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A new ferromagnetic thiospinel $CuCrZrS_4$ with re-entrant spin-glass behaviour

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ABSTRACT

A new thiospinel $CuCrZrS_4$ has been successfully synthesized by a solid-state chemical reaction. This $CuCrZrS_4$ exhibits ferromagnetic properties below the Curie temperature at $T_c = 60 \pm 2$ K. The appearance of irreversibility between field-cooled (F.C.) and zero-field cooled (Z.F.C.) magnetization is prominent below around 5 K in less than 150 Oe. The ac susceptibility χ_{AC} shows a rapid decrease below ≈10 K. This low-magnetic field behaviour indicates the existence of a reentrant spin glass phase below ≈10 K. The d.c. magnetic susceptibility above 100 K shows Curie-Weiss behaviour with the effective magnetic moment of 3.61 μ_B, which is a little less than the spin only value of 3.87 μ_B for Cr^{3+} ion. The asymptotic Curie temperature θ_p is approximately 65 K which is a little higher than T_c. The valence state is confirmed to be $Cu^+Cr^{3+}Zr^{4+}S^{2-}{}_4$ on the basis of magnetic properties. Electrical resistivity ρ shows a semiconducting temperature dependence over the temperature range 4.2 to 280 K with an activation energy of 6.84×10^{-3} eV in the higher temperature range 50 to 283 K.

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§ 1. INTRODUCTION

Sulphospinels exhibit a wide variety of physical properties that make them interesting from a scientific point of view, while oxyspinels are in general semiconductors with antiferromagnetic interactions (Van Stapele 1982). Magnetic materials encompass a rich variety of spin alignments. One of the normal thiospinels, $CuCr_2S_4$ has metallic conduction (Hahn *et al.* 1956, Bouchard *et al.* 1965, Itoh 1980, Oda *et al.* 2001) and is ferromagnetic with a Curie temperature $T_c = 377$ K with a saturation magnetization of about 5 μ_B / f.u. (Lotgering 1964a, Ohbayashi *et al.* 1968, Kanomata *et al.* 1970, Robbins et al. 1970, Belov *et al.* 1973). The origin of the magnetic moment has been the subject of controversy. The sulphospinel $CuCr_2S_4$ has the spinel type structure where Cu ions occupy the A (tetrahedral) sites and Cr ions occupy the B (octahedral) sites, as shown in figure 1.

The mixed-valence model of Cr ion has been proposed as $Cu^{+}Cr^{3+}Zr^{4+}S^{2-}_{4}$, (Lotgering 1964a, b, Lotgering and van Stapele 1967, Robbins *et al.* 1967, van Stapele and Lotgering 1970, Riedel and Horvath 1973, Van Stapele 1982, Krok-Kowalski *et al.* 2001), here a Cr^{3+} ion with 3 μ_B a Cr^{4+} ion with 2 μ_B and a Cu^{+} ion have a closed shell, where all the Cr ions align parallel with each other. Consequently the formula unit of $CuCr_2S_4$ has a net magnetic moment of $5\mu_B$. The metallic conduction and ferromagnetism have been attributed to a double exchange between Cr^{3+} and Cr^{4+} ions (Zener and Heikes 1953, Van Stapele 1982). This interpretation has been verified experimentally (Kimura *et al.* 2001).

On the other hand, the ionic valence state of $CuCr_2S_4$ can be described schematically $Cu^{2+}Cr^{3+}2S^{2-}4$, as two Cr^{3+} ions, where 3 electrons in the 3*d* shell with spin up, and a Cu^{2+} ion which is oriented antiparallel to the spin of Cr^{3+} ion (Goodenough 1967, 1969). Each Cr^{3+} ion has a moment of 3 μ_B and each Cu^{2+} ion has a moment of $1\mu_B$ in the opposite direction. As a result the formula unit of $CuCr_2S_4$ has a net magnetic moment of $5\mu_B$.

It is worthwhile to study magnetic properties of a new thiospinel $CuCrZrS_4$, which is a chemically modified compound from this $CuCr_2S_4$. This new compound $CuCrZrS_4$ has been first prepared by Padiou *et al.* (1980). They suggested the ferromagnetism of $CuCrZrS_4$. A ferromagnetic positive Weiss temperature, which is a rather crude and less accurate estimation of $\theta_p = 25$ K, is given from the Curie Weiss law without any detailed measurements.

We have successfully synthesized high-purity specimens of $CuCrZrS_4$ and clarified the ferromagnetic state. The magnitude of magnetic moment of $CuCrZrS_4$ is examined from a diagnostic point of view for the ionic valence state described above. The difference between field-cooled (F.C.) and zero-field cooled (Z.F.C.) magnetization is detected clearly below 5 K in less than 150 Oe. The ac susceptibility shows a rapid decrease below $\approx$10 K. These low magnetic field behaviour indicates a reentrant spin glass phenomenon in $CuCrZrS_4$. This reentrant behaviour from ferromagnetism to spin-glass transition resembles Au-Fe alloys (Coles *et al.* 1978), $Eu_xSr_{1-x}S$ (Maletta 1979, 1982), and Ni-Mn alloys (Abdul-Razzaq and Kouvel 1987). It is emphasized that the dilute ferromagnet of $CuCrZrS_4$ on the restricted

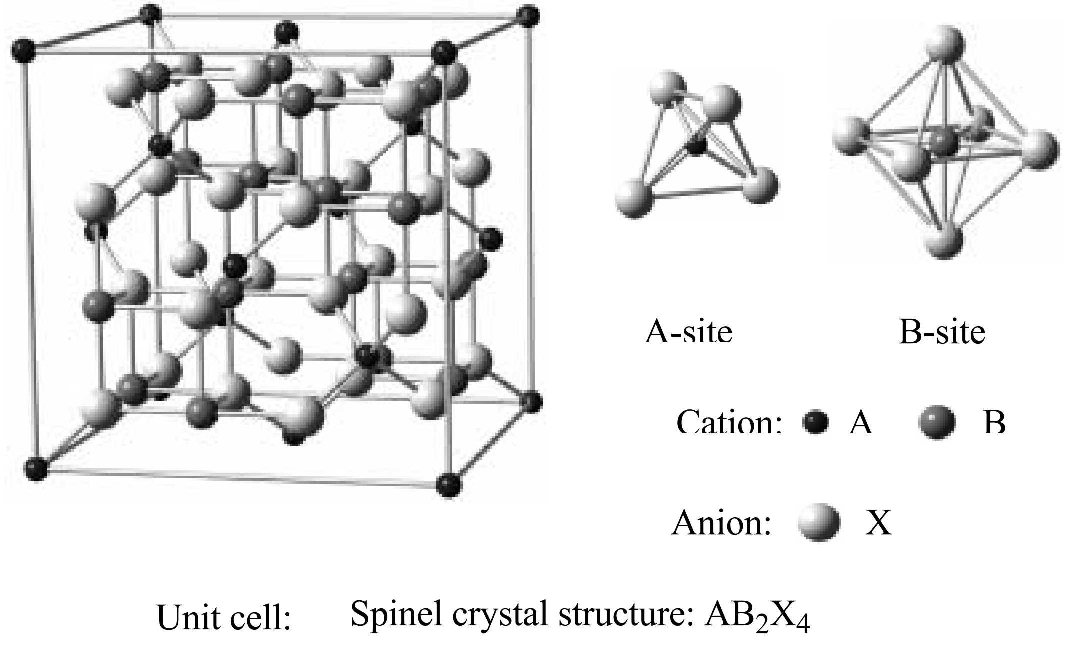

Figure 1. The cubic unit cell of spinel structure. Cu ions occupy the *A* (tetrahedral) sites and Cr or Zr ions occupy the *B* (octahedral) sites. Large circles indicate S ions.

sublattice of B-site of the spinel crystal structure reveals the reentrant spin glass characteristic, where Cr composition is 50 % on B-site. This $CuCrZrS_4$ is not a metallic alloy, and the magnetic disorder and geometrical frustration take place on the B-site; therefore $CuCrZrS_4$ would be a candidate for a typical insulating compound for a simple and transparent theoretical investigation.

§ 2. EXPERIMENTAL METHODS

The polycrystalline specimens were prepared by a direct solid-state reaction. Mixtures of high-purity fine powders of Cu (purity 99.99 %), Cr (99.99 %), Zr (99.9 %), S (99.999 %) with nominal stoichiometry were heated in sealed quartz tubes up to 1023 K and kept at this temperature for 7 days. The resultant powder specimens were reground, pressed into rectangular bars and then were heated at 1023 K for 2 days. The identification of the crystal structure and the determination of the lattice constants were carried out by powder X-ray diffraction method using Cu Kα radiation at room temperature. The resistivity ρ of sintered specimens with dimensions of about 2 mm×2 mm×10 mm was measured by a standard dc four-probe method over a temperature range 4.2 K to room temperature. The dc magnetization of powder specimens was measured with a Quantum

Design superconducting quantum interference device (r.f.-SQUID) magnetometer over a range of $2.0 \leq T \leq 300$ K. The ac magnetic susceptibility χ_{AC} was measured using a mutual inductance bridge at a frequency of 80 Hz and an amplitude of ac magnetic field of 5.0 Oe over the range $4.2 \leq T \leq 150$ K.

§ 3. RESULTS AND DISCUSSION

3. 1. *Crystal structure*

A powder X-ray diffraction pattern at room temperature confirms that $CuCrZrS_4$ has the normal-spinel type structure of single phase. The X-ray diffraction pattern is presented in figure 2. The value of unit cell parameter a =10.200 Å, obtained by the least square method. The indices, the comparisons of d spacings between calculated and observed values, and the observed intensities are listed in Table 1.

Table 1. Indices, observed and calculated values of d spacings and observed intensities for $CuCrZrS_4$ with the lattice constant a = 10.200 Å.

h	k	l	d_{obs}	d_{cal}	I_{obs}
1	1	1	5.9014	5.8852	23
2	2	0	3.6100	3.6039	22
3	1	1	3.0785	3.0734	100
4	0	0	2.5517	2.5484	45
3	3	1	2.3422	2.3385	2
4	2	2	2.0833	2.0807	6
5	1	1	1.9641	1.9617	31
3	3	3		1.9617	
4	4	0	1.8038	1.8020	50
5	3	1	1.7251	1.7230	3
6	2	0	1.6128	1.6117	2
5	3	3	1.5561	1.5545	8
4	4	4	1.4725	1.4713	3
7	1	1	1.4281	1.4274	1
5	5	1		1.4274	
6	4	2	1.3627	1.3622	2
7	3	1	1.3281	1.3271	7
5	5	3		1.3271	
8	0	0	1.2752	1.2742	3
6	6	0	1.2024	1.2013	1
8	2	2		1.2013	
7	5	1	1.1779	1.1770	4
5	5	5		1.1770	
8	4	0	1.1406	1.1397	4
9	1	1	1.1200	1.1196	1
7	5	3		1.1196	

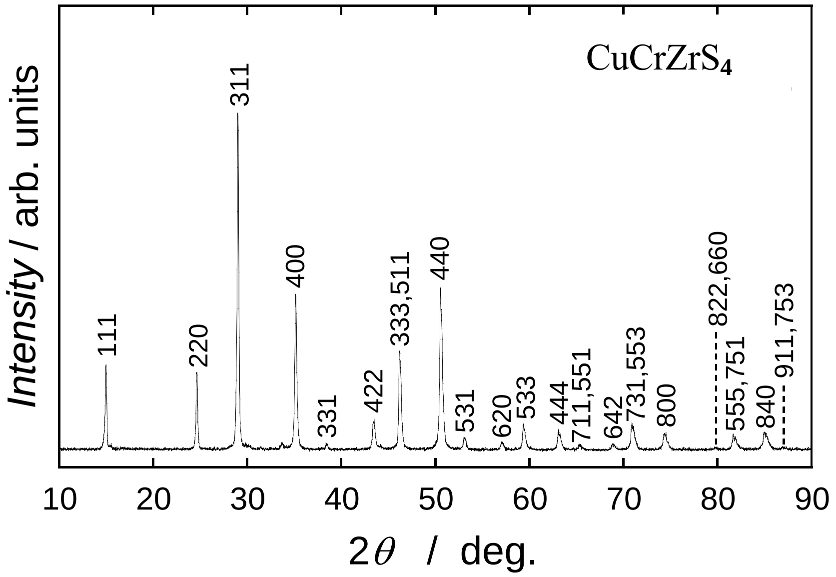

Figure 2. Powder X-ray diffraction pattern of $CuCrZrS_4$ at room temperature. The diffraction peaks can be indexed with cubic symmetry for the spinel structure.

3. 2. *Conductivity*

Figure 3 shows the temperature dependence of electrical resistivity ρ for the sintered specimen. The resistivity ρ exhibits a semiconducting behaviour. The value of ρ is of only relative significance because the measured resistivity depend on the filling density of the sintered specimen and on the grain boundaries. $CuCr_2S_4$ has metallic conductivity. The mixed valence state of Cr ions (Cr^{3+}-Cr^{4+}) results in the appearance of delocalized electrons due to the hopping between Cr^{3+} and Cr^{4+} ions. An electron jumps from the Cr^{3+} ion to the intervening sulfur ion, simultaneous with the jump of a second electron from the sulfur ion to the Cr^{4+} ion. If the concentration of Cr^{3+} and Cr^{4+} ions is comparable, an electron leaving a particular Cr^{3+} ion has an equal probability of jumping to any of Cr^{4+} ions which are its immediate neighbours. Thus, this double exchange interaction contributes to the electrical conduction. The introduction of Zr^{4+} ion into the B-site suppresses this interaction because of the existence of fixed valence state of Zr^{4+} ions. The Zr^{4+} ion substitution changes the character of conductivity from metallic to a semiconducting temperature dependence.

Figure 4 presents the conductivity $\sigma = 1/\rho$ as a function of $1/T$. The slope of the $\log\sigma$ vs. 1/T plot gives an activation energy $q = 6.84 \times 10^{-3}$ eV, obeying the equation of $\sigma = A\exp(-q / k_B T)$ in the temperature range 50-283 K as can be seen in figure 4. The straight slope breaks around 50 K. The experimental data σ can not be well reproduced by a single exponential formula for the wide measured temperature range. Around the Curie temperature $T_c = 60$ K, the resistivity does not indicate any anomaly but only a smooth variation of the semiconducting temperature dependence.

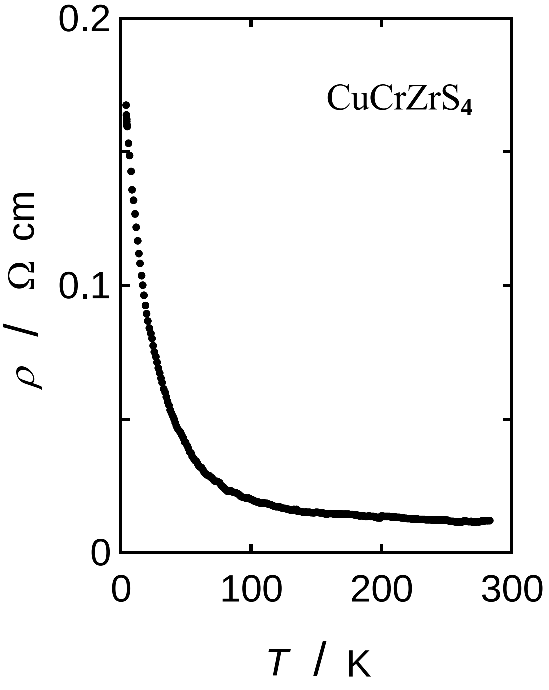

Figure 3. Temperature dependence of electrical resistivity ρ for a sintered $CuCrZrS_4$ specimen.

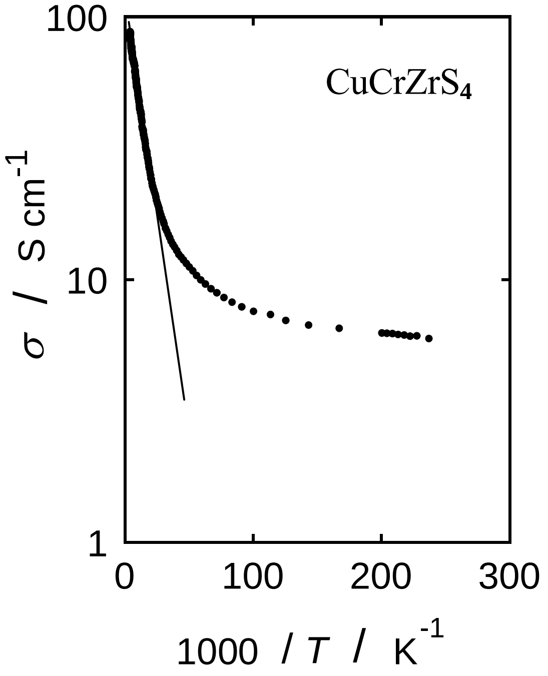

Figure 4. Temperature dependence of electrical conductivity $\sigma=1/\rho$ for a sintered $CuCrZrS_4$ specimen. The straight line indicates the result calculated for activation energy model for conduction.

3. 3. *Ferromagnetism*

It is noted that 4.2 K is a delicate temperature near the reentrant spin glass behaviour that is clearly detected in low-magnetic field with the separation between F.C. and Z.F.C. magnetization, which will be mentioned in the next section. The magnetization curves at 4.2 K are shown in figures 5 and 6. The demagnetizing field corrections for this *M-H* curve have not been made. This sample shows a narrow hysteresis loop. The residual magnetization is fairly small, and the coercive force is also very small as can be seen in figure 6. Saturated behavior at high magnetic field has not been observed. From figure 5, the magnitude of spontaneous magnetization is estimated from the extrapolation to zero field and found to be 1.11×10^3 emu / mol f.u., which assigns each Cr^{3+} ion to the value of magnetic moment n_B / Cr^{3+} ion to be 0.199 μ_B / f.u. The moment n_B refers gs = 3.0 μ_B expected for a Cr^{3+} free ion. The value of 0.199 μ_B is only 6.6 % of 3.0 μ_B. The magnetic moment is 0.347 μ_B / f.u. at 10 kOe. The magnetization is not saturated at 10 kOe. The magnetization is expressed as $M = M_0 + \chi H$. Any anomaly corresponding to a spin flip is not detected up to 10 k Oe.

More typical ferromagnetic properties will be expected over the temperature range $10 \leq T \leq 60$ K. A possible mechanism expected in the ferromagnetic state may be considered such as non-collinear spin alignment, for example in NiS_2 (Kikuchi 1979).

Figure 7 shows the result of the temperature dependence of the ac magnetic susceptibility χ_{AC}. The susceptibility rises rapidly at 60 K at which the temperature derivative $d\chi_{AC}/dT$ indicates the sharp anomaly, corresponding to the Curie temperature T_c. An anomaly is found below ≈10 K where the susceptibility drops with decreasing temperature, which is discussed in the next section as a reentrant spin glass.

Figure 8 presents the temperature dependences of the magnetization M and inverse magnetic susceptibility χ^{-1} which refers to $(M/H)^{-1}$ in a constant magnetic field 10.0 kOe. Figure 9 shows the results in 100.0 Oe, here the shallow decrease in M is seen below 10 K. The diamagnetic susceptibility is due to atomic cores and is estimated to be -1.85×10^{-4} emu/mol-f.u. for $CuCrZrS_4$ using the Pascal additive law (König 1976), and this magnitude is negligibly small. The susceptibility can be fitted to a modified Curie-Weiss law, $\chi = C / (T-\theta) +\chi_0$, where χ_0 is the temperature independent term, C is the Curie constant of the value of 1.55 K emu / mol f.u. and θ is the Weiss temperature. The value of θ refers to an asymptotic Curie temperature θ_p for a ferromagnet. The value of θ_p is approximately 65 K with ferromagnetic coupling, which is a little higher than T_c (60 K). The value of effective magnetic moment $\mu_{eff} = g\sqrt{s(s+1)}$ per formula unit is 3.61 extracted from the value of C. One Cr ion with a localized moment exists in each formula unit. The experimental result of μ_{eff} per one formula unit is obtained to be 3.61, which is a little less than 3.87 for the spin only value μ_{eff} / Cr^{3+} ion.

In addition, any indication of ferrimagnetic behaviour is not found. The characteristic ferrimagnetic curvature in χ^{-1} for a temperature not far above T_c is not detected. Our results of χ^{-1} show a completely straight line such as in figures 8 and 9, which is the feature of a ferromagnet. If the Cu ion would have a divalent state, which has s =1/2, anti-parallel to Cr

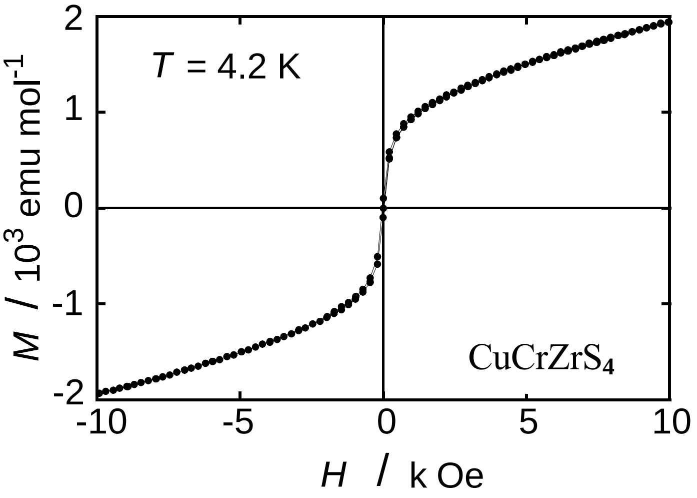

Figure 5. Magnetization curve for magnetic fields up to 10.0 kOe at 4.2 K.

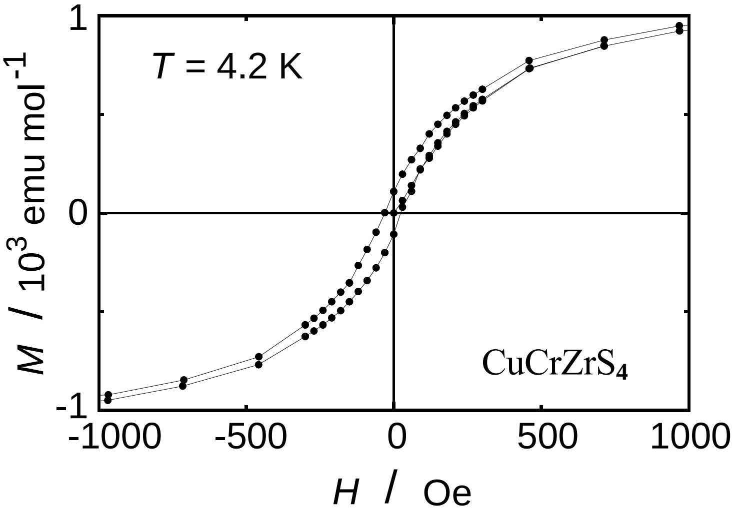

Figure 6. Magnetic hysteresis curve for magnetic fields up to 1.0 kOe at 4.2 K.

spins with ferrimagnetic coupling, then the curvature of the plot of χ^{-1} versus T should exhibit the characteristic asymptotic behaviour, which has not been observed. Therefore, these magnetic data lead to a conclusion that all the Cr ions possess a localized magnetic moment with $s = 3/2$, while Cu, Zr and S ions have basically no magnetic moment. These experimental results indicate strongly that the valence state of Cu ion is monovalent (Cu^+) and that of the Zr ion is tetravalent (Zr^{4+}), with both non-magnetic states.

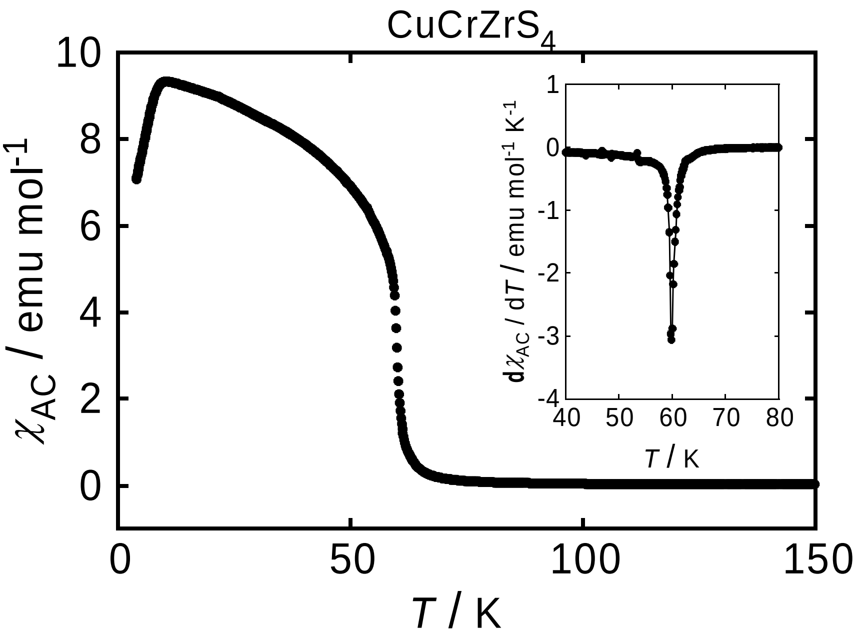

Figure 7. Temperature dependence of the ac magnetic susceptibility χ_{AC} for CuCrZrS$_4$ as a function of temperature. The demagetizing field corrections have been made. The inset shows the temperature derivative of χ_{AC}, which indicates the T_c at sharp negative peak.

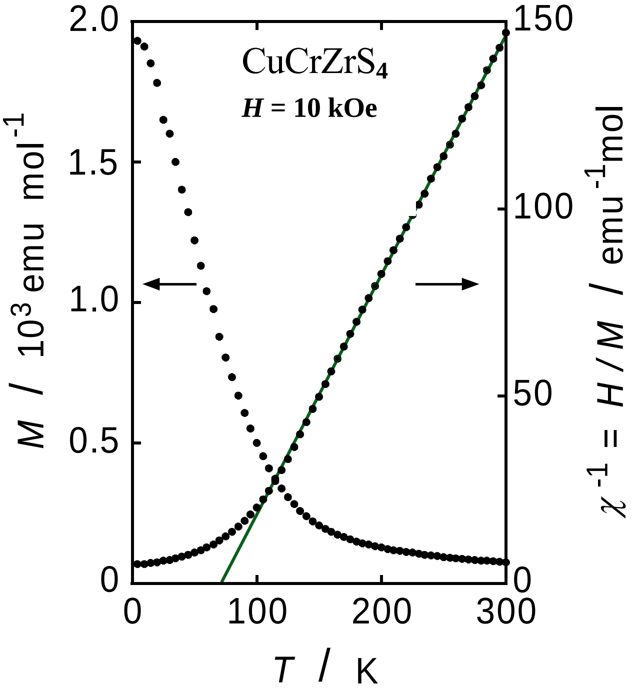

Figure 8. Temperature dependence of magnetization M and the inverse magnetic susceptibility $\chi^{-1} = (M/H)^{-1}$ for CuCrZrS$_4$ in a constant field of 10.00 kOe. The straight line is the Curie-Weiss law.

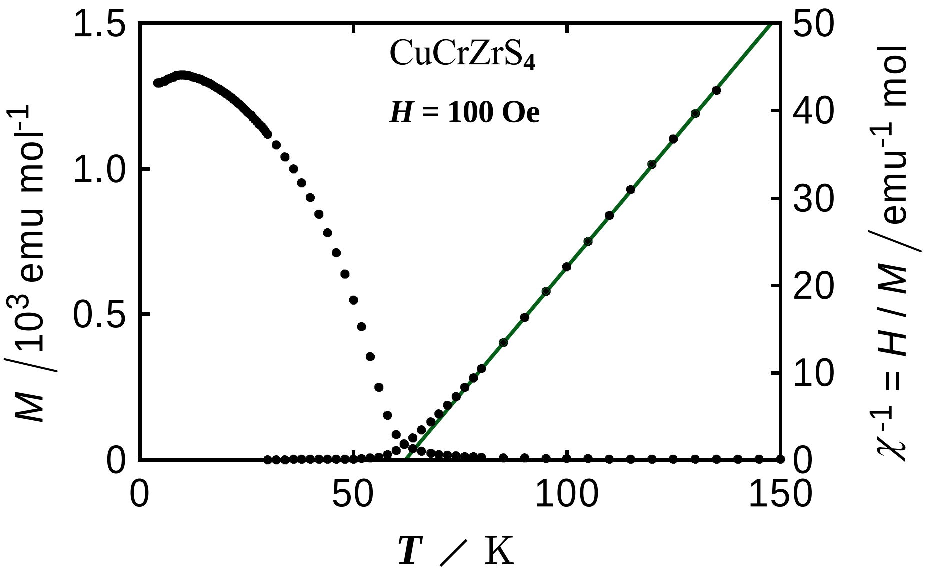

Figure 9. Temperature dependence of magnetization *M* and the inverse susceptibility χ^{-1} in a constant field of 100.0 Oe. This *M* is measured in field-cooled (F.C.) condition. The slight decrease in the magnetization below 10 K is detected; see text. The data on zero-field-cooled magnetization are not presented here, avoiding confusion.

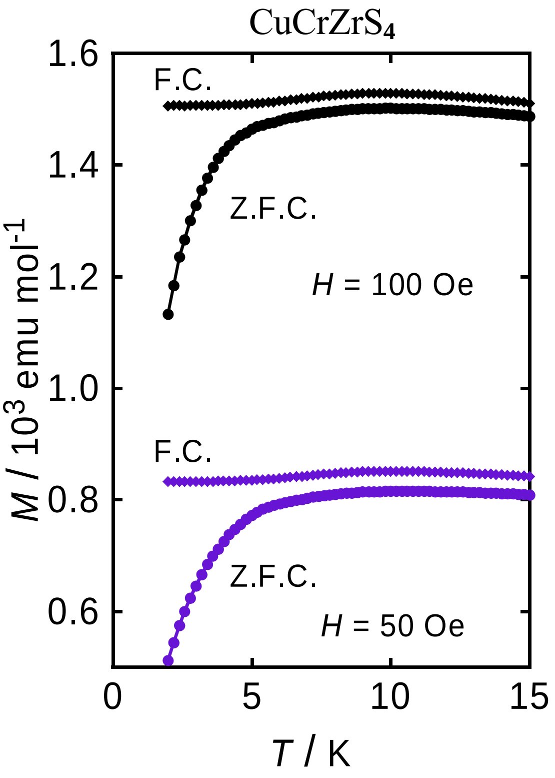

Figure 10. The difference between field-cooled (F.C.) and zero-field cooled (Z.F.C.) magnetization for a 100.0 Oe. F.C., field cooled; Z.F.C., zero-field cooled. The difference between the field-cooled and zero-field-cooled magnetization for the results at $T \geq 5$ K is larger in the lower magnetic field of 50 Oe than in a magnetic field of 100 Oe. The anomaly in χ_{AC} below 10 K corresponds to that of the zero-field-cooled magnetization.

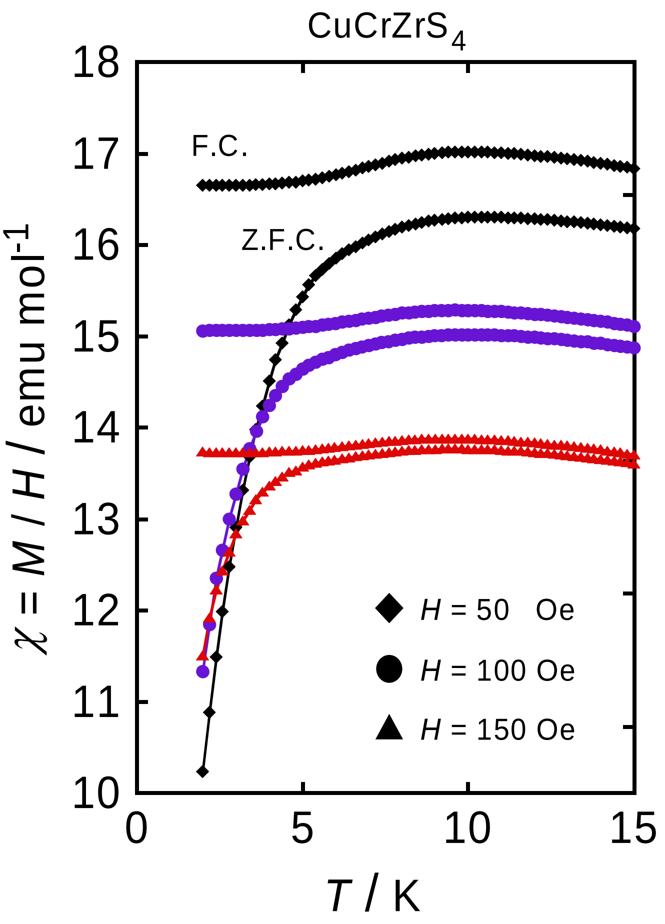

Figure 11. The difference between field-cooled and zero-field-cooled susceptibility for magnetic fields of 50, 100, and 150 Oe. F.C., field cooled; Z.F.C., zero-field cooled. The data in figures 10 and 11 are taken from the same specimen, which is different from the specimen used for figure 9.

3. 4. *Re-entrant spin glasses*

Figure 10 shows the appearance of an irreversible effect between field-cooled (F.C.) and zero-field cooled (Z.F.C.) magnetization in 50 and 100 Oe which is observed markedly below 5 K, such as Cu-Mn alloy (Nagata *et al.* 1979, Fischer and Hertz 1991, Mydosh 1993). The sudden drop in χ_{AC} below ≈10 K corresponds to the Z.F.C. magnetization. Figure 11 also presents the difference between F.C. and Z.F.C. magnetization at 150 Oe. This behaviour indicates a reentrant spin glass phase from the ferromagnetic state. The value itself of the difference between F.C. and Z.F.C. magnetization above 5 K decreases with increasing the external magnetic field.

It should be noted, first of all, that the breakdown of ferromagnetism and the reentrant transition to the spin glass phase in $CuCrZrS_4$ takes place in the dilute ferromagnetic system based on the pure ferromagnetic $CuCr_2S_4$ with T_c= 377 K. The magnetic phase diagram with respect to Zr composition has not been studied so far because this compound $CuCrZrS_4$ is new. The Curie temperature T_c decreases to 60 K in $CuCrZrS_4$, owing to 50 % dilution by Zr non-magnetic ion. The long range ferromagnetic order is depressed for the diluted system. This reentrant behaviour may be found only in the restricted Zr composition region around 50 % such as $Eu_xSr_{1-x}S$ (Maletta 1979, 1982). The specimen with a lower concentration of Zr shows strong ferromagnetic coupling with higher T_c without any reentrant phenomenon, while the lower one may reveal the simple transition from the high temperature paramagnetic to the spin glass phase at low temperature. The reentrant spin glass phase in $CuCrZrS_4$ originates from the random weak links of disordered clusters by dilution and by geometrical frustration. The B-sublattice in the spinel structure constructs a tetrahedral network. If the magnetic coupling is antiferromagnetic, then the spin alignment is highly unstable by the geometrical frustration even in the non-diluted system, such as the pyrochlore crystal structure.

It is conjectured that a tendency toward non-collinear coupling is introduced by the substitution of Zr ion into B-site, which is suggested by our magnetization results. Consequently, the long-range ferromagnetic order in $CuCrZrS_4$ is decoupled at lower temperature into the reentrant spin glass phase.

Finally we should like to point out that the study of the magnetic system for the compounds $CuCrTiS_4$ and $CuCrSnS_4$ is important because of the comparison with the present study. Furthermore, at the specimen preparation stage, the difference between the quenched and annealed specimens enables the spin glass phase to lead to critically different characteristics, because the location of Cr ion at B-site is random for quenched or the other distribution for annealed specimens. The present work is made on the annealed specimens. It is our hope that $CuCrZrS_4$ would be a candidate for an insulating compound for reentrant spin glass, expecting transparent statistical theoretical investigation in the near future.

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