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Crystal structure and electronic properties of CrAlGe

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ABSTRACT

First-principles total energy calculations indicate that CrAlGe prefers a $TiSi_2$-type structure to a Cu_2 Sb-type one and that its magnetic ground state is ferromagnetic. These predictions are in agreement with experimental observation. As a result of consideration of the disorder between Al and Ge, it is found that the magnetic moment on Cr locally varies from site to site, but a magnetization per formula unit is almost constant. The analysis of electronic structure indicates a possibility that a ferromagnetic $CrAl_{2-x}Ge_x$ ($0 \leq x \leq 1$) becomes half-metallic and that this nature is impervious to the disorder between Al and Ge.

1. Introduction

It is well known that the ternary compound MnAlGe is a ferromagnet ($T_C = 518$ K) with the Cu_2 Sb-type structure [1,2]. The Mn atoms form a based-centered tetragonal sublattice and two adjacent basal planes are separated by Al and Ge atoms (Fig. 1). The distance between Mn atoms along *c* axis (5.9 Å) is much larger than that in the basal plane (2.8 Å). Thus, this compound is a pseudo-two-dimensional magnetic material. Furthermore, this compound has a large uniaxial magnetic anisotropic constant (5.3 Merg/cm^{-3} at room temperature) [1]. Due to these characteristics, MnAlGe has attracted much attention and the following investigations are reported.

Motizuki et al. showed that the Fermi surface of MnAlGe has a strong two-dimensional character from ab-initio calculations [3]. Shibata et al. estimated the intra-layer and inter-layer exchange constants from the temperature dependence of the resonance frequency of Mn^{55} nuclei [4]. Mizukami et al. investigated several magnetic properties of MnAlGe epitaxial film, such as perpendicular magnetic anisotropy constant, saturation magnetization, magnetization precession etc [5]. There are several reports about substitution effects of Cr or Fe on the Curie temperature for MnAlGe [6–8].

Quite recently, a perfect substitution of Cr for MnAlGe, that is CrAlGe, were synthesized and its structural and magnetic properties was investigated by X-ray diffraction and magnetization measurements [9,10]. It was found that the ternary compound CrAlGe does not have a tetragonal Cu_2 Sb-type structure but has an orthorhombic $TiSi_2$-type one, where MnAlGe and Mn_{1-x} Cr_xAlGe ($x \leq 0.2$) has a tetragonal Cu_2 Sb-type one [8]. In this paper, the structural and magnetic properties of CrAlGe are examined from first-principles electronic calculations to gain deeper insight into this material.

2. Approach

The analysis of X-ray diffraction pattern suggested that CrAlGe has a $TiSi_2$-type cell with a space group of *Fddd* (No. 70) [11], where the Cr atom occupies the 8a:(0, 0, 0) and the Al and Ge atoms occupy the 16 g:(0, 0, z) with an occupancy of 0.5, respectively [9]. Although this indicates that the Al and Ge atoms occupy randomly the site of the cell in this study, we adopted the following simple cell with a space group of *C*222 (No. 21), where the Cr atoms occupy the 2a, 2c, and 4k sites, and the Al (Ge) atoms occupy the 4i and 4k' (4j and 4k") sites (see Fig. 1). In the latter section, we will discuss the effect of the atomic disorder between Al and Ge. In addition to a $TiSi_2$-type cell, a Cu_2 Sb-type cell with a space group of *P*4/*nmm* (No. 129) is also shown in Fig. 1, where the Cr, Al, and Ge atoms occupy the 2a, 2c, and 2c sites, respectively. In this study, we used the

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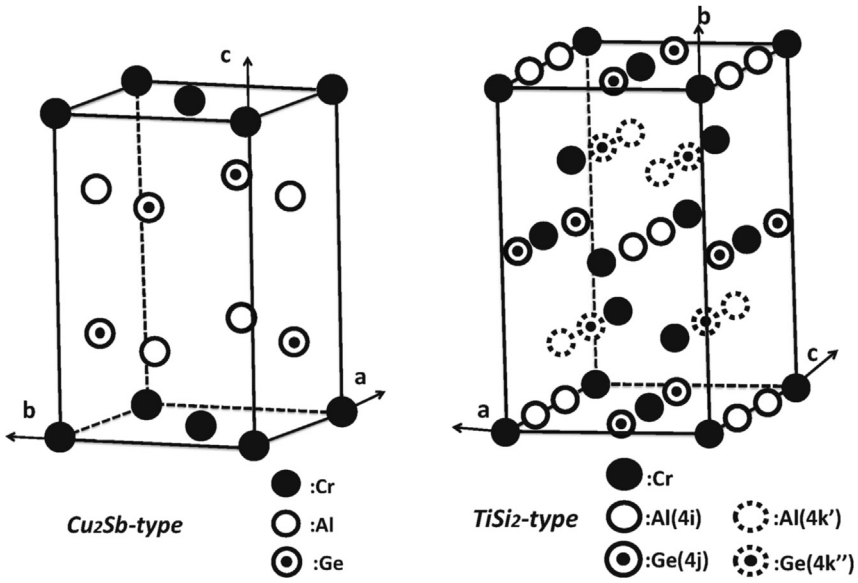

Fig. 1. Crystal structure of Cu_2 Sb and $TiSi_2$.

following values listed in Ref. [9] for the lattice constants of the cell and the atomic positions for the Al and Ge atoms: a=b= 3.913 Å, c= 5.933 Å, z= 0.273 (Al), z= 0.720 (Ge) for Cu_2 Sb-type; a= 4.770 Å, b= 8.725 Å, c= 8.254 Å, z= 0.3365 for $TiSi_2$-type. The atomic sites in three cells (Nos. 21, 70, 129) are summarized in Table 1.

First-principles electronic calculations are performed using the full-potential linearized augmented plane wave (FLAPW) method [12]. The generalized gradient approximation of Perdew *et al.* [13] is used for the exchange-correlation potential. The plane wave cutoff is 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, we used the values 2.45 a.u. for Cr and 2.17 a.u. for Al and Ge.

3. Results and discussions

3.1. Stable structure and magnetic properties

First, we consider a ground-state structure of CrAlGe, which has the lowest total energy. To this purpose, we estimated total energies of two structures with a ferromagnetic state, $TiSi_2$-type and Cu_2 Sb-type as shown in Fig. 1, where the former is experimentally suggested in Ref. [9], and the latter is well known to be the structure of MnAlGe. The result listed in Table 2 shows that the ferromagnetic $TiSi_2$-type structure has a lower total energy than the ferromagnetic Cu_2 Sb-type one. On the other hand, the result of MnAlGe shows that the ferromagnetic Cu_2 Sb-type structure has a lower total energy than the ferromagnetic $TiSi_2$-type one. These results are consistent with the experimental ones.

Concerning the magnetic properties, the magnetization per formula unit M(μ_B/f.u.), is reported to be 1.69 μ_B for MnAlGe [7]. This is in good agreement with our result, 1.74 μ_B. For magnetic moments of constituent atoms, the agreement between our results and previous ones is very good. On the other hand, the experimental value of M is 0.41 μ_B for CrAlGe [9], which is in bad agreement with our result, 1.00 μ_B.

To clarify this discrepancy, we also calculated an electronic structure of a ferrimagnetic $TiSi_2$-type structure. As listed in Table 2, our result of M is 0.07 μ_B. This value is also in bad agreement with the experimental one (0.41 μ_B). The total energy is a little higher than the ferromagnetic state (see Table 2), though it is lower than the ferromagnetic Cu_2 Sb-type structure. Simply, if ferromagnetic and ferrimagnetic states coexist with equal probability, then the

Table 1
Atomic sites in a cell with a space group, No 21, 70, or 129.

No. 21	2a	2c	4k	4i	4j
	(0, 0, 0)	(1/2, 0, 1/2)	(1/4, 1/4, z)	(0, 0, z)	(0, 1/2, z)
			(3/4, 1/4, −z)	(0, 0, -z)	(0, 1/2, −z)
No. 70	8a	16g			
	(0, 0, 0)	(0, 0, z)	(1/4, 1/4, z+1/4)		
	(1/4, 1/4, 1/4)	(0, 0, -z)	(1/4, 1/4, −z+1/4)		
No. 129	2a	2c			
	(0, 0, 0)	(0, 1/2, z)			
	(1/2, 1/2, 0)	(1/2, 0, −z)			

Table 2
Total energies (E_{tot}) and magnetic moments (in unit of μ_B) for Cu_2Sb and $TiSi_2$ structures. The lowest E_{tot} is taken to be 0 eV/atom. The previously reported data [3] are listed in the 6th column. The last column shows atomic positions in the $TiSi_2$ structure.

	CrAlGe			MnAlGe				
	Cu_2Sb	$TiSi_2$		Cu_2Sb		$TiSi_2$		
	Ferro	Ferro	Ferri	Ferro		Ferro	Ferri	
E_{tot}	0.04	0	0.02	0		0.10	0.05	
Cr/Mn	1.46	0.96	1.33	1.82	(1.90)	2.00	1.60	(2a)
		1.16	0.98			1.93	1.83	(2c)
		1.19	−0.99			2.03	−1.72	(4k)
Al	−0.01	−0.04	−0.00	−0.02	(−0.02)	−0.08	−0.00	(4i)
		−0.04	−0.01			−0.08	+0.00	(4k')
Ge	−0.05	−0.05	−0.01	−0.05	(−0.06)	−0.07	+0.00	(4j)
		−0.06	+0.01			−0.07	+0.00	(4k")
f.u.	1.41	1.00	0.07	1.74	(1.81)	1.69	+0.00	

Table 3
Starting spin magnetic moments of three different Cr atoms. The symbols, "+", "−", "0" mean that each value of the moments is positive, negative, and zero.

	1	2	3	4	5	6	7	8
Cr (2a)	+	−	+	−	+	−	0	0
Cr (2c)	−	+	+	+	0	0	+	−
Cr (4k)	+	+	0	0	+	+	+	+