Magnetic and Electronic Structures of Cobalt or Copper Substituted Mn_2Sb

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First-principles total-energy calculations have been performed for the hypothetical case of $x = 1$ in $\text{Mn}_{2-x}\text{X}_x\text{Sb}$ ($\text{X} = \text{Co}$ and Cu) for several magnetic states, using the full-potential linearized augmented plane wave method based on the generalized gradient approximation. The calculated total energy indicates that the Co (Cu) atom prefers the site Mn(I) to the site Mn(II) (Mn(II) to Mn(I)). This result of Co is consistent with the available neutron diffraction experiment. For CoMnSb where Co occupies the site Mn(I), the change of lattice constants (a and c) and c/a from AF2 to F is in good agreement with experimental trends. Our results indicate that the optimization of the ratio c/a (lattice distortion) is crucial to determine the most stable magnetic state and that the optimization of the atomic positions of the sites Mn(II) and Sb is also crucial. [doi:10.2320/matertrans.M2013327]

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1. Introduction

The compound Mn_2Sb with the tetragonal Cu_2Sb structure ($P4/nmm$) is ordered ferrimagnetically below 550 K.¹⁾ As shown in Fig. 1, it contains two crystallographically different Mn sites, i.e., Mn(I) and Mn(II), which are tetrahedrally and octahedrally surrounded by Sb atoms, respectively. The ferrimagnetic (FR) structure is formed by the antiparallel arrangement of the Mn(I) ($2.13\mu_B$) and Mn(II) ($3.87\mu_B$).¹⁾

The substitution of Co or Cu for Mn results in the appearance of a first-order magnetic phase transition from FR to the antiferromagnetic (AF) state at T_t as temperature decreases.²⁾ The FR to AF transition is accompanied with a large change in the volume,³⁻⁵⁾ resistivity,^{5,6)} magnetization,³⁻⁵⁾ etc. Application of magnetic field induces the first-order AF to FR transition, which is accompanied with large magnetoresistance, magnetostriction, etc.^{5,6)} Therefore, these compounds attract attention as a magnetic field controlled materials.

Recently, the phenomenon that a first-order phase transition is arrested by a magnetic field have been reported for magnetic materials, such as $\text{Ce}(\text{Fe}_{0.96}\text{Al}_{0.04})_2$,⁷⁾ $\text{Ni}_{45}\text{Co}_{5-\text{Mn}_{36.7}\text{In}_{13.3}}$.⁸⁾ This is so-called kinetic arrest (KA) effect. The KA effect is also reported for $\text{Mn}_{1.85}\text{Co}_{0.15}\text{Sb}$,⁶⁾ $\text{Mn}_{1.8}\text{Co}_{0.2}\text{Sb}$,⁵⁾ $\text{Mn}_{2-x}\text{Cu}_x\text{Sb}$.⁹⁾ It is very important to clarify the mechanism of the KA effect in the view of application of such magnetic field controlled materials.

In this paper, we investigate electronic and magnetic properties of $\text{Mn}_{2-x}\text{X}_x\text{Sb}$ ($\text{X} = \text{Co}$ and Cu) by a first-principles band calculation to expand our knowledge for the materials.

2. Approach

First-principles total-energy calculations have been performed by the full-potential linearized augmented plane wave (FLAPW) method.¹⁰⁾ For the exchange–correlation energy or its corresponding potential, we used the generalized gradient approximation (GGA) by Perdew *et al.* (PBE96).¹¹⁾ In the present study, the self-consistent calculation is performed using a $14 \times 14 \times 9$ k -point mesh. The plane-wave cutoff is $RK_{\text{max}} = 7.0$, where R is the smallest atomic sphere

Fig. 1 Crystal structure of Mn_2Sb and schematic representation of several magnetic structures.

radius and K_{max} is the magnitude of the largest K vector. For the atomic-sphere radius, we used such values as 2.24 a.u. for Mn, Co and Cu, and 2.13 a.u. for Sb. In the calculation of the equilibrium positions of the atoms in a cell, we used a reversed-communication trust-region Quasi-Newton method.¹⁰⁾

In this paper, we have dealt with the hypothetical case of $x = 1$ in $\text{Mn}_{2-x}\text{X}_x\text{Sb}$ ($\text{X} = \text{Co}$ and Cu), that is, the X atom occupies the site Mn(I) (denoted by XMnSb) or the site Mn(II) (MnXSb). For a magnetic phase, the following five structures shown in Fig. 1 are considered:¹²⁾ paramagnetic or non-magnetic (P), ferromagnetic (F), ferrimagnetic (FR) and two antiferromagnetic (AF1, AF2) states. The FR and AF1 structures are equal to those reported for Mn_2Sb ¹⁾ and Mn_2As ,¹³⁾ respectively.

For CoMnSb and MnCoSb , we started the calculation with an antiparallel alignment of the spin magnetic moments on Co and Mn, but did not obtain a self-consistent solution. A solution with a parallel alignment of the spin magnetic moments on Co and Mn is only obtained. Thus, in CoMnSb and MnCoSb , there exist only the F and AF2 states.

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Fig. 2 Total energy vs lattice constant a . The upper panels (a), (b), (c) show the results of CoMnSb (●) and MnCoSb (▲). The lower panels (d), (e), (f) show the results of CuMnSb (●) and MnCuSb (▲). The symbol ◇ denotes the lattice constant that gives a minimum total energy.

3. Results and Discussions

3.1 Site preference of Co and Cu

We have carried out total-energy calculations of hypothetical compounds for several magnetic states to gain insight in the site preference of Co and Cu atoms. The results of “energy vs a ” are shown in Fig. 2, where the following experimental values of Mn₂Sb are used for the ratio c/a and the atomic position parameters, u and v (see Fig. 1): $c/a = 1.608$, $u = 0.710$, $v = 0.279$.¹⁴⁾ Hereafter, we define “ V_A ” as the volume which gives the minimum energy in Fig. 2.

First we consider CoMnSb and MnCoSb. The Fig. 2 shows that the total energy of MnCoSb ($E(\text{MnCoSb})$) is lower than $E(\text{CoMnSb})$ in the P state and that $E(\text{CoMnSb}) < E(\text{MnCoSb})$ in F and AF2 states. This result indicates that the Co atom prefers the site Mn(I) to the site Mn(II) in a magnetic state. This is consistent with the report by Brown *et al.*¹⁵⁾ They showed that the Co atom occupies the site Mn(I) in Mn_{1.8}Co_{0.2}Sb from an analysis of the neutron diffraction experiment.

Second, we consider CuMnSb and MnCuSb. It is meaningless to distinguish F from FR (AF1 from AF2) because the magnetic moment on Cu is negligible (the value is less than $0.01\mu_B$). The Fig. 2 shows that $E(\text{MnCuSb}) < E(\text{CuMnSb})$ in all magnetic states. This result indicates the Cu atom prefers the site Mn(II) to the site Mn(I). Unfortunately, we can not confirm our result because the information about the site preference of Cu is not available.

3.2 Lattice deformation and atomic position

Before we have a discussion about our present results, we make some comments on the predictability of our total-energy calculation. (Concerning an accuracy of FLAPW method, see Ref. 16) for example.) We have obtained the

result¹⁷⁾ of $\Delta E = -0.06 \text{ eV/f.u.}$ ($+0.02 \text{ eV/f.u.}$) for Mn₂Sb (Mn₂As), where $\Delta E = E(\text{FR}) - E(\text{AF1})$. Here $E(\text{FR})$ and $E(\text{AF1})$ means a total energy for the FR and AF1 states, respectively (see Fig. 1). Although the energy difference between FR and AF1 is small, these results are consistent with the experimental reports^{1,13)} because the experimental observation shows that Mn₂Sb (Mn₂As) has the FR (AF1) state for its magnetic ground state. Concerning a lattice constant, the discrepancy between our results and experimental ones^{14,18)} is lower than 3% for Mn₂Sb and Mn₂As.

We show the result of a total energy as a function of c/a in Figs. 3(a) and 3(b) for CoMnSb and MnCuSb, respectively. In these figures, there are important three points (A, B, C). At the point A, the total energy is minimized as a function of a (see Fig. 2). The points B and C show the ratio c/a which gives minimum total energies before and after the optimization of atomic positions of Mn(II) and Sb for CoMnSb (Cu and Sb for MnCuSb) on the condition that $V = V_A$, where “ V ” means the unit-cell volume. The arrows in Fig. 3 show that the optimization of atomic positions at the point B decreases the total energy from the upper point to the lower point.

First we consider CoMnSb. At the point A, the total energy for the F state ($E(\text{F})$) is lower than $E(\text{AF2})$. However, $E(\text{AF2})$ is lower than $E(\text{F})$ after the optimization of c/a . Moreover, the optimization of atomic positions of Mn(II) and Sb brings the result that $E(\text{F}) \approx E(\text{AF2})$. These results indicate that the optimization of the lattice deformation and the atomic position is crucial in the determination of the stabilization of the two magnetic phases, F and AF2.

The result of MnCuSb is shown in Fig. 3(b). In this case, the relative stability of the two magnetic phases, F and AF is not changed by the optimization of the lattice deformation and the atomic position but the optimization of the atomic position leads to lower energy in both magnetic phases.

Fig. 3 Total energy vs c/a for F and AF2 of CoMnSb (F and AF of MnCuSb). The symbols $\bullet$ and $\circ$ ($\blacktriangle$ and $\triangle$) mean the results for F (AF2) (F (AF)). The points B and C show the ratio c/a which gives minimum energies before and after the optimization of atomic positions of Mn(II) and Sb for CoMnSb (Cu and Sb for MnCuSb). See text in detail.

Table 1 Volume of the unit cell (V) and lattice constants (a , c). The data are given at the points B and C in Fig. 3. The symbol Δ means $(F - AF2)/AF2 \times 100$ for CoMnSb and $(F - AF)/AF \times 100$ for MnCuSb. The lowest rows in CoMnSb and MnCuSb show the atomic position parameters, u and v (see Fig. 1).

CoMnSb	B			C		
	F	AF2	Δ (%)	F	AF2	Δ (%)
V ($\text{\AA}^3$)	94.903	95.496	-0.621	94.903	95.496	-0.621
a ($\text{\AA}$)	3.943	3.979	-0.900	3.979	4.005	-0.651
c ($\text{\AA}$)	6.104	6.032	+1.192	5.996	5.955	+0.685
c/a	1.548	1.516	+2.111	1.507	1.487	+1.345
u	0.710			0.738		
v	0.279			0.284		
MnCuSb	B			C		
	F	AF	Δ (%)	F	AF	Δ (%)
V ($\text{\AA}^3$)	97.897	97.749	+0.151	97.897	97.749	+0.151
a ($\text{\AA}$)	3.915	3.920	-0.134	3.919	3.930	-0.258
c ($\text{\AA}$)	6.389	6.362	+0.420	6.373	6.330	+0.671
c/a	1.632	1.623	+0.555	1.626	1.611	+0.931
u	0.710			0.722		
v	0.279			0.298		

In Table 1 we summarize the data such as the volume of the unit cell and lattice constants at the points B and C in Figs. 3(a) and 3(b). The atomic position parameters, u and v (see Fig. 1) are also listed in Table 1. In both of CoMnSb and MnCuSb, the change from AF2 (AF) to F at the point B is similar to that at the point C. The difference between CoMnSb and MnCuSb appears in the change of the volume of the unit cell (V) from AF2 (AF) to F, that is, the V shrinks from AF2 to F in CoMnSb but it expands from AF to F in MnCuSb. The change of lattice constants (a and c) and c/a is consistent with the experimental result for Mn_{1.8}Co_{0.2}Sb.³⁾

The calculated data for the magnetic moment of each atom in CoMnSb and MnCuSb are listed in Table 2, together with experimental data in Mn₂Sb and Mn_{1.9}Co_{0.1}Sb. Our previous calculated data in Mn₂Sb are shown in parentheses. (The absolute value of the magnetic moment on Sb is less than $0.06\mu_B$.) This table shows that the values of the magnetic moments of constituent atoms barely change from the point B to the point C except for the AF state in MnCuSb,

Table 2 Calculated magnetic moments on constituent atoms in CoMnSb and MnCuSb. The experimental data in Mn₂Sb and Mn_{1.9}Co_{0.1}Sb are also listed. Our calculate data for Mn₂Sb are shown in parentheses.

Magnetic moment, m/μ_B				
CoMnSb				
site	F (B)	AF2 (B)	F (C)	AF2 (C)
Co	0.85	1.00	1.08	1.08
Mn(II)	3.35	3.41	3.35	3.41
MnCuSb				
site	F (B)	AF (B)	F (C)	AF (C)
Mn(I)	-2.25	-2.17	-2.39	-2.33
Mn ₂ Sb		Mn _{1.9} Co _{0.1} Sb		
site	FR ¹⁾	FR ¹⁷⁾	AF1 ¹⁵⁾	
Mn(I)	-2.13	(-2.17)	-1.71	
Mn(II)	3.87	(3.39)	3.98	

that is, the values of the magnetic moments are not sensitive to the optimization of the atomic positions of Mn(II) and Sb.

The result that CoMnSb has the same magnetic moment on Mn(II), $3.4\mu_B$, as Mn₂Sb indicates that the magnetic moment on Mn(II) is not sensitive to the substitution of Co for Mn(I). This is consistent with experimental report.¹⁵⁾ Mn_{1.9}Co_{0.1}Sb has the almost same magnetic moment on Mn(II), $3.98\mu_B$, as Mn₂Sb ($3.87\mu_B$), irrespective of the fact that the magnetic moment on Mn(I) changes from $-2.13\mu_B$ on Mn(I) in Mn₂Sb to $-1.71\mu_B$ in Mn_{1.9}Co_{0.1}Sb.

If we estimate the magnetic moment on Mn(I) in Mn_{1.9}Co_{0.1}Sb from the data of CoMnSb, then we obtain the value of $-1.8\mu_B$. This is very close to the experimental one, $-1.71\mu_B$. This result indicates the Co atom occupies the site Mn(I) with magnetic moment $1\mu_B$.

For Mn_{1.82}Co_{0.18}Sb, it is reported that the electronic specific heat coefficient γ increases by $\approx 39\%$ at the critical field for the field induced AF-FR transition due to an increase in the density of states (DOS) at the Fermi energy.^{4,15)} Thus, we estimate DOS at the Fermi energy and γ for CoMnSb and MnCuSb, and shows results in Table 3. Here the γ can be derived from $D(E_F)$ using $\gamma = (1/3)\pi^2 D(E_F)k_B^2$ where k_B is the Boltzmann constant. This table shows that in both of CoMnSb and MnCuSb the DOS increases from AF2 (AF) to

Table 3 Density of states at the Fermi energy and electronic specific heat coefficient. The data are estimated at the points B and C in Fig. 3. The symbol Δ means $(F - AF2)/AF2 \times 100$ for CoMnSb and $(F - AF)/AF \times 100$ for MnCuSb.

DOS, $D/\text{states}\cdot\text{eV}^{-1}\cdot\text{f.u.}^{-1}\cdot\text{spin}^{-1}$ (Electronic specific heat coefficient, $\gamma/\text{mJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$)					
CoMnSb			MnCuSb		
	B	C		B	C
F	1.52 (7.17)	1.04 (4.90)	F	0.99 (4.66)	0.88 (4.16)
AF2	1.08 (5.08)	1.03 (4.87)	AF	0.69 (3.24)	0.82 (3.87)
Δ (%)	41	0.5	Δ (%)	44	7.3

F at the point B but the enhancement almost disappears at the point C. The experimental estimation of $\Delta \approx 39\%$ for $\text{Mn}_{1.82}\text{Co}_{0.18}\text{Sb}$ ^{4,15)} is very close to $\Delta = 41\%$ for CoMnSb at the point B (not at the point C). Further investigation is needed to clarify this point.

4. Conclusion

First-principles band-structure calculations have been carried out the hypothetical case of $x = 1$ in $\text{Mn}_{2-x}\text{X}_x\text{Sb}$ ($X = \text{Co}$ and Cu) for several magnetic states. The calculated total energy indicates that the Co atom prefers the site Mn(I) to the site Mn(II) in a magnetic state. This is consistent with the neutron diffraction experiment.¹⁵⁾ In the case of Cu, the Cu atom prefers the site Mn(II) to the site Mn(I) in all magnetic states. To confirm this calculated result, we hope for neutron diffraction measurements on Cu substituted Mn_2Sb .

For CoMnSb, the change of lattice constants (a and c) and c/a from AF2 to F is in good agreement with experimental trends.³⁾ Further, the magnetic moment on Mn(I) in $\text{Mn}_{1.9}\text{Co}_{0.1}\text{Sb}$ estimated from our data of CoMnSb is very close to the experimental one.¹⁵⁾

Our results indicate that the optimization of the ratio c/a is crucial to determine the most stable magnetic state and that the optimization of the atomic positions of the sites Mn(II) and Sb is also crucial.

In this study, we have only dealt with the case of $x = 1$. In order to compare with the experimental results such as $\text{Mn}_{1.8}\text{Co}_{0.2}\text{Sb}$,⁵⁾ $\text{Mn}_{1.9}\text{Cu}_{0.1}\text{Sb}$ ^{9,19)} etc., it is necessary to deal

with the case of a low amount of substitution of Co or Cu. First-principles calculations for this purpose are in progress.

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