Magnetic and Thermodynamic Properties of FeCr$_2$Se$_4$

Masakazu Ito$^1$, Takuro Ogawa$^1$, Sinpei Urakawa$^1$, Naotoshi Kado$^1$, and Norio Terada$^2$

$^1$Department of Physics and Astronomy, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan
$^2$Department of Electrical and Electronic Engineering, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan
E-mail: showa@sci.kagishima-u.ac.jp (M. Ito)

Abstract. Magnetic and thermodynamic properties of a selenide FeCr$_2$Se$_4$ have been investigated. Electric resistivity $\rho(T)$ shows insulator-type temperature dependence defined as $\partial \rho(T)/\partial T < 0$ in the range $2.5 < T < 300$ K. At $T_N \sim 200$ K, $\rho(T)$ has an inflection point associated with antiferromagnetic order. A cusp-like anomaly appears at $T_N$ in temperature dependence of dc-magnetic susceptibility $\chi(T)$. An effective magnetic moment $\mu_{eff} = 7.66$ is obtained from Curie constant $C$ and this value is close to the one ($\mu_{eff} = 7.35$) calculated from coupling of the Curie constant for Fe$^{2+}$ (spin angular momentum $S = 2$) and Cr$^{3+}$ ($S = 3/2$). At $T = 75$ K, $\chi(T)$ increases abruptly with decreasing $T$. Below 20 K, between the values $\chi(T)$ of zero-field-cooled (ZFC) and field-cooled (FC) show the irreversibility, and $\chi(T)$ of ZFC has a broad peak at 5 K. On the other hand, in the $T$ dependence of specific heat $C_P(T)$ in the range $1.5K < T < T_N$, although $\lambda$-type anomaly appears at $T_N$, an anomaly which indicates the additional magnetic phase transition is not observed.

1. Introduction

Chalcogenides with a generic formula $AB_2X_4$ ($A, B$: transition metal, $X$: chalcogen) have attracted the attention recently, because some of them show interesting physical properties suitable for application such as a colossal magnetoresistance (CMR). A ferrimagnetic semiconductor FeCr$_2$S$_4$ is one of them[1]. The FeCr$_2$S$_4$ compound has a cubic spinel structure with a space group $Fd\bar{3}m$. Meanwhile, an iron chromium selenide FeCr$_2$Se$_4$ has the Cr$_3$S$_4$-type monoclinic structure ($I2/m$) and shows the semiconductive transport property[2]. Temperature $T$ dependence of magnetization $M(T)$ has a cusp-type anomaly associated with an antiferromagnetic ordering at Néel temperature $T_N = 218$ K. In addition this, $M(T)$ shows unusual increasing below 75 K with decreasing $T$, namely, the ferrimagnetic-like behaviour appears in the low temperature range [3, 4]. Spin-glass like irreversibility behaviour between the magnetization of zero-field-cooled (ZFC) and field-cooled (FC) below $T_N$ has also been reported[5].

To investigate a magnetic excitation of FeCr$_2$Se$_4$, we have measured electric resistivity $\rho(T)$, dc-magnetic susceptibility $\chi(T)$, and specific heat $C_P(T)$. 

Published under licence by IOP Publishing Ltd
2. Experimental
The polycrystalline specimen of FeCr$_2$Se$_4$ was prepared by a direct solid-state reaction. High purity elements of Fe, Cr and Se were mixed in stoichiometric ratio and reacted in a quartz tube at 1000 °C for seven days. The powder specimen was reground, pressed into a pellet and sintered at 1000 °C for two days. Electric resistivity ρ(T) was measured by a conventional four-probe DC technique. Temperature T dependence of dc-magnetic susceptibility χ(T) were measured using a Quantum Design MPMS SQUID magnetometer. Specific heat $C_P$ in the temperature range between 1.5 and 250 K were measured using a home-built calorimeter, which is operated by an adiabatic heat pulse method[6].

3. Results
Temperature T dependence of electric resistivity ρ(T) of FeCr$_2$Se$_4$ in 2.5 < T < 300 K is shown in Fig. 1. ρ(T) shows semiconductive T dependence, which is determined as $\partial \rho / \partial T < 0$, in the whole temperature range. A kink-type anomaly appears at Néel temperature $T_N$ ~ 200 K. In 100 K < T < $T_N$ and $T_N$ < 300 K, ρ(T) obeys an activation-type definition, ρ(T) ∝ exp($-\Delta / k_B T$), where $k_B$ and $\Delta$ are Boltzmann constant and an activation energy, respectively. With decreasing T, the value of $\Delta / k_B$ change from 145 to 28 K as shown in an inset of Fig. 1. In T < 100 K, ρ(T) can not be described by the simple activation-type definition.

![Figure 1. Temperature T dependence of electric resistivity ρ(T) of FeCr$_2$Se$_4$. The inset is ln ρ(T) v. s. 1/T plot. Solid lines show an activation-type temperature dependence.](image)

Figure 2 (a) shows T dependence of dc-magnetic susceptibility χ(T) of FeCr$_2$Se$_4$ in the temperature range between 2.0 and 300 K. As reported previously, a cusp-like anomaly appears at $T_N$ = 200 K [3, 4, 5]. Although the system is in the antiferromagnetic ordered phase, with decreasing T, χ(T) increases rapidly at around 75 K. This makes expect the ferro- or ferrimagnetic phase transition. As shown by a solid line in the inset of Fig. 2, inverse susceptibility $\chi^{-1}(T)$ above $T_N$ can be fitted with the equation of mean-field theory for antiferro- and ferrimagnet,

$$\chi^{-1}(T) = 1/\chi_0 + (T^2 - a_0)/(C \cdot T - a_1),$$  (1)

here C is the Curie constant, and $a_0$, $a_1$ and $\chi_0$ are fitting parameters. The estimated value of effective magnetic moment $\mu_{eff}$ from C of fit result is 7.66$\mu_B$, here, $\mu_B$ is the Bohr magneton. This value is close to the one as considering the coupling of Fe$^{2+}$ (spin-angular momentum: $S_{Fe} = 2$ ) and Cr$^{3+}$ ( $S_{Cr} = 3/2$ ), $g\mu_B\sqrt{S_{Fe}(S_{Fe} + 1) + 2S_{Cr}(S_{Cr} + 1)} = 7.35\mu_B$ (here, g is a g-factor). As shown in Fig. 2(b), in T ≤ 25 K, χ(T) has the irreversibility between the values

Figure 2 (a) shows T dependence of dc-magnetic susceptibility χ(T) of FeCr$_2$Se$_4$ in the temperature range between 2.0 and 300 K. As reported previously, a cusp-like anomaly appears at $T_N$ = 200 K [3, 4, 5]. Although the system is in the antiferromagnetic ordered phase, with decreasing T, χ(T) increases rapidly at around 75 K. This makes expect the ferro- or ferrimagnetic phase transition. As shown by a solid line in the inset of Fig. 2, inverse susceptibility $\chi^{-1}(T)$ above $T_N$ can be fitted with the equation of mean-field theory for antiferro- and ferrimagnet,

$$\chi^{-1}(T) = 1/\chi_0 + (T^2 - a_0)/(C \cdot T - a_1),$$  (1)

here C is the Curie constant, and $a_0$, $a_1$ and $\chi_0$ are fitting parameters. The estimated value of effective magnetic moment $\mu_{eff}$ from C of fit result is 7.66$\mu_B$, here, $\mu_B$ is the Bohr magneton. This value is close to the one as considering the coupling of Fe$^{2+}$ (spin-angular momentum: $S_{Fe} = 2$ ) and Cr$^{3+}$ ( $S_{Cr} = 3/2$ ), $g\mu_B\sqrt{S_{Fe}(S_{Fe} + 1) + 2S_{Cr}(S_{Cr} + 1)} = 7.35\mu_B$ (here, g is a g-factor). As shown in Fig. 2(b), in T ≤ 25 K, χ(T) has the irreversibility between the values
of ZFC and FC procedures. The broad peak appears in $\chi(T)$ of ZFC at around 5 K. These magnetic properties are characteristics of spin-glass freezing.

![Graph](image)

**Figure 2.** (a) Temperature $T$ dependence of dc-magnetic susceptibility $\chi(T)$ of FeCr$_2$Se$_4$. The measurement was carried out in magnetic field $H = 5$ kOe. The inset shows inverse susceptibility $\chi^{-1}(T)$. The solid line is the best fit by the mean-field theory for the anti- and ferrimagnet. (b) The expanded plot of $\chi(T)$ in $2.0 < T < 25$ K.

Figure 3 shows $T$ dependence of specific heat $C_p(T)$ of FeCr$_2$Se$_4$ in $1.5 < T < 250$ K. At $T_N$, $C_p(T)$ shows small $\lambda$-type anomaly. In lower-temperature range, however, no anomaly indicating the additional magnetic phase transition is observed, even at $\chi(T)$ shows the rapid increase ($T \sim 75$ K ) and the broad peak in ZFC $\chi(T)$ ($T \sim 5$ K ). As shown in the inset of Fig. 3, $C_p(T)$ in $T < 20$K can be reproduced by the Debye-$T^3$ law, $C_p(T) \sim \beta T^3$, where, $\beta$ is a coefficient which is related to the lattice specific heat. This means that the low-$T$ range $C_p(T)$ is contributed from only the lattice part, and magnetic entropy released this temperature range is very small. Debye temperature $\theta_D = 261$ K is obtained from the relation $\beta = 12\pi^4 n N_A k_B / 5 \theta_D^5$, where $n$ is the number of atoms ( $n = 7$ in this system ), $N_A$ is Avogadro’s number, and $k_B$ is Boltzman’s constant.

4. Discussion

Because the magnetic excitation give a large influence on the temperature dependence of specific heat, it is unusual that only the lattice part contributes to the low-$T$ range $C_p(T)$ of FeCr$_2$Se$_4$, in spite of $\chi(T)$ shows the rapid increase and the irreversibility. Our results of specific heat possibly suggest the following things. Firstly, the ferrimagnetic like increase of $\chi(T)$ at 75 K
Figure 3. Specific heat as the function of $T$, $C_p(T)$, of FeCr$_2$Se$_4$. The inset is plot of $C_p(T)/T$ v.s. $T$. The solid line shows Debye-$T^3$ law.

does not come from the reduction of the thermal fluctuation of the spin moments on the Fe$^{2+}$ and Cr$^{3+}$ sub lattice. If the system has the large thermal magnetic fluctuation in the low-temperature range, $C_p(T)$ should have the large contribution from the magnetic part and does not obey the Debye-$T^3$ law any more. The increasing of $\chi(T)$ at 75 K probably due to the gradually changing an angle between the spin moments. Secondly, origin of the spin glass like irreversibility and the broad peak of $\chi(T)$ in low-$T$ is not the spin-glass freezing. In general, at spin-glass freezing temperature, $C_p(T)$ shows broad peak. In our result, however, any anomaly was not observed in the low-$T$ range. The irreversibility and broad-peak anomaly probably come from magnetic-domain rearrangement as seen in the spinel FeCr$_2$Se$_4$[7].

5. Conclusion
We investigated the magnetic and thermodynamic properties of FeCr$_2$Se$_4$. Dc-magnetic susceptibility $\chi(T)$ shows rapid enhancement at around 75 K, and broad peak in zero-field-cool process of $\chi(T)$ at 5 K. Because low-temperature specific heat $C_p(T)$ can be reproduced by just the lattice contribution, the origin of anomalies in $\chi(T)$ is not magnetic order or spin-glass freezing.

Acknowledgement
This work was supported by KAKENHI(Grant No. 23540393) from Japan Society for the Promotion of Science(JSPS).

References
[1] Ramirez A P, Cava R J and Krajewski J 1997 Nature (London) 386 156
[2] Valiev M, Kerimov I G, Babaev S K and Namazov Z M 1975 Inorg. Mater. 11 176
[3] Snyder G J, Caillat T and Fleurial J-P 2000 Phys. Rev. B 62 10185
[4] Kang J H, Kim S J, Lee B W and Kim C S 2006 J. Appl. Phys. 99 08F714.
[5] Goya G F and Sagredo V 2003 Solid State Commun. 125 247
[6] Ito M, Hisamatsu T, Rokkaku T, Shigeta I, Manaka H, Terada N and Hiroi M 2010 Phys. Rev. B 82 0244061
[7] Yang Z R, Tan S and Zhang Y H Appl. Phys. Lett. 79 (2001) 3645