Ab-Initio Calculation of the Basic Magnetic Properties of (Mn, Cr, V)-doped MgSiN$_2$

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Abstract. The current interest in the emerging field of semiconductor spintronics is mostly focused on transition metal-doped binary materials, e.g. Mn-doped GaAs, GaN, etc. Recently, however, the explorations of transition metal-doped ternary semiconductors have intensified, due to some experimental confirmations of high Curie temperature in chalcopyrite compounds. A density functional theory within generalized gradient approximation study was performed on (Mn, Cr, V)-doped ternary material MgSiN$_2$. Our results show Mn-doped MgSiN$_2$ to be antiferromagnetic for Mn$_{\text{Mg}}$ (Mn substitutes Mg site) and ferromagnetic for Mn$_{\text{Si}}$ (Mn substitutes Si site). On the other hand, (Cr, V)-doped MgSiN$_2$ was found to be ferromagnetic, independent of the substitution sites.

1. Introduction
In the past several years, the study of room temperature Diluted Magnetic Semiconductors (DMS) has attracted great interest. DMS are semiconductors that are doped with metal atoms. It is believed that the interaction among the spins of these atoms leads to a ferromagnetic state. DMS received considerable attention when Mn-doped GaAs was found to have a Curie temperature above 100 K [1]. Since then the intensity of DMS research, both theoretical and experimental, has multiplied. The study of room temperature DMS would lead to the quest of building the “spintronic” devices.

Thus far, research on transition metal (TM)-doped diluted magnetic semiconductor (DMS) systems has been focused primarily on the binary compound. Some of the best-studied binary systems include InAs, GaAs, and GaN. [1-5] Mn-doped GaN DMS, for example, has for some time, been predicted to have transition temperature well above 300 K. [1]

TM-doped ternary compounds have attracted much attention due to the recent experimental confirmations of high transition temperature ferromagnetism in, e.g., CdGeP$_2$, ZnGeP$_2$, ZnSnAs$_2$, CuGeSe$_2$, CdGeAs$_2$, and ZnSiAs$_2$ compounds. [6-10] Ternary compounds are interesting systems due to the fact that it is possible to substitute TM atoms in one (or both) of the two cation sites. Based on which site was substituted by the metal atom, the ferromagnetic (FM) or antiferromagnetic (AFM) state could be produced. In the case of M-doped (M = Mn, Cr, or V) II-IV-V$_2$ ternary compound, M$^{2+}$ will substitute a divalent (group II) cation site (M$_{\text{II}}$). In this case, the AFM spin arrangement is favored. On the other hand, if the M atom occupies the group IV cation site (M$_{\text{IV}}$), holes will be produced. Holes are expected to lead to ferromagnetism.

In this paper, we report the results of ab-initio calculations of the basic magnetic properties of M (M = Mn, Cr or V)-doped MgSiN$_2$. MgSiN$_2$ is a wide-band ternary semiconductor [11] with an interesting thermal property. Because of its high thermal conductivity, MgSiN$_2$ ceramic has recently
been suggested as an alternative to replace the traditional heat sink material, Al₂O₃, in integrated circuits. [12] The crystal structure and lattice parameters of MgSiN₂ are closely related to those of AlN, whose fabrication technology is already known. To understand the magnetic properties of this material, we first study the effect of M substitutions on cation sites (Mg or Si). It is interesting to see whether substitutional M_{II} or M_{IV} of a ternary compound could lead to ferromagnetism or antiferromagnetism. Secondly, we also study the effect of M concentrations (3.125% and 6.25%) on the magnetic ordering of this structure. In this case, the role played by substitutional M_{II} and M_{IV} in ferromagnetism of MgSiN₂, with respect to metal concentration, is studied.

2. Computational Method
First-principles total energy calculations of M-doped MgSiN₂ were performed using the ABINIT code. [13-14] ABINIT is a plane-wave-based pseudopotential density functional theory (DFT) code. Specifically, the generalized gradient approximation (GGA) of DFT has been used in our calculations. The GGA is a widely used approximation for the exchange correlation functional in DFT and has proven to be very successful in predicting many material properties.

For our calculations, the GGA-PBE from Fritz-Haber-Institute (Troullier-Martins scheme) has been used for all elements. The automatic generation of k points in the Irreducible Brillouin Zone of 2 X 2 X 2 Monkhorst-Pack grids has been performed. The system was studied in a 2 X 2 X 1 supercell containing 64 atoms (accommodating 32 cations and 32 anions). The cutoff energy of the plane-wave basis set was fixed at 25 Ha.

The crystal structure of MgSiN₂ used in our calculations is orthorhombic. Its unit cell contains 16 atoms, compared to only 4 atoms in, e.g., wurtzite GaN. Its space group is Pna2₁ (No.33). The following lattice constants have been used in our calculations: a = 5.2977 Å, b = 6.473 Å and c = 5.0139 Å. These parameters were obtained using a structural optimization calculation and in good agreement with the result found elsewhere. [15]

3. Results and Discussion
We substituted M atoms to replace either the group II (M_{II} or M_{Mg}) or group IV (M_{IV} or M_{Si}) atoms. For each substitutional case, the total energy for both the ferromagnetic (FM) and antiferromagnetic (AFM) spin alignments were calculated. To study the effect of metal concentration on MgSiN₂, we considered the following two cases: (i) 2 metal atoms in MgSiN₂ (corresponds to x = 3.125%); and (ii) 4 metal atoms in MgSiN₂ (corresponds to x = 6.25%). For each case of transition-metal concentration, we calculated the total energy of the systems for both the FM and AFM spin alignments.

| Metal concentration | Metal type | Substitutional site: Mg | Substitutional site: Si |
|---------------------|------------|-------------------------|-------------------------|
|                     |            | ∆E (meV/atom) | Magnetic structure | ∆E (meV/atom) | Magnetic structure |
| 3.125%              | Mn         | -3.26        | AFM                  | 20.16        | FM                  |
|                     | Cr         | 9.37         | FM                   | 7.27         | FM                  |
|                     | V          | 4.53         | FM                   | 3.13         | FM                  |
| 6.25%               | Mn         | -0.83        | AFM                  | 9.44         | FM                  |
|                     | Cr         | 2.16         | FM                   | 1.81         | FM                  |
|                     | V          | 1.73         | FM                   | 3.46         | FM                  |

Table 1 shows the results of our calculations. The energy gain per magnetic ion, ∆E, can be expressed as ∆E = E(AFM) – E(FM), where E(AFM) denotes the total energy of the AFM state and E(FM) denotes the total energy of the FM state. The positive value of ∆E implies a FM state is
preferred, while the negative value of $\Delta E$ implies an AFM state is preferred. The unit used for $\Delta E$ is meV/atom. Our results show different magnetic orderings, depending on which sites were substituted by the M atoms. Independent of the metal concentration, the substitutional $\text{Mn}_{\text{Mg}}$ does lead to AFM interactions (negative $\Delta E$), while the substitutional $\text{Mn}_{\text{Si}}$ leads to FM interactions (positive $\Delta E$). On the other hand, (Cr, V)-doped MgSiN$_2$ was found to prefer the FM state, independent of the substitution sites and concentration.

**Table 2.** The relationship between magnetic property and the number of 3d electrons in each substitutional case. We have assumed that metal atoms are $\text{M}^{2+}$ and $\text{M}^{4+}$ when they substitute for Mg and Si, respectively. The AFM state is preferred in the case of (Mg, Mn)SiN$_2$ because the electron configuration is half-filled ($d^5$) and super-exchange interaction prevails. On the other hand, in the cases of $d^1$ to $d^4$, the FM state is preferred because there are plenty of donors available.

Since the case of (Mn, Cr, V)$_\text{Si}$ always leads to ferromagnetism, we show in Figure 1 the calculated values of $\Delta E$ with respect to (Mn, Cr, V) concentrations. Except for the case of $V_{\text{Si}}$, the value of $\Delta E$ decreases as we increase the concentration from 3.125% to 6.25%. Thus, adding more dopants into Si site could reduce the stabilization of the FM state in both Mn- and Cr-doped MgSiN$_2$. In a recent theoretical calculation, Mn-doped MgSiN$_2$ with high (12.5%) Mn concentration was found to have antiferromagnetism if Mn atom substitutes the group IV (Si) site. [16] Finally, independent of its concentration, $\Delta E(\text{Mn}) > \Delta E(\text{Cr or V})$. According to the mean-field approximation, the Curie temperature ($T_c$) is proportional to the value of $\Delta E$. This, in turn, means Mn-doped MgSiN$_2$ would produce the highest $T_c$, compared to (Cr or V)-doped MgSiN$_2$.

![Figure 1. The calculated values of $\Delta E$ versus metal concentration.](image-url)
4. Conclusion
Using the first principles DFT within the GGA, we have studied the basic magnetic properties of (Mn, Cr, V)-doped MgSiN$_2$. Our calculations show, Mn-doped MgSiN$_2$ to be antiferromagnetic for Mn$_{Mg}$ (Mn substitutes Mg) and ferromagnetic for Mn$_{Si}$ (Mn substitutes Si). Independent of the metal concentration, both (Cr, V)$_{Mg}$ and (Cr, V)$_{Si}$ lead to ferromagnetism. Increasing metal concentration into both sites, however, was predicted to lower the stabilization of the FM state, especially in Mn- and Cr-doped MgSiN$_2$.

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