Magnetic properties of weak itinerant electron ferromagnet CrAlGe

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Abstract. Magnetic properties for CrAlGe with an orthorhombic TiSi₂-type structure were investigated under ambient pressure and hydrostatic pressure. CrAlGe is ferromagnetic at the temperature below Curie temperature \(T_C\) of 80 K and has the spontaneous magnetic moment \(p_s\) of 0.41 \(\mu_B/\text{f.u.}\) at 5 K and the effective moment \(p_{\text{eff}}\) of 1.89 \(\mu_B/\text{f.u.}\) under ambient pressure. For the temperature \(T\) below 30 K, the decrease in \(p_s(T)/p_s(5\text{K})^2\) was proportional to \(T^2\). However, the decrease in \(p_s(T)/p_s(5\text{K})^2\) was proportional to \(T^{4/3}\) for \(30 \text{K} < T < T_C\). The ratio \(p_{\text{eff}}/p_s\) was consistent with the theoretical curve of the generalized Rhodes-Wohlfarth plot (Takahashi plot). Obtained results suggest that CrAlGe is a weak itinerant electron ferromagnet. By applying a high pressure of 1 GPa, \(T_C\) decreased by approximately 10 K.

1. Introduction

It was reported that ferromagnetic MnAlGe with the tetragonal Cu₂Sb-type structure is one of the promising candidates for the application of high-density memory and spintronics devices [1]. In this crystal structure, as shown in Fig. 1(a), Mn atoms occupy the 2a-site that locates two-dimensionally at \(c\)-plane, resulting a large uniaxial magnetic anisotropy of about \(10^6 \text{ J/m}^3\) along \(c\)-axis [2-4]. The spontaneous magnetic moment \(p_s\) is 1.70 \(\mu_B/\text{f.u.}\) and the Curie temperature \(T_C\) is 518 K [2-4]. It was reported that Cr substitution for Mn in Mn₁₋ₓCrₓAlGe (\(x \leq 0.2\)) with the Cu₂Sb-type structure enhanced \(p_s\) and \(T_C\) [3, 4]. However, it has been unclear why the magnetic properties improve by Cr substitution for Mn in Mn₁₋ₓCrₓAlGe. In order to understand the Cr substitution effect on the magnetic properties of Mn₁₋ₓCrₓAlGe, it is important to study the fundamental properties of CrAlGe as well as Mn₁₋ₓCrₓAlGe systematically. However, the structural and magnetic properties of CrAlGe had been not characterized in detail, whereas ternary phase diagram of Cr-Al-Ge at 673 K shows existence of CrAlGe phase as an equilibrium state [5, 6]. Quite recently, Yoshinaga et al. suggested that CrAlGe has not the Cu₂Sb-type but the orthorhombic TiSi₂-type structure, as shown in Fig. 1(b). Furthermore, they reported that CrAlGe with the TiSi₂-type structure is a weak itinerant electron magnet [7].

In this paper, the experimental results on the magnetic properties of polycrystalline CrAlGe is presented. The magnetic data suggest that the Curie temperature and the magnetic moment of CrAlGe are suppressed by applying high pressure. The results obtained under ambient pressure are discussed based on Takahashi’s spin fluctuation theory.
2. Experimental procedure
Polycrystalline CrAlGe was prepared by induction melting of a mixture composed from appropriate amounts of pure elements (Cr, 99.99%; Al, 99.99%; Ge, 99.99%). The as-cast sample was annealed at 1073 K for 1 day and then quenched into iced water. Powder x-ray diffraction (XRD) experiments were carried out using Cu-Kα radiation at room temperature. For determining the crystal structure and the x-ray reflection indices, the observed diffraction patterns were analyzed by comparison with calculated patterns using a Powder Cell program [8]. The magnetization $M$ measurements under ambient pressure were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) for $5 \leq T \leq 390$ K and magnetic fields $H$ up to 5 T at IMR. The magnetization under a hydrostatic pressure of 1 GPa was measured using the SQUID magnetometer and a clamp-type piston cylinder pressure cell at ISSP.

3. Results and discussion
Figure 2 shows the experimental XRD pattern (a) and the calculated XRD pattern for the orthorhombic TiSi$_2$-type structure (b) [7]. The parameters used for the calculated XRD pattern of the TiSi$_2$-type structure are listed in Table 1. In this study, we assumed that Cr atom occupied the 8a-site, and both atoms of Al and Ge were at the 16f-site by the same occupancy in the TiSi$_2$-type structure. As seen in this Fig. 2, the calculated XRD is in good agreement with the experimental XRD pattern (a). All the diffraction peaks were indexed as a single phase of the TiSi$_2$-type structure. The lattice parameters were determined to be $a = 0.4770$ nm, $b = 0.8254$ nm and $c = 0.8725$ nm.

Figure 3 shows the magnetization curves in magnetic fields up to 5 T (a) and the isothermal $M^2$ vs.
Table 1. Used parameters of TiSi$_2$-type structures for CrAlGe [7].

| Atom | Wyckoff | x (nm) | y (nm) | z (nm) | Occupancy |
|------|---------|--------|--------|--------|-----------|
| Cr   | 8a      | 0      | 0      | 0      | 1         |
| Al   | 16f     | 0      | 0.3365 | 0      | 0.5       |
| Ge   | 16f     | 0      | 0.3365 | 0      | 0.5       |

$H/M$ plots (Arrott plot) (b) the at several temperatures. The magnetization curves for $T \leq 80$ K show the ferromagnetic behaviour. The spontaneous magnetic moment $p_s$ at 5 K was determined to be 0.41 $\mu_B$/f.u. (0.41 $\mu_B$/Cr) by Arrott plot. We estimated $p_s^2$ at several temperatures from the Arrott plot analysis for $T \leq 90$ K, as shown in Fig. 3 (b). The Curie temperature $T_C$ was determined to be 80 K as the temperature at which $p_s^2$ passes the origin, as shown in Fig. 4.

Figure 4 shows the temperature dependence of the reciprocal susceptibility $1/\chi$ ($1/\chi$ vs. $T$ plot) for $T > 150$ K [7]. The susceptibility $\chi$ was deduced from the temperature dependence of the magnetic moment in a magnetic field of 5 T. The observed $1/\chi$ vs. $T$ plot is well expressed by the Curie-Weiss

Figure 3. Magnetization curves (a) and $M^2$ vs. $H/M$ plots (Arrott plot) (b) of CrAlGe at several temperatures. Spontaneous magnetic moment $p_s$ was determined by the linear extrapolation to $H/M = 0$ for the $M^2$ vs. $H/M$ plots.

Figure 4. $p_s^2$ vs. $T$ plot for $60 \leq T \leq 90$ K. The solid line is least-squares fits to $p_s^2$. 

![Figure 3](image1.png)

![Figure 4](image2.png)
law, and the paramagnetic Curie temperature \( \theta_p \) and the effective magnetic moment \( p_{\text{eff}} \) were determined to be 95 K and 1.89 \( \mu_B/\text{Cr} \), respectively.

The Curie-Weiss law is concluded from the Weiss theory (called localized electron model) which assumes a fixed magnetic moment per atom [9]. The effective magnetic moment \( p_{\text{eff}} \) deduced from the Curie constant and the spontaneous magnetic moment per atom of the ground state \( p_s \) have the following relation:

\[
p^2_{\text{eff}} = g^2 S(S+1), \quad p_s = gS,
\]

where \( g \) and \( S \) are \( g \)-factor and the spin angular momentum, respectively. It is well known that the experimental results on many magnetic metals and alloys, which are not represented based on the localized electron model, also show the Curie-Weiss low. In addition, the value of \( p_c \) is calculated from \( p_{\text{eff}} \) using \( p_{\text{eff}}^2 = p_s(p_s+2) \), and in general, \( p_c/p_s \) for ferromagnetic metals with high Curie temperature is nearly unity [9]. On the other hand, \( p_c/p_s \) for weak itinerant-electron-ferromagnets (WIEF) with low Curie temperature becomes very large [9].

In this study, it was found that CrAlGe had magnetic properties with \( T_C = 80 \) K, \( \theta_p = 95 \) K, \( p_c = 0.41 \mu_B/\text{Cr} \) at 5 K and \( p_{\text{eff}} = 1.89 \mu_B/\text{Cr} \). That is, \( p_c/p_s \) is larger than unity, indicating that CrAlGe is one of WIEF. In order to clarify the origin of the magnetic properties of CrAlGe, it is important to analyze the magnetic data based on Takahashi’s spin fluctuation theory for WIEF [10-12]. Therefore, we estimated the parameters \( T_0 \) and \( T_\lambda \) which are characterized by the energy width of the dynamical spin fluctuation spectrum and the dispersion of the static magnetic susceptibility in the wave vector space, respectively. The quantitative values of \( T_0 \) and \( T_\lambda \) can be deduced from the experimental data of the Arrott plot on the basis of Takahashi’s theory. The analysis method for CrAlGe was presented in the previous paper in detail [7]. These parameters were estimated to be \( T_0 = 1.0 \times 10^3 \) K, \( T_\lambda = 4.0 \times 10^3 \) K and \( \eta = (T_C/T_0)^{1/3} = 0.43 \) by the magnetization process (Arrott plot) at 5 K. These values are comparable to those of typical WIEF such as MnSi, ZrZn\(_2\), Ni\(_3\)Al, (Fe, Co)Si, etc. [12].

| \( p_s (\mu_B) \) | \( p_{\text{eff}} (\mu_B) \) | \( p_c (\mu_B) \) | \( p_{\text{eff}}/p_s \) | \( p_c/p_s \) | \( T_C (\text{K}) \) | \( T_0 (\text{K}) \) | \( T_C/T_0 \) |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| CrAlGe         | 0.413           | 1.89            | 1.13            | 4.58            | 2.75            | 80              | 1028            | 0.078           |

**Figure 5.** Temperature dependence of the reciprocal susceptibility \( 1/\chi \) [7].
The obtained $\eta$ (= 0.43) of CrAlGe was small, which is consistent with Takahashi's theory for WIFE [12]. In this case, according to Takahashi's theory, $[p_s(T)/p_s(0)]^2$ follows the $T^{4/3}$-dependence in the temperature range below $T_c$ except for very low temperature at which the $T^2$-dependence is observed. In Fig. 6(a) and (b), $[p_s(T)/p_s(5K)]^2$ vs. $T^2$ and $T^{4/3}$ plots are shown, respectively. As seen in Fig. 6(a) and (b), $[p_s(T)/p_s(0)]^2$ shows a $T^2$-dependence at low temperature side and a $T^{4/3}$-dependence in the wide temperature range below $T_c$. By using the low temperature data for $5 \leq T \leq 30$ K, $T_A$ is estimated to be $3.8 \times 10^4$ K, which is in good agreement with the value $(4.0 \times 10^4$ K) determined by the magnetization process at 5 K, as mentioned above. Consequently, the magnetization process of CrAlGe at 5 K and the temperature dependence of the spontaneous magnetic moment are consistent with Takahashi's theory. The obtained values of the parameters are summarized in Table 2.

It is reported that the small amount of Cr substitution for Mn atom of MnAlGe with the tetragonal Cu$_2$Sb-type structure enhanced $p_s$ and $T_c$ [3, 4]. However, $p_s$ (= 0.413 $\mu_B$/f.u.) and $T_c$ (= 80 K) of fully substituted compound CrAlGe with the orthorhombic TiSi$_2$-type were much lower than those ($p_s$ = 1.70 $\mu_B$/f.u. and $T_c$ = 518 K) of MnAlGe with the tetragonal. This is probably due to the change of the crystal structure. That is, it is supposed that the unique properties of Mn$_{13}$Cr$_{17}$Al$_6$Ge$_{20}$ originate from the magnetic characters of Mn and Cr atoms located two-dimensionally in $c$-plane of the tetragonal Cu$_2$Sb-type structure.

It is well known that Rhodes-Wohlfarth plot ($p_s/p_s$ vs. $T_c$ plot) is able to categorize the ferromagnets which are the localized electron model and the itinerant electron model [13]. In addition to this, recently, $p_{lo}/p_s$ vs. $T_c/T_0$ plot (Takahashi plot) was also proposed by Takahashi.

Figure 7 shows the Rhodes-Wohlfarth plot (a) and the Takahashi plot (b), respectively. The solid curve in Fig 8 (b) is the theoretical curve. As seen in Fig. 8 (a) and (b), CrAlGe is not a localized electron ferromagnet but WIEF, and the position of CrAlGe is in agreement with the curve in the Takahashi plot (b), compared with the curve in the Rhodes-Wohlfarth plot (a). This result suggests that the magnetic properties of CrAlGe depend strongly on the parameters proposed in Takahashi's spin fluctuation theory. In other words, the magnetic properties of CrAlGe originate the quantum spin fluctuation. As seen in Fig. 8 (b), however, it seems that the position deduced from our experimental results for CrAlGe is slightly deviated from the theoretical curve in Takahashi plot. This is may be due to the magnetic anisotropy of the sample. In the case of WIEF with the magnetic anisotropy, the parameters $T_0$ and $T_A$ have to be modified slightly.

![Figure 6](image-url)
Finally, we present the pressure effect on the magnetic properties of CrAlGe. Figure 8 shows the temperature dependence of the magnetization ($M$-$T$ curve) at a magnetic field of 1 T under 0.1 MPa (ambient pressure) and 1 GPa. In these measurements, $T_C$ was defined as the peak of the temperature derivative of $M$-$T$ curves ($dM/dT$). As seen in Fig. 8, $M$ at 5 K and $T_C$ decreased by about 5% and 10 K, respectively, when a high pressure of 1 GPa was applied. As discussed above, the magnetic properties of CrAlGe originate from the nature of WIEF. When a hydrostatic pressure was applied to CrAlGe, the cell volume decreases. If the electronic band structure of CrAlGe represents the magnetic properties at 0 K (lowest temperature), this volume contraction leads the increase of the bandwidth and the density of states in the vicinity of the Fermi level. This change of the band structure probably causes the enhancement of the spin fluctuation and the decrease of $M$ and $T_C$.

Figure 8. Temperature dependence of the magnetization at a magnetic field of 1 T under 0.1 MPa and 1 GPa.

4. Conclusions
CrAlGe has an orthorhombic TiSi$_2$-type structure with the lattice parameters of $a = 0.4770$ nm, $b = 0.8254$ nm and $c = 0.8725$ nm at room temperature. The spontaneous magnetic moment, effective
magnetic moment and Curie temperature of CrAlGe were determined to be $p_s = 0.41 \mu_B$/Cr at 5 K, $p_{\text{eff}} = 1.89 \mu_B$/Cr and $T_C = 80$ K, respectively. By analyzing magnetic data, the parameters $T_0$ and $T_A$ were estimated to be $1.0 \times 10^3$K and $4.0 \times 10^3$K, respectively. The ratio $p_{\text{eff}}/p_s$ was consistent with the theoretical curve of the generalized Rhodes-Wohlfarth plot (Takahashi plot: $p_{\text{eff}}/p_s$ vs. $T_C/T_0$ plot). Obtained results suggested that CrAlGe is a weak itinerant electron ferromagnet expressed well by Takahashi’s spin fluctuation theory. It was found that the magnetic moment and the Curie temperature decreased by applying high pressure.

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