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Dual irreversible behavior of temperature dependence of magnetization in the spinel-type $Cu_{1-x}Ag_xCrSnS_4$

Shoichi Nagata*, Takahiro Ishikawa, Shuji Ebisu

Department of Materials Science and Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan

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A spinel-type compound $CuCr_2S_4$ has the Curie temperature $T_c \simeq 380$ K. A family $(Cu_{1-x}Ag_x)(Cr_{0.50}Sn_{0.50})_2S_4$ indicates a double non-magnetic substitution on *A*- and *B*-sites in the spinel, with a fixed composition of 0.50 on *B*-site. An exotic hump anomaly of the magnetization arises over 30–130 K, while a conventional spin-glass behavior is observed below $T_g = 17$ K. Irreversible behavior between zero-field-cooled (ZFC) and field-cooled (FC) magnetizations has been detected in these two different temperature regions $T < 17$ K and 30 K $< T <$ 130 K. Experimental fine specification for causing this hump will be presented, with an emphasis on the sample preparation. The hump emerges from the restricted composition $0.45 \leq x \leq 0.58$ with annealing procedure, on the contrary, the quenched specimen extinguishes this hump. Magnitude of the hump varies intensely with applied magnetic field. A simple model to explain this novel hump will be discussed on the basis of the ionic radius of the substituted elements.

1. Introduction

A spinel-type mother compound $CuCr_2S_4$ has the Curie temperature $T_c \simeq 380$ K [1–5]. The formula unit has a net magnetic moment close to $5.0\mu_B$. Fig. 1 shows the spinel crystal structure. The exchange interaction of $CuCr_2S_4$ has been evaluated based on the molecular field theory, where only Cr ion ($S = 3/2$) on *B*-site has magnetic moment. In the Hamiltonian $H = -2JS_iS_j$, six nearest neighbor (nn) exchange interaction is $J_1 = 52$ K with ferromagnetic coupling, and 12 next nearest neighbor (nnn) one is $J_2 = -13$ K with antiferromagnetic one [6,7].

The substitution of non-magnetic element for Cr ion suppresses strongly the ferromagnetic nature of $CuCr_2S_4$. The random substitution on *B*-site, $Cu(Cr_{1-y}M_y)_2S_4$ (where M=Ti [8], Zr [9–15], Hf [16], Sn [17–25]) has been extensively studied. Specimen with $y \simeq 0.50$ reveals spin-glass behavior below 20 K for all these non-magnetic substitution on *B*-site.

On the other hand, it is rare to find non-magnetic substitution for Cu on the *A*-site, except for $Ag(Cr_{0.50}Sn_{0.50})_2S_4$ with Ag replacing Cu [26–28]. In this study, we have accomplished a preparation of non-magnetic random substitutions on both *A*- and *B*-sites in the spinel structure. These double substitutions $Cu_{1-x}Ag_xCrSnS_4$, which is the same notation as $(Cu_{1-x}Ag_x)(Cr_{0.50}Sn_{0.50})_2S_4$, have been carried out over the entire range of $0.00 \leq x \leq 1.00$. Here, the Cr–Sn composition is fixed with y=0.50 on *B*-site.

Since only Cr ions have the magnetic moment, the substitution of Ag for Cu seems not to exhibit a peculiar change of the magnetic properties. An unconventional upturn hump anomaly, for the temperature dependence of the magnetization $M(T)$, has been observed for $Cu_{0.50}Ag_{0.50}CrSnS_4$ in the previous work [17]. Nevertheless, sample specification, for leading this novel hump, has not been ascertained so far.

This work focuses on the detailed sample specification concerning with composition range of x for causing the hump of $M(T)$, and in particular a difference between annealed and quenched specimens. The experimental evidence for this hump in $M(T)$ will be provided, with the emphasis of sample preparation. A simplified model to interpret this hump anomaly will be given.

2. Experimental

Polycrystalline samples of $(Cu_{1-x}Ag_x)(Cr_{0.50}Sn_{0.50})_2S_4$ were prepared using solid-state reaction in sealed quart ampoules [8,17,28]. For all the annealed procedure, these samples were heated to 1023−1053 K and kept for 4 days, then were annealed at 673 K for 4 h. The preparation of the quenched specimens will be mentioned below.

The dc magnetization measurements were performed with rf-SQUID magnetometer (quantum design MPMS). A remanent magnetic field was removed before the measurement. Both temperature dependences of zero-field-cooled (ZFC) magnetization $M_{ZFC}(T)$ and field-cooled (FC) magnetization $M_{FC}(T)$ have been measured [29].

* Corresponding author.
E-mail address: nagatas@almond.ocn.ne.jp (S. Nagata).

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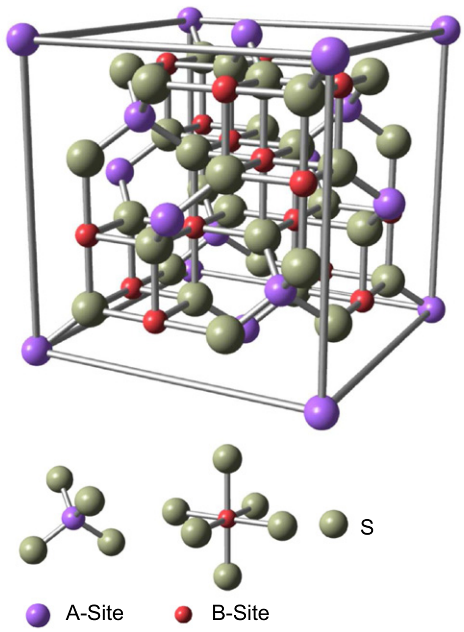

Fig. 1. Spinel crystal structure.

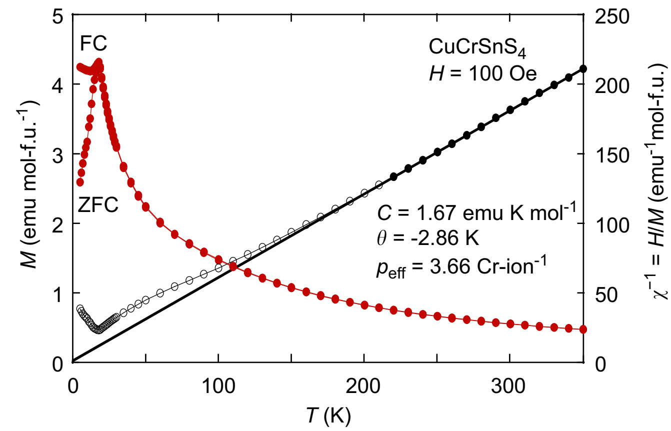

Fig. 2. Temperature dependence of magnetization and the inverse susceptibility in a magnetic field of 100 Oe for $CuCrSnS_4$.

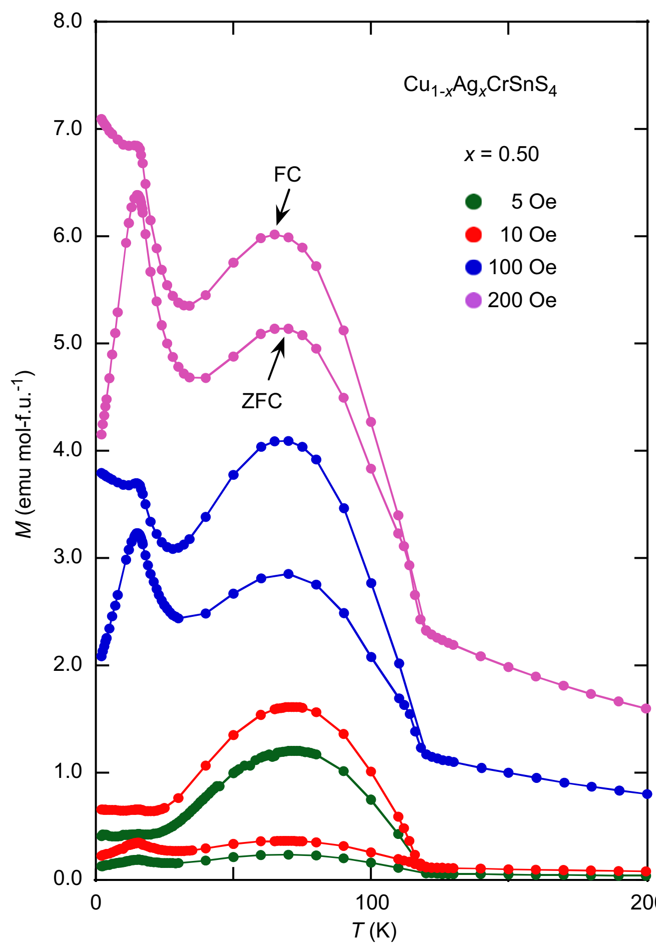

Fig. 3. Field variation of $M(T)$ over 5–200 Oe for $x=0.50$. The data in higher fields than 200 Oe have been given by Ishikawa [17].

3. Results

3.1. Structure characterization

The Rietveld analysis from X-ray diffraction (XRD) data confirms the spinel-type structure for $Cu_{1-x}Ag_xCrSnS_4$ over the entire composition $0.0 \le x \le 1.0$. The representative results have been previously reported [17], excepting the quenched specimens. All the measured samples, both of annealed and quenched, have a single phase within the X-ray data, then exclude impurity effect. The site preference problem has been examined in detail, consequently Cu or Ag occupy *A*-site, while Cr or Sn occupy *B*-site. The random distribution of the substituted elements, in both of sites Ag for Cu on *A*-site and Sn for Cr on *B*-site, has been verified, by using the Rietveld simulation with RIETAN-2000 [17,30].

3.2. Annealed samples

Fig. 2 represents the temperature dependence of magnetization $M(T)$ as well as the inverse magnetic susceptibility of $CuCrSnS_4$, where susceptibility is defined as $\chi=(M/H)$. The spin-glass behavior is observed below $T_g=17$ K. The result fits the Curie–Weiss law in high temperatures. The value of effective Bohr magneton number p_{eff} Cr-ion^{-1} is obtained to be 3.66, which is close to the value of 3.87 as a free Cr^{3+} ion. The asymptotic Weiss temperature θ has a value of -2.86 K. The results of $M(T)$ for $x=0.45$ has been reported [17]. A germination of the anomaly of $M(T)$ is seen in 10 and 20 Oe above T_g in the region of $T_g \le T \le 110\,K$ for $x=0.45$, indicating the difference between $M_{ZFC}(T)$ and $M_{FC}(T)$.

Fig. 3 demonstrates the field dependence of $M(T)$ over 5–200 Oe for $x=0.50$, and Fig. 4 for $x=0.58$ over 10–200 Oe. The conventional spin-glass behavior remains below $T_g \simeq 17$ K. The hump spreads over 30–130 K, with irreversibility between $M_{ZFC}(T)$ and $M_{FC}(T)$. Figs. 3 and 4 exhibit clearly an irreversible behavior of $M(T)$ over two different temperature regions $T < 17$ K and 30 K $< T <$ 130 K. The hump is suppressed in higher fields and collapsed down, indicating a tiny trace quantity of the anomaly where $M_{ZFC}(T)$ and $M_{FC}(T)$ coincide with each other [17]. Fig. 5 shows the results for $x=0.60$. The hump anomaly becomes extinct for the composition $x=0.60$.

Fig. 6 exhibits a variation for the magnitude of hump in 100 Oe. The composition range, yielding the upturn hump anomaly, is restricted in $0.45 \le x \le 0.58$. The most pronounced hump anomaly has been observed for $x=0.50$, and the data of the higher fields are given by Ishikawa [17]. For the outside composition regions $x < 0.45$ and $x > 0.58$, $M(T)$ shows the absence of any hump behavior, whereas it holds the spin-glass behavior below