

# Magnetic and thermodynamic properties of the thiospinel compound $\text{CuCrZrS}_4$

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(Received 27 September 2006; published 13 December 2006)

We have carried out dc magnetic susceptibility, magnetization and specific-heat measurements on thiospinel  $\text{CuCrZrS}_4$ . Below  $T_C^*=51$  K, dc magnetic susceptibility and magnetization data show ferromagnetic behavior with a small spontaneous magnetization  $0.36\mu_B/\text{f.u.}$  In dc magnetic susceptibility, large and weak irreversibilities are observed below  $T_f=6$  K and in the range  $T_f < T < T_C^*$ , respectively. We found that there is no anomaly as a peak or step in the specific heat at  $T_C^*$ .

DOI: [10.1103/PhysRevB.74.214412](https://doi.org/10.1103/PhysRevB.74.214412)

PACS number(s): 75.50.-y, 75.60.Ej, 65.40.Ba, 75.10.Nr

## I. INTRODUCTION

Chalcogenide spinels with the generic chemical formula  $AB_2X_4$  are well known to show a number of interesting physical properties. For example,  $\text{CuRh}_2\text{S}_4$  (Refs. 1–4) and  $\text{CuRh}_2\text{Se}_4$  (Refs. 2–5) are superconductors,  $\text{CuIr}_2\text{S}_4$  shows a temperature-induced metal-insulator transition due to a new type charge ordering,<sup>6–8</sup> and  $\text{FeCr}_{2-x}\text{In}_{2(1-x)}\text{S}_4$  shows a reentrant spin-glass behavior from a long-range antiferromagnetic order.<sup>9</sup> Recently, we found the amazing phenomenon of a pressure-induced superconductor-insulator transition in  $\text{CuRh}_2\text{S}_4$ .<sup>10,11</sup>  $\text{CuCr}_2\text{S}_4$ , the parent compound to  $\text{CuCrZrS}_4$ , is a metallic compound, which shows a ferromagnetic transition at a Curie temperature  $T_C=377$  K with a saturation magnetization of  $5\mu_B/\text{f.u.}$ <sup>12–15</sup> The  $B$  site Cr ions in  $\text{CuCr}_2\text{S}_4$  have valences  $\text{Cr}^{3+}$  (spin-angular momentum  $S=3/2$ , magnetic moment  $m=3\mu_B$ ) and  $\text{Cr}^{4+}$  ( $S=1$ ,  $m=2\mu_B$ ).<sup>14–17</sup> This mixed valence state of Cr ions results in the metallic conductivity of  $\text{CuCr}_2\text{S}_4$ . Ferromagnetism with  $5\mu_B/\text{f.u.}$  in this compound is attributed to the double-exchange interaction between the  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  cations via the conduction electrons.<sup>18–20</sup>

High-purity specimens of  $\text{CuCrZrS}_4$  were recently synthesized and investigated through transport and magnetic measurements by Iijima *et al.*<sup>21</sup> When Zr ions occupy half of the  $B$  sites of  $\text{CuCr}_2\text{S}_4$ , the temperature dependence of the electric resistivity changes from metallic to semiconducting with an energy gap of 79 K. The Curie temperature simultaneously decreases to 60 K. In addition, spin-glass behavior is observed below the freezing temperature  $T_f=10$  K, namely,  $\text{CuCrZrS}_4$  shows reentrant spin-glass freezing from the long-range ferromagnetic order. It has been confirmed that the ionic configuration of this compound is  $\text{Cu}^{1+}\text{Cr}^{3+}\text{Zr}^{4+}\text{S}_4^{2-}$ . In this paper, we report the dc magnetic susceptibility, magnetization, and specific heat of  $\text{CuCrZrS}_4$ . These results suggest that the ferromagnetic behavior of  $\text{CuCrZrS}_4$  is not caused by the usual long-range ferromagnetic order.

## II. EXPERIMENTAL

A polycrystalline specimen was prepared by a direct solid-state reaction as described previously.<sup>21</sup> High-purity fine powders of Cu (99.99%), Cr (99.99%), Zr (99.9%), and

S (99.999%) were mixed in stoichiometric ratio and were reacted in a quartz tube at 1023 K for seven days. A powder specimen was reground, pressed into a rectangular bar with an aspect ratio of 1:5, and sintered at 1023 K for two days. From x-ray Rietveld analysis at 300 K, it is confirmed that the distribution of Cr and Zr ion on the  $B$  site in  $\text{CuCrZrS}_4$  is disordered. The magnetic measurements were carried out using a Quantum Design MPMS SQUID magnetometer. The dc magnetic susceptibility was measured as a function of temperature in  $2 \leq T \leq 300$  K during warm up after cooling to 2 K both in the zero field (ZFC) and in the measuring field of  $H=100$  Oe (FC). The magnetization in the magnetic-field range between  $-45$  and  $45$  kOe at several temperatures between 2 and 120 K was measured after ZFC. The magnetic measurements were carried out along the long axis of the shape. Specific heat  $C_p$  measurements in the temperature range between 1.8 and 150 K were carried out using a Quantum Design PPMS, which is operated by the thermal relaxation method.  $C_p$  is derived by measuring the thermal relaxation time  $\tau$ , which is proportional to  $C_p^{-1}$ .

## III. RESULTS

### A. Magnetic properties

Figure 1(a) shows the temperature  $T$  dependence of dc magnetic susceptibility  $\chi$  and inverse susceptibility  $\chi^{-1}$  of  $\text{CuCrZrS}_4$  at 100 Oe in the temperature range between 2 and 300 K. With decreasing  $T$ ,  $\chi$  increases rapidly below  $T_C^*=51$  K as seen at the Curie temperatures for ordinary ferromagnetic compounds.  $T_C^*$  was defined as the minimum point of  $\partial\chi/\partial T$ . As shown by the solid line in Fig. 1(a), magnetic susceptibility above 75 K can be fitted by the Curie-Weiss law,  $\chi=C/(T-\theta)$ , with a paramagnetic Curie temperature  $\theta=57$  K and a Curie constant  $C=1.515$  emu K/mol. The positive  $\theta$  means the magnetic interaction in the system is ferromagnetic. The effective magnetic moment  $\mu_{\text{eff}}$  obtained from  $C$  is  $3.48\mu_B$ , which is close to the value of  $3.87\mu_B$  expected for the free  $\text{Cr}^{3+}$  ion. As was pointed out by Iijima *et al.*,<sup>21</sup> a large irreversibility between  $\chi_{\text{FC}}$  and  $\chi_{\text{ZFC}}$  is observed in the low-temperature range as shown in Fig. 1(b). This behavior is suggestive of spin-glass freezing. The value of plateau in  $\chi_{\text{FC}}$  below 10 K is about 10% of a ferromagnetic demagne-

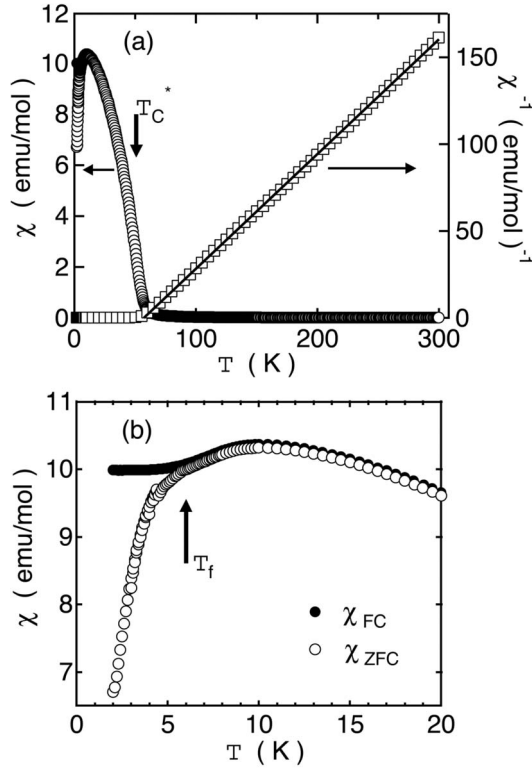


FIG. 1. (a) Temperature dependence of the dc magnetic susceptibility  $\chi$  and the inverse susceptibility  $\chi^{-1}$  under magnetic field  $H=100$  Oe in the temperature range  $2 \leq T \leq 300$  K. The solid line is the best fit by Curie-Weiss law. (b) An expanded plot of  $\chi$  between 2 and 20 K. The closed and open circles represent  $\chi$  measured with field cooled (FC) and zero-field cooled (ZFC), respectively.

tization plateau expected for the shape of our sample.<sup>22</sup>

In order to discuss the irreversibility in more detail, the difference of magnetic susceptibility  $\Delta\chi (= \chi_{FC} - \chi_{ZFC})$  is calculated and shown in Fig. 2.  $\Delta\chi$  shows an abrupt increase below  $T_f = 6$  K with decreasing  $T$ .  $\Delta\chi$  has a nonzero value even in the range  $T_f \leq T \leq T_C^*$  as shown in the inset of Fig. 2.

Figure 3(a) shows the magnetization  $M$  vs field  $H$  curve

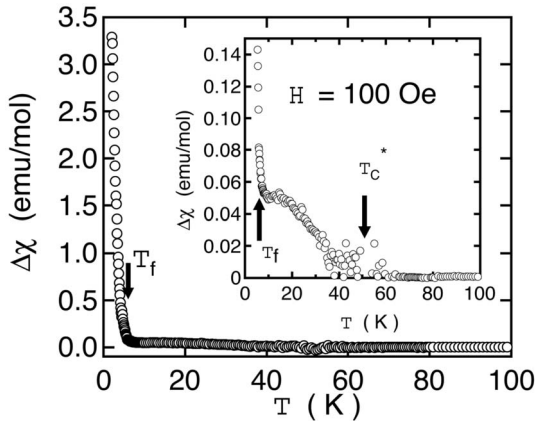


FIG. 2. Difference of magnetic susceptibility  $\Delta\chi$  as a function of  $T$  in the range  $2 \leq T \leq 100$  K. The inset is a plot of  $\Delta\chi$  with expanded vertical scale.

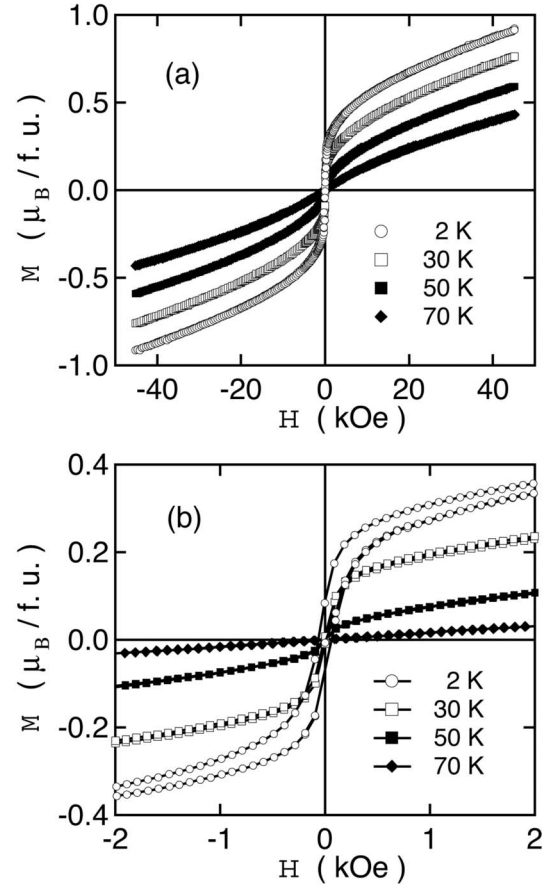


FIG. 3. Magnetization as a function of the magnetic field  $H$  at representative temperatures. (a)  $M(H)$  in the range  $-45 \leq H \leq 45$  kOe. (b) An expanded plot of  $M(H)$  in the range  $-2 \leq H \leq 2$  kOe.

of  $\text{CuCrZrS}_4$  at 2, 30, 50, and 70 K in the range  $-45 \leq H \leq 45$  kOe.  $M$  is not saturated in field up to 45 kOe even at lowest temperature. A clear hysteresis loop is observed in the lower  $H$  region at 2 K as shown in Fig. 3(b). The loop has a small coercive force of  $H \sim 50$  Oe, which is defined as the field necessary to restore zero magnetization.

A modified Arrott plot analysis was employed to investigate the spontaneous magnetic moment  $M_S$  of  $\text{CuCrZrS}_4$ . This analysis is based on the Arrott-Noakes equation<sup>23</sup> for the ferromagnetic material given by

$$\left(\frac{H}{M}\right)^{1/\gamma} = \frac{T - T_C}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta}. \quad (1)$$

Here  $T_C$  is the Curie temperature,  $\beta$  and  $\gamma$  are critical exponents, and  $M_1$  and  $T_1$  are constants depending on the material. According to Eq. (1), the isotherm of  $M(H)$  should be a set of parallel straight lines in a modified Arrott plot, in which  $M^{1/\beta}$  is plotted versus  $(H/M)^{1/\gamma}$ .<sup>23–28</sup> To construct this plot, it is necessary to determine the critical exponents  $\beta$  and  $\gamma$ . Initially, in order to do this, the scaling plot  $|M|/|t|^\beta$  vs  $|H|/|t|^{(\beta+\gamma)}$  with the reduced temperature  $t = (T - T_C)/T_C$  was attempted for the  $M(H)$  of  $\text{CuCrZrS}_4$ . For the ferromagnetic material, by taking the optimal values of  $\beta$ ,  $\gamma$ , and  $T_C$ , all

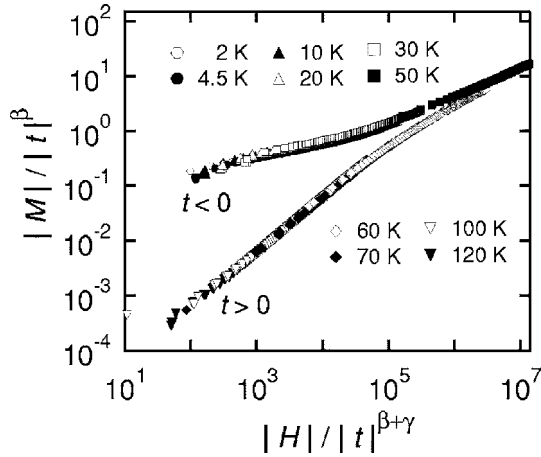


FIG. 4. Scaling plot of  $|M|/|t|^\beta$  vs  $|H|/|t|^{\beta+\gamma}$  with  $\beta=1.30$ ,  $\gamma=0.95$ , and  $T_C=52$  K on the logarithmic scale.

data points below  $T_C$  ( $t < 0$ ) converge to a curve, whereas the data points above  $T_C$  ( $t > 0$ ) converge to another one.<sup>23,24,28</sup> Figure 4 shows the  $|M|/|t|^\beta$  plot as a function of  $|H|/|t|^{\beta+\gamma}$  on the logarithmic scale with  $\beta=1.30$ ,  $\gamma=0.95$ , and  $T_C=52$  K. All isotherms of  $M(H)$  converge to two branches of curves depending on the sign of  $t$ . The value of  $T_C$  obtained from this analysis is close to the value of  $T_C^*$  determined by  $\chi$ . The modified Arrott plot using  $\beta$  and  $\gamma$  obtained from the scaling analysis  $M^{1/\beta}$  vs  $(H/M)^{1/\gamma}$  is shown in Fig. 5. In the high-field region, all isotherms show the linear dependence with a parallel slope. The dotted lines are linear extrapolations of  $M^{1/\beta}$ .  $M_S$  as a function of  $T$  is determined from the intercepts on the  $M^{1/\beta}$  axis of the dotted lines in Fig. 5. Figure 6 shows  $M_S$  extracted from the modified Arrott plot analysis. Below 52 K, CuCrZrS<sub>4</sub> has  $M_S$ . The value of  $M_S$  at 0 K estimated from Fig. 6 is  $0.36\mu_B/\text{f.u.}$  This value is only  $\sim 12\%$  of that expected for a  $\text{Cr}^{3+}$  ion.

### B. Thermodynamic properties

Figure 7(a) shows the temperature dependence of specific heat  $C_p(T)$  of CuCrZrS<sub>4</sub> in the range  $1.8 \leq T \leq 400$  K. At 300 K,  $C_p(T)$  reaches 85% of that estimated from the Du-

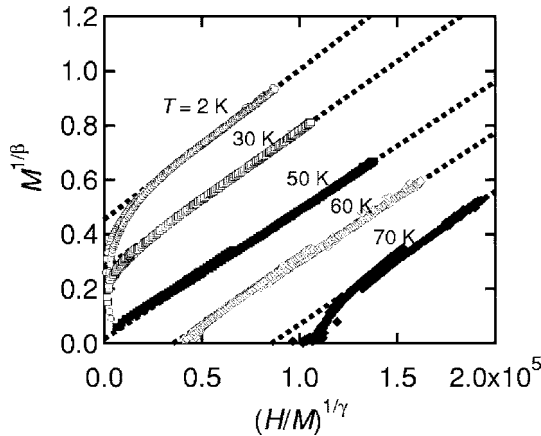


FIG. 5. Modified Arrott plot for CuCrZrS<sub>4</sub> at representative temperatures. The dotted lines are linear fits in the higher-field region.

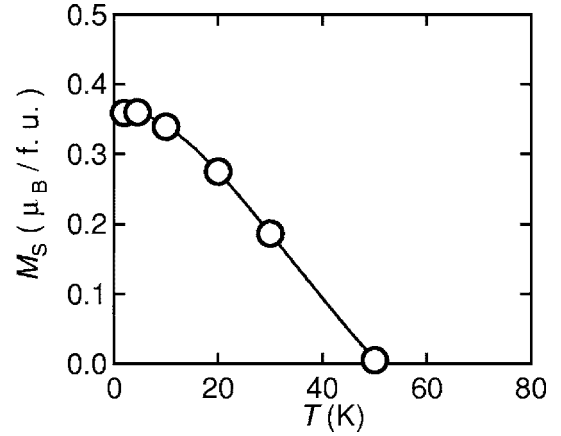


FIG. 6. The temperature dependence of the spontaneous magnetic moment determined by the modified Arrott plot analysis. The solid line is a guide to the eyes.

long and Petit law ( $\sim 175$  J/K mol). Remarkably, neither a peak or a step is observed in  $C_p$  at  $T_C^*$  as shown in Fig. 7(b), despite that clear ferromagnetic behavior is observed from the magnetic properties. In general, specific-heat measurements with a relaxation method are not suitable for obtaining the absolute value of  $C_p$ , which has a large temperature dependence around the first-order transition, because the thermal relaxation process cannot be fitted by a simple exponential time- $t$ -dependence equation,  $\exp(-\tau/t)$ . However, we can confirm whether there is an anomaly in  $C_p$ . The absence of an anomaly in the specific heat at  $T_C^*$  is still unclear. This unusual behavior will be discussed later. Figure 7(c) is the plot of  $C_p/T$  as a function of  $T$ . A broad hump appears around  $T_f$ . It is well known that the specific heat of spin-glass systems such as (Eu, Sr)S (Ref. 29) and AuFe (Ref. 30) do not show a discontinuity as seen in the first- and second-order transition but rather a broad hump around the spin-glass freezing temperature. Our result suggests that spin-glass freezing occurs below  $T_f$ .

## IV. DISCUSSION

### A. Spin-glass behavior at low temperature

In general, spin-glass freezing originates from the frustration of the magnetic interaction in the system. We will discuss the frustration in CuCrZrS<sub>4</sub>. As mentioned above, CuCr<sub>2</sub>S<sub>4</sub> has metallic conductivity, which is attributed to the mixed valence of Cr ions ( $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$ ) and the ferromagnetism due to the double-exchange interaction between Cr ions via conduction electrons. When half of the Cr ions of CuCr<sub>2</sub>S<sub>4</sub> are substituted by Zr ions, the electric configuration is  $\text{Cu}^{1+}\text{Cr}^{3+}\text{Zr}^{4+}\text{S}_4^{2-}$ , and the transport properties become semiconductive.<sup>21</sup> This behavior can be explained by a variable range-hopping (VRH) conduction.<sup>31</sup> This means that the number of conduction electrons in CuCrZrS<sub>4</sub> decrease with decreasing temperature. The decrease in the number of conduction electrons gives rise to the reduction of the double-exchange interaction and relative enhancement of the super-exchange antiferromagnetic interaction between  $\text{Cr}^{3+}$  cations via  $\text{S}^{2-}$  anions at low temperature. The  $\text{Cr}^{3+}$  cations in

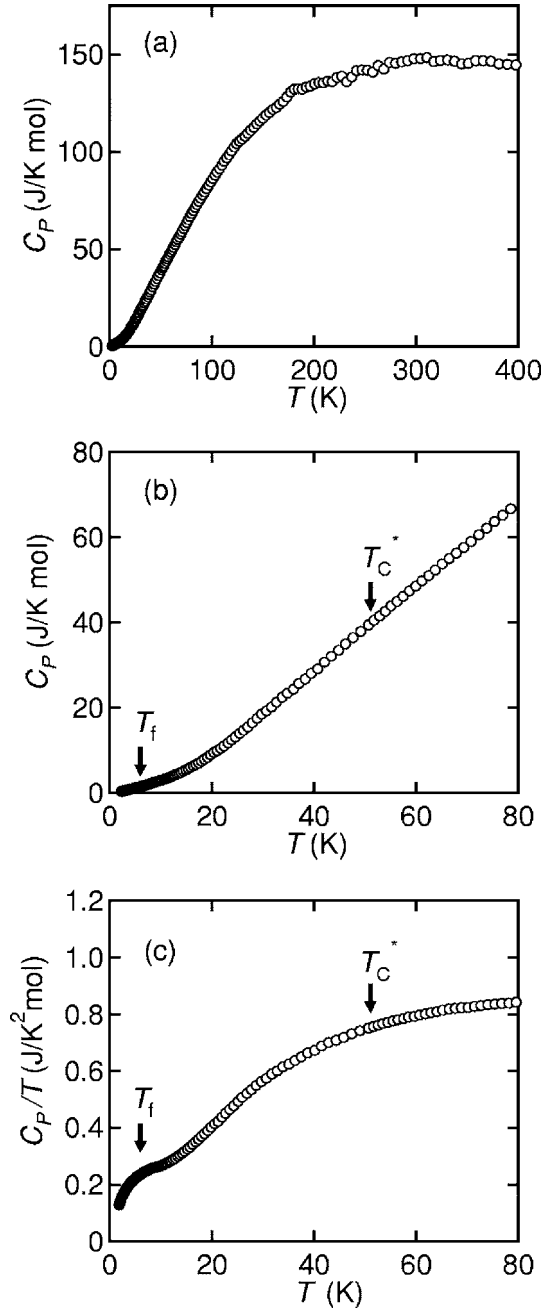


FIG. 7. (a) Temperature dependence of specific heat  $C_P$  in the range  $1.8 \leq T \leq 400$  K. (b) An expanded plot of  $C_P(T)$  in the range  $1.8 \leq T \leq 80$  K. (c) Temperature dependence of specific-heat divided temperature  $C_P/T$  in the range  $1.8 \leq T \leq 80$  K.

$\text{CuCrZrS}_4$  have a tetrahedral network with each  $\text{Cr}^{3+}$  cations. When the interaction between  $\text{Cr}^{3+}$  cations is antiferromagnetic, the tetrahedral network causes strong geometrical frustration in the system. This is similar to behavior in the pyrochlore crystal structure.<sup>32</sup> Finally, let us mention about a thiospinel compound  $\text{CdCr}_{2x}\text{In}_{2-2x}\text{S}_4$ . Dupuis *et al.* reported that this compound shows the reentrant spin-glass freezing from ferromagnetic phase in  $0.15 < x < 0.85$ .<sup>33</sup> As the origin of the frustration in  $\text{CdCr}_{2x}\text{In}_{2-2x}\text{S}_4$ , they pointed out the enhancement of the superexchange antiferromagnetic interaction by the substitution of In ions for magnetic Cr ions in the B site.

### B. Specific heat

Now we discuss why there is no anomaly at  $T_C^*$  in  $C_P(T)$  from the viewpoint of the phase with and without the ferromagnetic long-range order below  $T_C^*$ .

In the first case, one can consider the coexistence of the itinerant and the localized spins in the  $t_{2g}$  orbital. Some of Cr compounds have large density of states (DOS), which predominantly consist of one of the  $t_{2g}$  in 3d orbital of the Cr ions close to below the Fermi level that is occupied by the localized spins.<sup>34,35</sup> On the other hand, other  $t_{2g}$  orbitals are strongly hybridized with  $p$  orbitals of the anions in the compound and form the dispersive bands, which have the itinerant spins. This picture leads to the coexistence of the localized and the itinerant spins in the  $t_{2g}$  orbital electrons. The itinerant spins that belong to the  $d(t_{2g})-p$  hybridized bands tend to polarize the localized spins because of Hund's rule coupling, resulting in a ferromagnetic exchange interaction, which is often called a self-doped double-exchange interaction.<sup>35</sup> This mechanism is very similar to that of the double-exchange interaction between the localized  $t_{2g}$  electrons and the itinerant electrons in the  $d(e_g)-p$  hybridized bands in the Zener model.<sup>36</sup> Recently, Granado *et al.* studied the neutron scattering and specific heat of  $\text{LaCrSb}_3$ .<sup>37</sup> They reported that  $\text{LaCrSb}_3$  shows the ferromagnetic long-range order at  $T_C = 126$  K and nevertheless no peak or step appears in specific heat at  $T_C$ . They suggested that unconventional magnetic behavior results from the localized spins, which are strongly polarized even above  $T_C$  by the self-doped double-exchange interaction. This situation can be responsible for entropy transfer to higher temperature, and released entropy at  $T_C$  is small. Consequently, an anomaly in  $C_P$  at  $T_C$  is too small to be observed. If the localized moments in  $\text{CuCrZrS}_4$  are strongly polarized by the itinerant electrons due to a mechanism similar to that of ferromagnetism in  $\text{LaCrSb}_3$ , no anomaly at  $T_C^*$  in specific heat might be explained. This situation based on the self-doped double-exchange interaction, however, is expected to arise in the compound with a highly anisotropic crystal structure, such as the layered compound  $\text{LaCrSb}_3$ .<sup>37</sup> The thiospinel compound  $\text{CuCrZrS}_4$  has an isotropic cubic structure. Judging from this, the scenario of the coexistence of the itinerant and the localized spins in the  $t_{2g}$  orbital as seen in  $\text{LaCrSb}_3$  is likely to be ruled out.

As the second case, we suggest the possibility of successive spin-glass freezing at  $T_f$  and  $T_C^*$ . Existence of small ( $T_f \leq T \leq T_C^*$ ) and large ( $T \leq T_f$ ) irreversibility in  $\Delta\chi$  is similar to successive spin-glass freezing seen in the spin-glass material  $\text{Ni}_{0.42}\text{Mn}_{0.58}\text{TiO}_3$ .<sup>38</sup> As mentioned in Sec. IV A, this system has competing ferromagnetic and antiferromagnetic exchange interactions. With decreasing  $T$ , the number of conduction electrons decrease, and the superexchange interaction gradually grows stronger. This promotes a variation of the strength of geometric frustration with decreasing  $T$ , and might be the origin of the successive spin-glass freezing. If spin-glass freezing occurs below  $T_C^*$ , no discontinuity at  $T_C^*$  in specific heat, would be observed. Unfortunately, the broad hump around  $T_C^*$  in specific heat, which is characteristic of spin-glass freezing, is not observed due to the difficulty of separating the phonon contribution from the total specific heat. Ferromagnetic features observed in the magnetic prop-



erties might be originated from the spin-glass phase with the small ferromagnetic spin components. In order to clarify why no discontinuity at  $T_C^*$  in specific heat is observed, detailed studies are needed.

## V. CONCLUSION

We have studied the magnetic and thermodynamic properties of the thiospinel compound  $\text{CuCrZrS}_4$ , which has been reported to show long-range ferromagnetic order at 60 K and spin-glass freezing at 10 K. The dc magnetic susceptibility and magnetization curve show ferromagnetic behavior below  $T_C^*=51$  K with a small spontaneous magnetization  $0.36\mu_B/\text{f.u.}$  at  $T=0$  K. With decreasing temperature, the

irreversibility in dc magnetic susceptibility appears at  $T_C^*$ , and increases abruptly at  $T_f=6$  K. In specific heat, no magnetic discontinuity is observed in the temperature range we measured. We discussed the origin of no magnetic discontinuity in specific heat from the viewpoint of the phase with and without the ferromagnetic long-range order below  $T_C^*$ .

## ACKNOWLEDGMENTS

This work was partially supported by Grant-in-Aids for COE Research (Grant No. 13CE2002), the Scientific Research (Grants No. 16740205, No. 17340113) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and aid funds from Energia, Inc. (Hiroshima) and the Asahi Glass Foundation (Tokyo).

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