks A, B, and C at the same position. Preedge peak A can be interpreted as the transition of Mn 1s core electron to the Mn 3d states and the white line peak B is attributed to the electron transition from Mn 1s states to the vacuum level. It can be observed that the calculated XANES spectrum of ZnO with substitutional Mn almost reproduces the experimental spectra of
Zn$_{0.96}$Mn$_{0.04}$O and Zn$_{0.96}$Mn$_{0.04}$O:N. These results have confirmed that the Mn ions were substitutionally incorporated into the ZnO lattice, and no Mn-related secondary phase is formed. The sensitivity of Mn K-edge XANES to the N dopant substitution was checked by replacing one neighboring O atom of Mn in ZnO:Mn with one N atom in the simulations. The calculated XANES spectra remained almost identical before and after the N substitution, indicating the insensitivity of Mn K edge.

In order to determine the relation of enhanced magnetism and the effect of the doped N atoms, the N K-edge XANES spectrum of the Zn$_{0.96}$Mn$_{0.04}$O:N film was compared with that of N-doped ZnO cited from Ref. 33 [Fig. 9]. It can be seen that the XANES spectra of N-doped ZnO present four characteristic peaks $a$, $b$, $c$, and $d$ at 401.0, 403.8, 409.5, and 420.0 eV, respectively. Peak $a$ is the white line peak while the post-edge peaks $b$, $c$, and $d$ arise from the multiple-scattering around the central N atom. Evidently, the XANES features of Zn$_{0.96}$Mn$_{0.04}$O:N are similar to those of N-doped ZnO. Thus, the calculated spectrum of the Zn$_{1-x}$Mn$_x$O with one O atom replaced by N atom can reproduce the main features of the experimental XANES spectrum of the Zn$_{0.96}$Mn$_{0.04}$O:N film, implying the substitutional occupation of N dopants.

The calculated densities of states (DOSs) in the close configuration for the Mn-doped ZnO and the (Mn,N)-codoped ZnO are illustrated in Fig. 10. For the Mn-doped ZnO, neither Mn nor O introduces DOS at the Fermi level despite the hybridization between the Mn 3d and O 2p states [Fig. 10(a)]. Therefore, the superexchange interaction between the neighboring Mn$^{2+}$ ions is antiferromagnetic in character. The competition between the ferromagnetic interaction (arising from BMP) and the antiferromagnetic coupling of the neighboring Mn atoms explains why the moment (0.3μB/Mn) in Zn$_{0.96}$Mn$_{0.04}$O is much smaller than the expected value of 5μB/Mn for a free Mn$^{2+}$ ion. As N atoms replace some of the O sites in the Mn-doped ZnO, the total energy calculations revealed that the Mn and N atoms prefer to exist as the nearest neighbors [34]. Moreover, the Mn 3d partial DOSs are strongly hybridized with the N 2p states at the Fermi level in the band gap [Fig. 10(b)]. This strong p-d interaction leads to a ferromagnetic coupling between the two Mn ions connected by an intervening N atom. The codoping of both Mn and N in Zn$_{1-x}$Mn$_x$O:N changes the Mn–Mn antiferromagnetic interactions to ferromagnetic coupling in the close configuration. Consequently, this enhances the magnetic moment per Mn (1.4μB/Mn) in the Zn$_{0.96}$Mn$_{0.04}$O:N thin film.

4. Mn-doped GaN

In this section, the structural and electronic investigation on Mn-doped GaN magnetic semiconductors was performed [35,36]. Ga$_{1-x}$Mn$_x$N DMSs with a thickness of 300 nm and Mn content ranging from
1.0 to 10 at.%, were grown on semi-insulating GaAs (001) substrates at 680 °C using plasma-assisted molecular beam epitaxy (PA-MBE). Hall-effect measurements unambiguously showed that the as-prepared Ga$_{1-x}$Mn$_x$N samples have strong \( p \)-type conductivity with the hole density of about $10^{18} \text{ cm}^{-3}$. XRD studies demonstrated that the Mn-doped GaN thin films have zinc-blende (ZB) structure [37].

Figure 11 shows Mn K-edge XANES spectra of ZB structural Ga$_{1-x}$Mn$_x$N thin films and Ga K-edge XANES spectrum of crystalline GaN. It can be observed that there are three strong peaks of A (16.8 eV), B (26.3 eV), and C (64 eV) in the post-edge region of Mn K-edge for the Ga$_{0.99}$Mn$_{0.01}$N. The XANES spectrum of crystalline GaN also presents three strong peaks located at the same positions as those of Ga$_{0.99}$Mn$_{0.01}$N, but their intensities are quite different. Moreover, a strong peak A1 (2.0 eV) in the edge region appears for Ga$_{0.99}$Mn$_{0.01}$N, but it is absent for GaN. These features will further be shown in Fig. 11 from XANES calculation, and the peaks A1 and B are the fingerprint peaks for the Mn atoms located in the substitutional sites of Ga$_{1-x}$Mn$_x$N DMS. Increasing the Mn concentration of Ga$_{1-x}$Mn$_x$N to 0.025, peak A1 is reduced in intensity and peak B is split into two small peaks B1 and B2. This implies that Mn atoms occupy some new sites with the increase of Mn doping concentration. At the higher Mn content of 0.10, no A1 and B peaks appear in the XANES spectrum of Ga$_{1-x}$Mn$_x$N.

![Figure 11. The Mn K-edge XANES spectra of Ga$_{1-x}$Mn$_x$N thin films and Ga K-edge XANES spectrum of crystalline GaN.](image)

![Figure 12. Comparison of the Mn K-edge XANES spectra from theoretical calculations and the experimental XANES spectra for Ga$_{1-x}$Mn$_x$N.](image)

In order to investigate the XANES spectra of ZB structural Ga$_{1-x}$Mn$_x$N DMS, we have attempted to model four representative Ga$_{1-x}$Mn$_x$N clusters for the XANES calculations, such as the substitutional Mn$_{Ga}$, the interstitial Mn$_{I}$, the Mn$_{Ga}$-Mn$_{I}$ dimer and the Mn$_{4}$ cluster by FEFF8.2 code. Figure 12 displays the Mn K-edge XANES spectra for these models. It is evident that the XANES features for the Mn atoms locating at the substitutional and interstitial sites are quite different. For the substitutional Mn in (Ga,Mn)N DMS, three fingerprint peaks A1, A and B are obvious. Preedge peak A1 can be regarded as the transition of Mn 1s core electron to the hybridization orbital of Mn 3d and N 2p states. Moreover, the peak B is the strongest in height and width. In contrast, for the interstitial Mn, the A1 peak in the pre-edge region disappears, instead a shoulder peak as indicated by an arrow appears, and the position of peak B shifts to higher energy and its height is significantly lower than that of peak A. In the substitutional Mn sites, Mn atoms are coordinated by four N neighbors, while in the case of interstitial Mn the four nearest neighbors of Mn are Ga atoms. The difference between the substitutional and interstitial Mn sites in their nearest neighbors consequently produces the different multiple-scattering contributions that are attributed to the distinct features in their B peaks in the post-
edge XANES spectra. It can be observed that the calculated XANES spectrum of GaMnN with substitutional Mn perfectly reproduces the experimental spectrum of Ga$_{0.990}$Mn$_{0.010}$N. Hence, we can deduce that most of Mn atoms in Ga$_{0.990}$Mn$_{0.010}$N with a low Mn dopant occupy the substitutional positions of the Ga sites in GaN. The calculated XANES spectrum for the Mn$_{Ga}$-Mn$_{I}$ dimer is similar to that of the substitutional Mn in the region of the peak A, but the fingerprint peak A1 in the pre-edge region is absent and the peak B is obviously reduced in height. A pre-edge shoulder peak as indicated by an arrow can also be observed. The calculated XANES spectrum of Mn$_{Ga}$-Mn$_{I}$ dimer and the experimental spectrum of Ga$_{0.975}$Mn$_{0.025}$N look similar in shape, suggesting that a substantial part of Mn atoms, besides the substitutional Mn, may exist in the form of Mn$_{Ga}$-Mn$_{I}$ dimer in the Ga$_{0.975}$Mn$_{0.025}$N. In fact, the Mn-Mn distance (1.93 Å) in Mn-Mn dimer is equal to the Mn-N bond length (1.93 Å) in the substitutional GaMnN. Both the Mn-Mn and Mn-N coordinations give rise to the nearest peaks at almost the same position in $R$-space. These two overlapped peaks make the EXAFS analysis not sensitive enough to exclude the existence of minority of Mn in the form of dimer. In contrast, the minority of Mn-Mn dimer in Ga$_{0.975}$Mn$_{0.025}$N can be easily detected by XANES owing to its sensitivity to the electronic structure. For the XANES spectrum of Mn cluster embedded in the GaN matrix, only very broad peaks appear in the post-edge region. This feature looks like that of the heavily Mn-doped sample Ga$_{0.900}$Mn$_{0.100}$N, implying the prominent existence of Mn clusters in Ga$_{0.900}$Mn$_{0.100}$N.

Figure 13. Total and partial DOS of various Mn occupations in GaN: (a) substitutional Mn$_{Ga}$, (b) interstitial Mn$_{I}$, (c) Mn$_{Ga}$-Mn$_{I}$ dimer, and (d) Mn$_{4}$ cluster.

Fig. 13 (a) indicates the DOS of the substitutional Mn$_{Ga}$, whose 3$d$ states are split into a doubly degenerate $e$ band and a triply degenerate $t_{2}$ band. As for the interstitial Mn$_{I}$ which is surrounded by four nearest-neighbor Ga atoms, the hybridization between Mn 3$d$ and Ga 4$p$ states also splits the Mn 3$d$ states into a doubly degenerate $e$ and a triply degenerate $t_{2}$ states [Fig. 13(b)]. The Fermi level falls into the $d_{z}^{\uparrow}$ band, the spin-up and spin-down $d_{z}$ states are located at $-1.3$ eV and are almost symmetric. A comparison of Figs. 15 (a) and (b) indicates that the $d_{z}^{\frac{1}{2}}$ band of substitutional Mn is located deeply inside the gap, forming highly localized electronic states; while for interstitial Mn, the $d_{z}$ states are substantially mixed with the conduction band (CB), leading to a less localized electronic states at the Fermi level. These significantly different features of the $d_{z}$ states between the substitutional and interstitial Mn can well explain the distinct pre-edge features of their XANES spectra as shown in Fig. 12. For the Mn$_{Ga}$ adopting a $d^{5}$ configuration, the $d_{z}^{\frac{1}{2}}$ states are fully occupied and the transition of Mn...
1s electron to the unoccupied \(dt^{↓}\) states is permitted. This gives rise to a single pre-edge peak \(A_1\). In contrast, for Mn, the participation of Mn \(dc\) states in the lowest part of the CB can not lead to a pronounced pre-edge peak, but a shoulder peak as indicated by an arrow in Fig. 12.

Regarding the Mn\textsubscript{Ga}+Mn\textsubscript{i} dimer, the DOS shown in Fig. 13(c) indicates that the \(d\) bands of Mn\textsubscript{Ga} shift downward by about 1eV because of the presence of Mn\textsubscript{i}. Once again the unoccupied \(d\) states of Mn\textsubscript{Ga} and Mn\textsubscript{i} mix with the lowest part of the CB, resulting in a pre-edge shoulder peak in its XANES spectrum as indicated by an arrow in Fig. 13. In addition, the electronic properties of a Mn\textsubscript{i} cluster embedded in GaN matrix were also calculated. The DOS shown in Fig. 13(d) manifests that the Mn \(d\) states form a continuous band structure above the Fermi level. This band structure is broad in energy, and its highest part mixes with the CB. Therefore, the XANES spectrum of the Mn\textsubscript{i} cluster in the near-edge region, which is associated with the transition of Mn 1s electron to the unoccupied 4p-like states, exhibits a rather broad peak \(A\).

5. Mn-doped Si

In this section, the occupation, magnetism, and electronic property of Mn dopants in silicon were systematically investigated [38]. A number of typical Mn distribution models, including the single doping, the poly-substitutional, the poly-interstitial as well as the substitutional-interstitial complexes, were considered. The energetically favorable configurations are schematically shown in Figure 14. The associated formation energies, spin moments, and magnetic states are listed in Table 1. For the doping of a single Mn in Si lattice, three high-symmetry sites, including one substitutional Mn\textsubscript{Si} and two interstitial sites Mn\textsubscript{T} (tetrahedral \(T\)) and Mn\textsubscript{O} (octahedral \(O\)) are considered. As expected, Mn\textsubscript{T} with a formation energy of 2.32 eV/Mn and a magnetic moment of 2.54 \(\mu_B\)/Mn is more energetically favored than the other two configurations. And the Mn\textsubscript{Si} site with a formation energy of 2.78 eV/Mn is lower in energy than the Mn\textsubscript{O} site by 130 meV. Therefore, based on the calculated formation energies, it is predicted that the isolated Mn\textsubscript{O} plays an unimportant role in Mn-doped Si system; and the presence of the Mn\textsubscript{T} is more likely than the Mn\textsubscript{Si} from the viewpoint of thermodynamics.

For substitutional \(n\)-Mn\textsubscript{Si} doping, it is found that the configuration where two Mn atoms are the nearest neighbors with a distance of 2.35 Å is the most favorable structure [see Fig. 14(a)], with two Mn atoms in an AFM alignment. Except the above close configuration, the FM state is lower in energy than AFM and nonmagnetic counterparts as the Mn-Mn distance in the pair Mn\textsubscript{Si} doping structure increases beyond 2.35 Å [Table 1]. This reconfirms the viewpoint that the FM interaction in substitutionally Mn-doped Si is long-ranged [39]. As for the interstitial poly-Mn doping, the most favorable configuration is that the two Mn atoms occupy two next nearest neighboring interstitial positions with a Mn-Mn distance of 3.84 Å as shown in Fig. 14(e), and the FM state is favored with a mean spin moment of 2.70\(\mu_B\)/Mn.

In contrast, the calculated formation energies clearly show that the Mn\textsubscript{T} atoms in the 3-Mn\textsubscript{T} and 4-Mn\textsubscript{T} structures shown in Figs. 16(f) and 16(g) prefer to cluster with each other.

Finally, our systematic study shows that Mn\textsubscript{Si} and Mn\textsubscript{T} ions in substitutional-interstitial complexes also prefer to occupy adjacent sites. The energetically favored configurations for each \(n\) \((n=1-4)\) are
displayed in Figs. 16(h)-16(k). The calculated formation energies for these structures are listed in Table 1. Strikingly, the formation energy for the Mn$_T$-Mn$_{Si}$-Mn$_T$ (1.89 eV/Mn) is the lowest, suggesting the Mn$_T$ and Mn$_{Si}$ ions in Mn-doped Si system prefer to form such a complex under equilibrium conditions. Interestingly, the formation energies for these (Mn$_T$)$_n$-Mn$_{Si}$ complexes are found to be overall lower than those for all substitutional or interstitial structures, suggesting such type of complex doing is generally favored in Mn$_x$Si$_{1-x}$ system. Table 1 shows that the magnetic ground states for (Mn$_T$)$_n$-Mn$_{Si}$ complexes are FM, except the (Mn$_T$)$_3$-Mn$_{Si}$ structure [Fig. 14(j)] with a mean spin moment of 1.50\(\mu_B\)/Mn. The most favorable Mn$_T$-Mn$_{Si}$-Mn$_T$ cluster of these configurations has a spin moment of 2.34\(\mu_B\)/Mn. The other two configurations, i.e., Mn$_T$-Mn$_{Si}$ and (Mn$_T$)$_2$-Mn$_{Si}$, also have relatively larger spin moments of 2.00\(\mu_B\)/Mn and 2.40\(\mu_B\)/Mn, respectively. Therefore, based on our first-principles calculations, it is predicted that in Mn-doped Si system the globally most favorable configuration is the substitutional-interstitial clusters, whose presence will notably enhance the magnetizations and change the electrical characters of the materials. These findings provide specific theoretical comprehension for different processing method adopted in experiments, and thus describe a general picture for understanding numerous intriguing observations in the Mn$_x$Si$_{1-x}$ DMS materials recently prepared.

6. Conclusions
In summary, the XAFS technique combining with the first-principles calculations were used to discover the dopants distributions, local atomic structures, electronic properties, and ferromagnetism origin for a variety of ZnO-, GaN-, and Si-based DMSs. Based on our results, we have established a pathway to understand the microscopic origin of ferromagnetism in the DMS materials from the viewpoint of experimental determination and theoretical calculations, which can thus assist in the further design of materials for possible spintronic applications.

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