The Magnetic Properties of (Cr, V)-doped ZnGeN$_2$

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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 (Cr, V)-doped ternary material ZnGeN$_2$. Our results show that both Cr- and V-doped ZnGeN$_2$ to be ferromagnetic, independent of the substitution sites. Formation of half-metallic ferromagnetism is also possible in this type of material.

1. Introduction
The subject of spintronics [1] – electronics based on the spin rather than charge – has attracted great interests. For practical applications, however, any candidates of spintronics materials need to have room temperature ferromagnetism. Additionally, it would also be a major advantage if these new materials already have an existing technology-base in other applications.

Thus far, the 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]

The 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] The ternary 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, ferromagnetic (FM) or antiferromagnetic (AFM) state could be produced. In the case of M-doped (M = Cr or V) II-IV-V$_2$ ternary compound, M$^{2+}$ will substitute a divalent (group II) cation site (M$_{II}$). In this case, the AFM spin arrangement is favored. On the other hand, if the M atom occupies the group IV cation site (M$_{IV}$), holes will be produced. Holes are expected to lead to ferromagnetism.

Ternary semiconductors have been known for their unique nonlinear optical properties. An example of materials in this category is the wide-band semiconductor ZnGeN$_2$. The crystal structure and lattice parameters of ZnGeN$_2$ are closely related to those of wurtzite GaN, whose fabrication technology is already known. As a matter of fact, ZnGeN$_2$ has been found to be useful as an alternative of GaN for optoelectronic devices. [11-13] Thus, the achievement of room temperature ferromagnetism in ZnGeN$_2$ would make it possible to integrate magnetic and optical effects for future spintronics applications.
In this paper, we report the results of ab-initio calculations on magnetic properties of M \((M = \text{Cr or V})\)-doped \(\text{ZnGeN}_2\). To understand the magnetic properties of this material, we first study the effect of M substitutions on cation sites (Zn or Ge). It is interesting to see whether substitutional M\(_{\text{II}}\) or M\(_{\text{IV}}\) of a ternary compound could lead to ferromagnetism or antiferromagnetism. Secondly, we also study the effect of Mn concentrations (3.125\%, 6.25\%, and 12.5\%) on the magnetic ordering of this structure. In this case, the role played by substitutional Mn\(_{\text{II}}\) and Mn\(_{\text{IV}}\) in ferromagnetism of \(\text{ZnGeN}_2\), with respect to metal concentration, is studied.

2. **Computational Method**

First-principles total energy calculations of M-doped \(\text{ZnGeN}_2\) were performed using the ABINIT code. \([14-15]\) 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 \(2 \times 2 \times 2\) Monkhorst-Pack grids has been performed. The system was studied in a \(2 \times 2 \times 2\) supercell containing 128 atoms (accommodating 64 cations and 64 anions). The cutoff energy of the plane-wave basis set was fixed at 18 Ha.

The crystal structure of \(\text{ZnGeN}_2\) 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 Pna2\(_1\) (#33). The following lattice constants have been used in our calculations: \(a = 6.5238\ \text{Å}, b = 5.5242\ \text{Å}\) and \(c = 5.2608\ \text{Å}\). These parameters were obtained using a structural optimization calculation and in good agreement with the experimental results. \([16-17]\]

3. **Results and Discussion**

We substituted M atoms to replace either the group II (M\(_{\text{II}}\) or M\(_{\text{Zn}}\)) or group IV (M\(_{\text{IV}}\) or M\(_{\text{Ge}}\)) 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 \(\text{ZnGeN}_2\), we considered the following three cases: (i) 2 metal atoms in \(\text{ZnGeN}_2\) (corresponds to \(x = 3.125\%\)); (ii) 4 metal atoms in \(\text{ZnGeN}_2\) (corresponds to \(x = 6.25\%\)); and (iii) 8 metal atoms in \(\text{ZnGeN}_2\) (corresponds to \(x = 12.5\%\)). For each case of transition-metal concentration, we calculated the total energy of the systems for both the FM and AFM spin alignments.

Table 1 shows the results of our calculations. The energy gain per magnetic ion, \(\Delta E\), can be expressed as \(\Delta E = E(\text{AFM}) - E(\text{FM})\), where \(E(\text{AFM})\) denotes the total energy of AFM state and \(E(\text{FM})\) denotes the total energy of FM state. Positive value of \(\Delta E\) implies a FM state is preferred, while negative value of \(\Delta E\) implies and AFM state is preferred. The unit used for \(\Delta E\) is meV/atom.

Our results show similar magnetic ordering. Independent of the metal concentration, both (Cr, V)-doped \(\text{ZnGeN}_2\) prefer FM state.

Figure 1 shows the calculated values of \(\Delta E\) with respect to (Cr, V) concentrations. Two important results can be stated. First, for all type of dopants, the value of \(\Delta E\) decreases as we increase the metal concentration. Thus, adding more dopants into either site in the dilute limit of up to \(x = 12.5\%\) reduces the stabilization of FM state. The second important result is, independent of its concentration, \(\Delta E(\text{Cr}) > \Delta E(\text{V})\). This means Cr-doped \(\text{ZnGeN}_2\) would produce the highest \(T_c\), compared to V-doped \(\text{ZnGeN}_2\).

In Figure 2, we show the calculated total density of states (DOS) of \(\text{Zn}(\text{Cr},\text{Ge}_{1-x})\text{N}_2\) \((x = 6.25\%)\) for the FM state. At the Fermi level \((E_F)\), one spin channel shows a clean band while the other spin channel shows a narrow band. This result shows formation of half-metallic ferromagnetism in this type of material. Half-metallicity behaviour was also shown to appear in Mn-doped \(\text{ZnGeN}_2\). \([18]\]
Table 1. Magnetic configurations of (Cr, V)-doped ZnGeN$_2$. In this table, FM means ferromagnetic configuration and AFM means antiferromagnetic configuration. Positive $\Delta E$ means FM configuration is favorable.

| Metal concentration | Metal type | Substitutional site: Zn $\Delta E$ (meV/atom) | Substitutional site: Ge $\Delta E$ (meV/atom) | Magnetic structure | Magnetic structure |
|---------------------|------------|---------------------------------------------|---------------------------------------------|-------------------|-------------------|
| 3.125% Cr           | 134.75     | FM                                          | 82.09                                       | FM                | 3.12% Cr          |
| 3.125% V            | 105.81     | FM                                          | 30.55                                       | FM                | 3.12% V           |
| 6.25% Cr            | 137.86     | FM                                          | 85.08                                       | FM                | 6.25% Cr          |
| 6.25% V             | 96.81      | FM                                          | 32.17                                       | FM                | 6.25% V           |
| 12.5% Cr            | 100.43     | FM                                          | 46.91                                       | FM                | 12.5% Cr          |
| 12.5% V             | 52.93      | FM                                          | 22.64                                       | FM                | 12.5% V           |

Figure 1. The calculated values of $\Delta E$ versus (Cr, V) concentrations.

Figure 2. Calculated total density of states (DOS) for Zn(Cr$_x$Ge$_{1-x}$)N$_2$ with $x$ = 6.25%.
4. Conclusion
Using the first principles DFT within the GGA we have studied the magnetic properties of (Cr, V)-
doped ZnGeN$_2$. Our calculations show, independent of the metal concentration, both (Cr, V)$_{Zn}$ and
(Cr, V)$_{Ge}$ lead to ferromagnetism. Increasing metal concentration into both sites, however, was
predicted to lower the stabilization of FM state. We also show formation of half-metallic
ferromagnetism is possible in this type of material. The existence of half-metallicity addresses the
prospect for using ferromagnetic ZnGeN$_2$ in spintronics applications.

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