Spin-glass and novel magnetic behavior in the spinel-type $Cu_{1-x}Ag_xCrSnS_4$

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ABSTRACT

A dual non-magnetic substitution system on A- and B-sites in the spinel structure has been studied. The mother compound is a ferromagnet $CuCr_2S_4$ with the Curie temperature $T_c \simeq 380$ K. A system of $Cu_{1-x}Ag_xCrSnS_4$, which is the same notation as $(Cu_{1-x}Ag_x)(Cr_{0.50}Sn_{0.50})_2S_4$, has been prepared over the entire range of $0.00 \leq x \leq 1.00$ although the Cr-Sn sublattice is unchanged in the fixed composition of 0.50 on B-sites. All these compounds exhibit the spin-glass phase with the freezing temperature T_g approximately at 16 K in 100 Oe. Since only Cr ions have the magnetic moment on the B-sites, the substitution of Ag for Cu on the A-sites does not influence strongly the spin-glass freezing behavior over the whole composition range. Nevertheless, the magnetization of $Cu_{1-x}Ag_xCrSnS_4$ with $x = 0.50$ and 0.55 cause a broad upturn hump over 30–130 K where the spin-glass phase is broken. Strong magnetic field dependence of this hump anomaly has been observed with an irreversibility between zero-field-cooled (ZFC) and field-cooled (FC) magnetizations even though above T_g. The hump is suppressed in higher fields and collapsed down at approximately 1.0 kOe with a tiny trace quantity of the anomaly where the difference between the ZFC and FC processes disappears. The specimen with $x = 0.45$ shows a small hump anomaly in low field < 20 Oe which corresponds to a precursor of the huge anomaly for $x = 0.50$. The hump anomaly could be attributed to a formation of the cluster-glass. The spin-clusters are embedded in the matrix of spin-glass elements in high degree of disorder without long-range order. All the spins eventually are frozen below T_g. The strange magnetic freezing originates from the delicate dual substitutions. The mechanism of the anomaly is far from a complete picture and remains enigmatic.

1. Introduction

Thiospinels exhibit a wide variety of physical properties. One of these spinels, $CuCr_2S_4$ is a compound of great interest as it shows ferromagnetism. $CuCr_2S_4$ is a metallic ferromagnet with a Curie temperature $T_c \simeq 380$ K. Versatile features of this typical ferromagnet have been investigated as a mother compound for the substitution effects. The formula unit has a net magnetic moment close to $5.0\mu_B$. It has been established that $CuCr_2S_4$ has the mixed valence as $Cu^+Cr^{3+}Cr^{4+}S_4^{2-}$, here Cr^{3+} ion with $3\mu_B$ and Cr^{4+} ion with $2\mu_B$, and a Cu^+ ion has the closed shell. The Cr ions align parallel each other, as a result the formula unit of $CuCr_2S_4$ has a net magnetic moment of $5\mu_B$ [1–5].

The chemically modified mixed valence spinel on B-sites, $CuCrZrS_4$, [6–11] has provided a way to spin-glass phase. A common characteristic of the spinel families $Cu(Cr_{1-x}M_x)_2S_4$ (where M = Ti, Zr, Hf) is that the substitution of M element for Cr atom proceeds from ferromagnetic to spin-glass behavior [12,13]. It would be a natural extension and expectation that $4+$

valence ion of Sn^{4+} is a candidate of the substitution for Cr on the B-sites. The quaternary spinel $CuCrSnS_4$ has been studied extensively [14–21].

A spinel-type $AgCr_2S_4$ has never been synthesized so far, because of the difficulty of synthesis. The occupation of Ag atom on the A-sites in the spinel compound is rarely seen. A few spinel compounds exist with occupying Ag atom on the A-sites [22,23]. The Ag based spinels $Ag(Cr_{1-x}Sn_x)_2S_4$ ($x = 0.50$, 0.60, and 0.70) have been successfully prepared recently and the results of the spin-glass characteristics have been reported [24].

We have focused the present study on the non-magnetic Ag substitution for Cu on the A-sites although the Cr-Sn sublattice is unchanged in the fixed composition for B-sites. Here 50% Cr and 50% Sn atoms are distributed randomly on the octahedral B-sites [25]. Single-phase specimens with the dual substitution were obtained after optimization of the sintering conditions. This system of $Cu_{1-x}Ag_xCrSnS_4$, which indicates the same notation as $(Cu_{1-x}Ag_x)(Cr_{0.50}Sn_{0.50})_2S_4$, can be prepared over the entire range of $0.00 \leq x \leq 1.00$.

The first stage of experiments is to find how strongly or weakly the spin-glass phase is influenced by non-magnetic Ag substitution. This expectation has become true because the spin-glass behavior does not vary over the whole composition range with

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the freezing temperature T_g approximately at 16 K in 100 Oe. Since only Cr ions have the magnetic moment on the B-sites, the substitution of Ag for Cu on the A-sites does not strongly influence the magnetic properties.

Nevertheless, we have discovered a strange upturn hump anomaly in the temperature variation of magnetization M for the compositions of $x = 0.50$ and 0.55. This hump anomaly arises in the temperature region between 30 and 130 K, above the freezing temperature T_g. This upturn hump is seen in rather low field and eventually suppressed in higher field than approximately 1.0 kOe. The temperature and field dependences of this hump anomaly of M have been examined.

A possibility of formation of the cluster-glass in the matrix of spin-glass elements will be proposed, because an irreversibility effect was detected for the field application. The isothermal magnetic hysteresis loops were measured for $x = 0.50$ at several temperatures. The results of these $M-H$ curves indicate also specific features. The present study is mainly concerned with the experimental finding in the dc magnetization measurements for $x = 0.50$.

2. Experimental methods

The initial study of sample preparations is reported by Hasegawa [24]. The highest purity specimens were produced by different heat treatments as shown in Fig. 1. The precise sintering temperature has to be adapted for each composition. This empirical method can lead to the optimum condition for synthesis of the high purity specimens of $Cu_{1-x}Ag_xCrSnS_4$. These specimens were heated to the specific temperature as indicated in Fig. 1 and kept at these temperatures for 4 days, then were annealed at 673 K for 4 h. All the prepared specimens were found to be stable under air after the synthesis. The identification of crystal structure and the determination of lattice constants were carried out by X-ray powder diffraction (XRD) using Cu Kα radiation at room temperature. The XRD data were analyzed by the Rietveld simulation method with RIETAN-2000 [25].

The dc magnetization measurements of powder specimens were performed with a quantum design superconducting quantum interference device (rf-SQUID) magnetometer over the temperature range over 2.0–350 K. For many specimens, the experimental results showed the appearance the irreversible effect between the zero-field-cooled (ZFC, initial magnetization, after cooling the sample to the lowest temperature in zero field, a field was applied and the data were taken with increasing temperature) and the field-cooled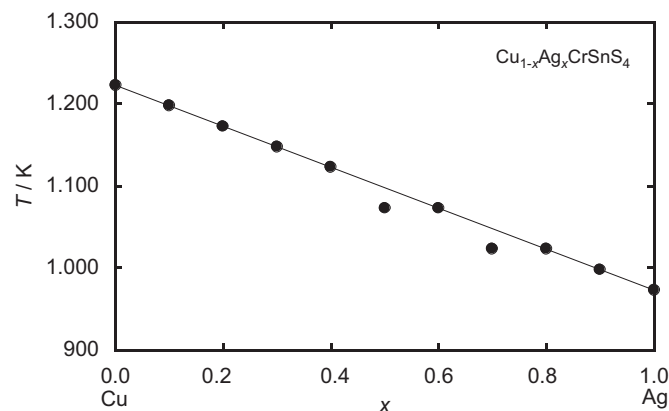 (FC, application of field before cooling) magnetizations [26]. The isothermal magnetic hysteresis curves were measured in the ZFC and FC processes at several temperatures. The demagnetizing field corrections have not been applied to any of our magnetic data because of the small magnitude of the magnetization.

3. Results and discussion

3.1. Lattice constant

X-ray data have been analyzed in terms of a cubic spinel structure with the space group $Fd\bar{3}m$ (No. 227). The X-ray diffraction (XRD) patterns at room temperature give evidence that all the $Cu_{1-x}Ag_xCrSnS_4$ have the spinel type structure. Representative diffraction profiles are shown in Fig. 2. The Rietveld simulation method with RIETAN-2000 verifies the random distribution in the A- and B-sites, respectively [25]. The site preference is exactly examined and confirmed that Cu and Ag occupy at only A-sites and Cr and Sn atom occupy at B-sites. Occupation percentage and the randomness are verified. However, the Rietveld refinement to adjust the inter atomic distances has not been done in this substitution system.

More detailed discussion concerned with distribution will be mentioned in later subsection for the specific specimen with $x = 0.50$. The lattice constant, a, obtained by the least square method, varies as shown in Fig. 3 at room temperature. Here, these values of x are given by the initial stoichiometry of the reacting constituents. The lattice constant increases linearly with increasing Ag substitution x and obeys Vegard's law. The unit sell
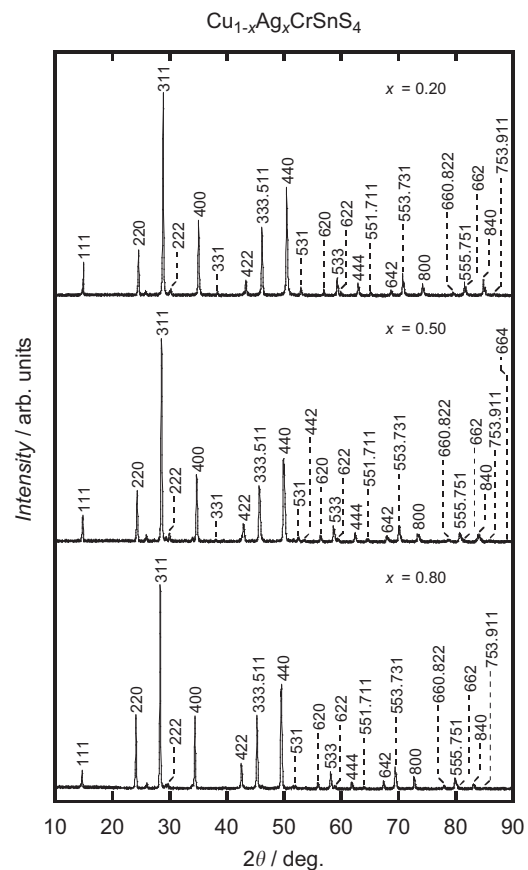

Fig. 1. Optimum condition of the heat treatment for the sample preparation of $Cu_{1-x}Ag_xCrSnS_4$.

Fig. 2. X-ray diffraction profiles of $Cu_{1-x}Ag_xCrSnS_4$ for powdered specimens with $x = 0.20$, 0.50, and 0.80 at room temperature.