Ab-initio Study of the Magnetic Properties of $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ ($\text{X} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$)

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The effect of the substitution of V, Cr, and Fe on the magnetic properties of MnAlGe ternary compounds has been investigated by first-principles electronic calculations. The total energy differences (ΔE s) between the ferromagnetic and nonmagnetic states varied in a similar trend to the variation in their experimental Curie temperatures. Thus, ΔE can be used to make an approximate and systematic estimation of the effect that atomic substitution or the addition of a fourth element will have on the Curie temperature. The results show that the magnetization of MnAlGe compounds (or the magnetic moment of Mn) is sensitive to the variation of the distance between the Mn layer and its adjacent layer comprising Al and Ge atoms. A large distance between the layers corresponds to a large magnitude of magnetization.
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1. Introduction

It is well known that the ternary compound MnAlGe is a ferromagnet with a Cu_2Sb -type structure.^{1–3)} Its Curie temperature (T_c) is known to be 518 K. The Mn atoms form a base-centered tetragonal sublattice with two adjacent basal planes separated by Al and Ge atoms (see Fig. 1). The distance between the Mn atoms along the c axis (5.9 Å) is much larger than the distance between the corner and center Mn atoms on the basal plane (2.8 Å). The MnAlGe compound has a large uniaxial magnetic anisotropic constant $5.3 \times 10^5 \text{ J/m}^3$ at room temperature¹⁾ and $9.7 \times 10^5 \text{ J/m}^3$ at 0 K.⁴⁾ Because of this characteristic, MnAlGe has potential applications in spintronic devices.⁵⁾

Recently, Umetsu *et al.*⁶⁾ investigated the effect of substitution of Mn atoms with either Cr or Fe atoms on the magnetization (M) and T_c of MnAlGe compounds. They observed that substitution by Cr atoms increases M and T_c of $(\text{Mn}_{0.8}\text{Cr}_{0.2})\text{AlGe}$ compound compared to the MnAlGe compound. Two further studies also reported the effect of substituting Mn atoms by V, Cr, and Fe atoms on M and T_c for MnAlGe.^{7,8)} All the above-mentioned three studies reported a similar trend in the variation of T_c with Mn atom substitutions. However, there is some observed discrepancy concerning the variation of M with two reports^{7,8)} citing that substitution by Cr decreases M compared to the MnAlGe compound.

In this study, we set to investigate the cause of this observed discrepancy on the behavior of M . To achieve this, we performed first-principles calculations of electronic structure of $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ ($\text{X} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$).

2. Approach

To replace a quarter of the Mn atoms in MnAlGe, we used a double-volume cell with space group $\text{P}\bar{4}m2$ (No. 115), with the following lattice vectors: $\vec{a}_1 = \vec{a} = (a, 0, 0)$, $\vec{b}_1 = \vec{b} = (0, a, 0)$, and $\vec{c}_1 = 2\vec{c} = (0, 0, 2c)$, where $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the original lattice vectors of the Cu_2Sb -type MnAlGe unit cell. The atomic sites and positions for this double-volume cell are listed in Table 1.

Fig. 1 Crystal structures of MnAlGe (left) and $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ (right).

Table 1 Atomic sites and positions of $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$.

atom	site	position	atom	site	position
X	1a	(0,0,0)	Al1	2g	(1/2,0,z ₁)
Mn1	1b	(1/2,1/2,0)	Al2	2g	(1/2,0,z ₂)
Mn2	1d	(0,0,1/2)	Ge1	2g	(1/2,0,z ₃)
Mn3	1c	(1/2,1/2,1/2)	Ge2	2g	(1/2,0,z ₄)

The lattice constants $a_1 (= b_1)$, c_1 and the atomic positions were estimated according to the following four steps. In the first step, the total energy (E_{tot}) was calculated as a function of a_1 by fixing the c_1/a_1 constant and the atomic position values to the experimental values (see Table 2). Then, we estimated the lattice constant $(a_1)_{\text{min}}$ (or cell volume V_{min}) that minimizes E_{tot} . In the second step, we calculated E_{tot} as a function of c_1/a_1 by fixing the cell volume and the atomic position values to V_{min} and the experimental values, respectively. This was followed by estimating the value of $(c_1/a_1)_{\text{min}}$ that minimizes E_{tot} . In the third step, using $(c_1/a_1)_{\text{min}}$ and the experimental atomic positions, V_{min} was re-calculated. In the fourth step, we estimated the optimal atomic positions by minimizing the forces acting on the atoms using V_{min} and $(c_1/a_1)_{\text{min}}$.

The optimal data (referred to as “opt”) on lattice constants and atomic positions for $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ ($\text{X} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$) are listed in Table 2. The initial values of the lattice

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Table 2 Optimal values of the lattice constants (Å) and atomic positions. The third and fifth rows show the values corresponding to the optimal and experimental values of MnAlGe.

	X	a_1	c_1	z_1	z_2	z_3	z_4
opt	V	3.932	12.032	0.1528	0.6450	0.3643	0.8557
	Cr	3.939	11.826	0.1466	0.6467	0.3617	0.8609
	Mn	3.922	11.744	0.1465	0.6460	0.3608	0.8608
	Fe	3.926	11.609	0.1406	0.6476	0.3591	0.8655
exp ^{a)}		3.913	11.866	0.1365	0.6365	0.3600	0.8600

^{a)} Ref. [2]

constants and atomic positions, which correspond to the experimental data,²⁾ are also listed in the same table (Table 2) (referred to as “exp”).

The first-principles calculations on electronic structure were performed using the full-potential linearized augmented plane wave method.⁹⁾ The generalized gradient approximation developed by Perdew *et al.*¹⁰⁾ was used for the exchange-correlation potential. The plane wave cutoff was $RK_{max} = 7.0$, where R is the smallest atomic sphere radius and K_{max} is the magnitude of the largest K vector. For the atomic sphere radius, the following values were used: 2.45 a.u. for the 3d transition metals and 2.17 a.u. for Al and Ge.

3. Results and Discussion

3.1 Magnetic moments per formula unit

The values of the M per formula unit for $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ are shown in Fig. 2, along with the experimental data reported by three separate groups.^{6–8)} Data estimated using the optimal parameters listed in Table 2 show that M reaches a maximum at $X = \text{Mn}$. This trend (referred to as Trd-Mn) is similar to the experimental data reported by two research groups,^{7,8)} but it differs from the data reported by the third group.⁶⁾ The third group’s findings indicate that M reaches a maximum at $X = \text{Cr}$ rather than at $X = \text{Mn}$ (referred to as Trd-Cr). We estimated M using the experimental parameters and found that the M reaches a maximum at $X = \text{Cr}$. Therefore, using the first-principles electronic structure calculations, two reported trends for M (Trd-Mn and Trd-Cr) were demonstrated.

Fig. 2 Magnetic moments per formula unit of $(\text{Mn}_{1-x}\text{X}_x)\text{AlGe}$ ($X = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$). The circles and crosses are our data at $x = 0.25$ estimated using the experimental and optimal data in Table 2, respectively. The triangles ($x = 0.2$), diamonds ($x = 0.1$), and squares ($x = 0.1$) are the experimental data obtained from Refs. 6), 7), and 8), respectively.

The main difference in the two trends (Trd-Mn and Trd-Cr) was attributed to the large decrease in M of MnAlGe from $1.95 \mu_B$ for Trd-Mn to $1.74 \mu_B$ for Trd-Cr. The values of magnetic moments of the constituent atoms were noted as follows: for Trd-Mn, Mn $2.01 \mu_B$, Al $-0.02 \mu_B$, Ge $-0.05 \mu_B$; and for Trd-Cr, Mn $1.82 \mu_B$, Al $-0.02 \mu_B$, Ge $-0.05 \mu_B$. Thus, the difference in M is mainly because of the difference in the magnetic moment of Mn ($m(\text{Mn})$).

The optimal and experimental structures show that the neighboring atoms of Mn in MnAlGe are four Al atoms, four Ge atoms, and four Mn atoms as the first, second, and third nearest neighbors, respectively. The distances between the atoms from the optimal (experimental) structure are $d(\text{Al}) = 2.55$ (2.54) Å, $d(\text{Ge}) = 2.61$ (2.57) Å, and $d(\text{Mn}) = 2.77$ (2.77) Å, where $d(X)$ is the distance between Mn and the nearest X atom. This indicates that the differences in $d(\text{Al})$ and $d(\text{Ge})$ are responsible for the two different M trends (Trd-Mn and Trd-Cr). A detailed investigation of the relation between $d(\text{Al})$ or $d(\text{Ge})$ and $m(\text{Mn})$ is outlined in Sect. 3.3.

3.2 Curie temperature

The energy differences (ΔE) for the optimal $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ structure (referred to as $\Delta E(\text{opt})$) were estimated as follows: $\Delta E = E(P) - E(F)$, where $E(P)$ and $E(F)$ are the total energies (eV/f.u.) in the paramagnetic and ferromagnetic states, respectively. The ΔE for the experimental $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ structure were also estimated (referred to as $\Delta E(\text{exp})$). The calculated $\Delta E(\text{opt})$, $\Delta E(\text{exp})$ and the experimental data for the T_c are shown in Fig. 3. Figure 3 shows that $\Delta E(\text{opt})$ and $\Delta E(\text{exp})$ follow a similar trend and reach a maximum at $X = \text{Cr}$. Moreover, this trend is similar to that of the experimental data for T_c .

The relationship between T_c and the lattice constants (a and c) was discussed by Umetsu *et al.*⁶⁾ Figure 4 shows the relationships between $\Delta E(\text{opt})$ and the lattice constants (a and c), along with the experimental data for T_c . The change of $\Delta E(\text{opt})$ (~ 0.1) is observed to occur in a narrower range of a (~ 0.02 Å) than c (~ 0.1 Å). This fact indicates that ΔE is more sensitive to variations in a than c . Moreover,

Fig. 3 Curie temperature (T_c) and energy difference ($\Delta E = E(P) - E(F)$) of $(\text{Mn}_{1-x}\text{X}_x)\text{AlGe}$ ($X = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$). $E(P)$ and $E(F)$ are the total energies (eV/f.u.) in the paramagnetic and ferromagnetic states, respectively. The circles and crosses are our data, ΔE , at $x = 0.25$ estimated using the experimental and optimal data in Table 2, respectively. The triangles ($x = 0.2$), diamonds ($x = 0.1$), and squares ($x = 0.1$) are the experimental data obtained from Refs. 6), 7), and 8), respectively.

Fig. 4 Curie temperature (T_c , triangles) and energy difference ($\Delta E = E(P) - E(F)$, crosses) as a function of the a (top) and c (bottom) lattice constants. $E(P)$ and $E(F)$ are the total energies (eV/f.u.) in the paramagnetic and ferromagnetic states, respectively. The crosses are our data of $(\text{Mn}_{1-x}\text{X}_x)\text{AlGe}$ ($\text{X} = \text{Cr}, \text{Mn}, \text{Fe}$) at $x = 0.25$ estimated using the optimal data in Table 2. The experimental data for T_c are from Ref. 6).

$\Delta E(a)$ is inclined upward left from Fe to Mn and upward right from Mn to Cr. However, $\Delta E(c)$ is inclined upward right from Fe to Mn, and also upward right from Mn to Cr. These characteristics can be observed in the relationships between T_c and the lattice constants (a and c). Thus, it can be said that the dependency of ΔE on the lattice constants (a and c) is similar to that for T_c . Also, the discrepancies between the optimal and experimental lattice constants (a and c) are less than 0.4% and 1.3% for a and c , respectively.

The above results indicate that ΔE is useful to approximately estimate the trend of T_c .

3.3 Magnetic moment of Mn

In this section, we discuss several investigations of $m(\text{Mn})$ in MnAlGe . Instead of using a double-volume cell, we used an original unit cell [$P4/nmm$ (No. 129)] of Cu_2Sb -type MnAlGe (see Fig. 1), where Mn is located at $(0, 0, 0)$ and $(0.5, 0.5, 0.5)$, Al is located at $(0.0, 0.5, z_1)$ and $(0.5, 0.0, -z_1)$, and Ge is located at $(0.0, 0.5, z_2)$ and $(0.5, 0.0, -z_2)$. First, we expanded a or c by 1% in the optimal cell to investigate the relationship between the lattice constant and the magnetic moment. The value of $m(\text{Mn})$ increases only by less than $0.04 \mu_B$ (from $2.01 \mu_B$ to 2.05 (2.04) μ_B in the case of $a(c)$). However, we exchanged the atomic positions z_1 and z_2 between the optimal and experimental cells, and the unexpected result was obtained. Using the atomic positions z_1 and z_2 of the optimal cell for the experimental cell results in increasing of $m(\text{Mn})$ from $1.82 \mu_B$ to $2.04 \mu_B$. In contrast, using the atomic positions z_1 and z_2 of the experimental cell

Table 3 Atomic positions, magnetic moments (μ_B), and shortest distances ($\text{\AA}$) between X and Mn in MnAlGe .

position	moment		distance		
			X		
$z_1 (= 1 - z_2)$	Mn	f.u.	Mn	Al	Ge
0.2750	1.756	1.674	2.773	2.540	2.540
0.2908	2.171	2.090	2.773	2.600	2.600
0.3011	2.335	2.235	2.773	2.640	2.640

for the optimal cell results in decrease of $m(\text{Mn})$ from $2.01 \mu_B$ to $1.80 \mu_B$. These considerable changes indicate that $m(\text{Mn})$ is sensitive to the position of Al or Ge in relation to Mn.

To clarify the relationship between $m(\text{Mn})$ and the position of Al or Ge in relation to Mn, we artificially shifted the positions of Al and Ge on the condition $z_2 = 1 - z_1$ for simplicity. Thus, the Mn layers are separated by two layers comprising Al and Ge atoms (see Fig. 1). The values of $m(\text{Mn})$ are listed in Table 3, along with the shortest atomic distances between Mn, Al, and Ge. Here, the Mn atoms on the corner and center sites of the basal plane have the shortest Mn–Mn distance ($d(\text{Mn})$). The corner Mn atom on the basal plane and Al (or Ge) in the adjacent layer have the shortest Mn–Al distance $d(\text{Al})$ (or $d(\text{Ge})$). In Table 3, we set the smallest z_1 value to be 0.275 because it gives the same $d(\text{Al}) = 2.54 \text{\AA}$ as in the experimental cell. Table 3 shows that an increase in $d(\text{Al})$ (or $d(\text{Ge})$) corresponds to an increase in $m(\text{Mn})$ value, even though $d(\text{Mn})$ is unchanged. It should also be noted that the $m(\text{Mn})$ value drastically changes.

We investigated the relationship between $m(\text{Mn})$ and $d(\text{Al})$ (or Ge) from the perspective of the electronic structure but did not obtain a definitive correlation. This may be because hybridization between the Mn-3d state and the Al-3p state or Ge-4p state is weak as shown by Motizuki *et al.*¹¹⁾ from first-principles calculations. Further investigation is required to confirm this assumption.

3.4 Observed discrepancy of the behavior of M

It was shown in Sect. 3.1 that the main difference existing in two different M trends (i.e., Trd-Mn and Trd-Cr) obtained from the first-principles calculations is attributed to the large decrease of M (about $0.2 \mu_B$) from Trd-Mn to Trd-Cr in MnAlGe . Furthermore, it was found that the difference in M is mainly arising from the difference in $m(\text{Mn})$. In Sect. 3.3, we showed that a change in $d(\text{Al})$ (or $d(\text{Ge})$) corresponds to a change in $m(\text{Mn})$. By the way, as shown in Fig. 2, the main difference existing in the two different M trends obtained from experimental data is attributed to the large increase of M (about $0.2 \mu_B$) from Trd-Mn to Trd-Cr in $(\text{Mn}_{1-x}\text{Cr}_x)\text{AlGe}$.

To clarify the relationship existing between M (or $m(\text{Mn})$ and $m(\text{Cr})$) and the position of Al or Ge in relation to Mn in $(\text{Mn}_{1-x}\text{Cr}_x)\text{AlGe}$, further first-principles calculations were performed for $(\text{Mn}_{0.75}\text{Cr}_{0.25})\text{AlGe}$. In this case, the following unit cell was chosen because Al and Ge each has only a single atomic site in this cell, and a quarter of the Mn atoms in MnAlGe can be replaced. The lattice vectors of the unit cell used with space group $P42m$ (No. 111) are $\vec{a}' = \vec{a}_1 + \vec{b}_1$, $\vec{b}' = -\vec{a}_1 + \vec{b}_1$ and $\vec{c}' = 0.5\vec{c}_1$. The atomic sites in the cell are as follows: 1a $(0, 0, 0)$ for Cr; 1d $(0.5, 0.5, 0)$ and 2e $(0.5, 0, 0)$ for Mn; 4n $(0.25, 0.75, z_1)$ for Al; 4n $(0.25, 0.75, z_2)$ for Ge.

Table 4 Atomic positions, magnetic moments (μ_B), and shortest distances ($\text{\AA}$) between X and Mn (or Cr) in $(\text{Mn}_{0.75}\text{Cr}_{0.25})\text{AlGe}$. The fourth column shows a weighted average values of the magnetic moments of Cr and Mn.

position $z_1 (= 1 - z_2)$	moment				distance		
	Cr	Mn	a.v.	f.u.	Mn/Cr	Al	Ge
0.2708	1.720	1.933	1.880	1.824	2.785	2.540	2.540
0.2866	1.793	2.179	2.083	2.006	2.785	2.600	2.600
0.2968	1.829	2.331	2.206	2.118	2.785	2.640	2.640

The values of $a_1 (= b_1)$ and c_1 are fixed as 3.939 and 11.826 $\text{\AA}$, respectively, which are the optimal values for $(\text{Mn}_{0.75}\text{Cr}_{0.25})\text{AlGe}$ (see Table 2). Furthermore, we artificially shifted the positions of Al and Ge using the condition $z_2 = 1 - z_1$ for simplicity, and set the atomic position z_1 at the value that produces the same $d(\text{Al})$ as in the case of MnAlGe .

The results are listed in Table 4. Table 4 shows that an increase in $d(\text{Al})$ (or $d(\text{Ge})$) corresponds to an increase in M value (or $m(\text{Mn})$ and $m(\text{Cr})$ values), even though $d(\text{Mn})$ is unchanged. Furthermore, it is seen that the M value changes drastically. These characteristics are the same as those of MnAlGe . This indicates that the difference existing in $d(\text{Al})$ and $d(\text{Ge})$ is one of causes of the observed discrepancy in the behavior of M .

4. Summary

We have investigated the effect of the substitution of V, Cr, and Fe on the magnetic properties of MnAlGe ternary compounds for $(\text{Mn}_{0.75}\text{X}_{0.25})\text{AlGe}$ ($\text{X} = \text{V}, \text{Cr}, \text{Fe}$) by first-principles calculations. We found that the total energy differences (ΔE s) between the ferromagnetic and paramagnetic (nonmagnetic) states have similar trends as exhibited by the experimental Curie temperatures of the system. Thus, ΔE can be used to make an approximate and systematic estimation of the effect that atomic substitution or the addition of a fourth element will have on the Curie

temperature. Our calculations also obtained similar trends as those exhibited by the experimental magnetization of the system.

Moreover, we found that the magnetization of MnAlGe (or the magnetic moment on Mn) is sensitive to the distance between the Mn layer and its adjacent layer comprising Al and Ge, wherein a large distance corresponds to a large magnetization. We therefore indicated the possibility that the differences in the positions of the Al and Ge atoms in relation to the Mn atom induce the observed discrepancy of the behavior of the magnetization of $(\text{Mn}_{1-x}\text{X}_x)\text{AlGe}$.

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