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Substitution effect on the two-dimensional triangular-lattice system $CuCrS_2$

N Tsujii and H Kitazawa

National Institute for Materials Science, Sengen 1-2-1, Tsukuba, 305-0047, Japan

E-mail: TSUJII.Naohito@nims.go.jp

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Abstract

We have studied the magnetic susceptibility and specific heat of polycrystalline $CuCr_{1-x}V_xS_2$, the mother compound of which, $CuCrS_2$, has a nearly two-dimensional structure in which the triangular-lattice CrS_2 layer and the Cu-ion layer are stacked alternately. The temperature dependence of the magnetic susceptibility revealed that only the Cr ions have local magnetic moment, and the V ions are nonmagnetic. $CuCrS_2$ shows a long-range antiferromagnetic ordering at $T_N = 39$ K, which is found to be suppressed quickly by the V substitution. Above $x = 0.2$, the ordered state is replaced by a spin-glass behaviour with the transition temperature T_g decreasing gradually with increasing x. T_g is one order of magnitude smaller than the Weiss temperature θ, implying the dominant effect of geometrical frustration. The specific heat C of the spin-glass system, $CuCr_{0.7}V_{0.3}S_2$ ($x = 0.3$), is found to vary as $C \propto T^2$ below 10 K, similarly to those two-dimensional spin-liquid systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Inorganic compounds with nearly two-dimensional structure have attracted extensive attention since they often show interesting and important properties, both scientifically and industrially. The compound $CuCrS_2$ has a layered structure, as is shown in figure 1. The CrS_2 layers are sandwiched by Cu-ion layers [1, 2]. The Cu ion is monovalent and has no magnetic moment, while the Cr ion is trivalent with a localized moment $S = 3/2$ [1]. It is reported that $CuCrS_2$ exhibits antiferromagnetic ordering at $T_N = 39$ K [1, 3], and its magnetic structure is relatively complex with a helical-type arrangement [4]. It is notable that the Cr ions form a triangular lattice within the layer; thereby one can expect the effect of geometrical frustration.

There are some reports about the substituted system $CuCr_{1-x}M_xS_2$ with M = V [5] and Mn [6] up to $x = 0.2$. The authors reported that in much more highly substituted samples ($x \geqslant 0.2$), another phase like Cu_3VS_4 appears, and concluded that the solubility limit is $x = 0.2$

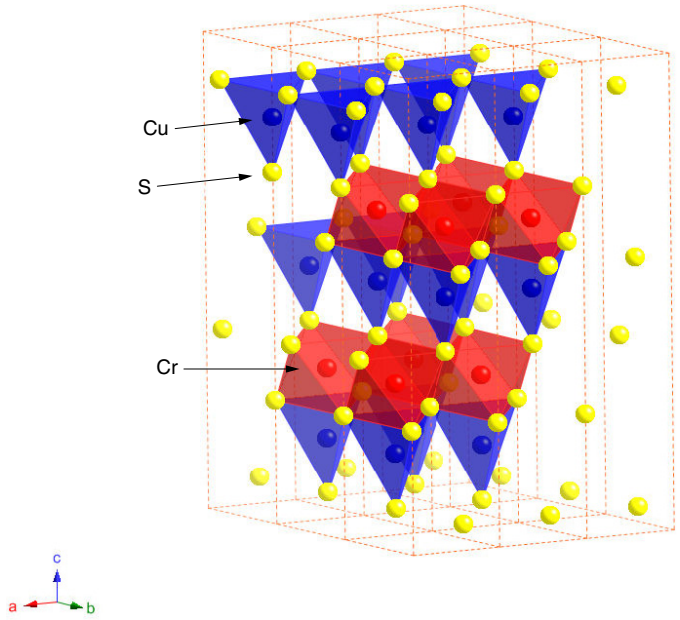

Figure 1. Crystal structure of $CuCrS_2$.

for both V and Mn [5, 6]. However, our recent studies have revealed that for $CuCr_{1-x}V_xS_2$, single-phased samples are obtained in a much larger composition range, $0 \leqslant x \leqslant 0.8$ [7], though the end compound $CuVS_2$ does not exist [8]. This difference would probably be due to the different reaction temperatures employed [7].

Here we present our results of magnetic and thermal properties of the substituted system $CuCr_{1-x}V_xS_2$.

2. Experimental details

Polycrystalline samples of $CuCr_{1-x}V_xS_2$ were prepared by a solid-state reaction in evacuated quartz tubes at high temperatures. Stoichiometric amounts of Cu_2S, Cr_2S_3 and V_2S_3 were mixed and ground in a mortar, pressed into pellets, and sealed in evacuated quartz tubes. These procedures were carried out under argon atmosphere in order to avoid oxidation. The tubes were heated at 850 °C for four days with intermittent grinding. Powder x-ray diffraction patterns was obtained to check the sample quality. As was reported previously, high-temperature reaction yielded a wide single-phased region, $0 \leqslant x \leqslant 0.8$ [7].

The magnetic susceptibility was measured with a SQUID magnetometer in the temperature range 2–300 K under a field of 1 kOe. Specific heat was measured by a relaxation method using a physical property measurement system from Quantum Design Co.

3. Results and discussion

In figure 2, the magnetic susceptibility of $CuCr_{1-x}V_xS_2$ is shown. Note that the susceptibility is plotted as χ_{Cr}, normalized value by the Cr concentration, $1-x$. All the samples show Curie–Weiss behaviour, $\chi = \frac{C}{T-\theta} + \chi_0$, where C, θ, χ_0 are the Curie constant, Weiss temperature,

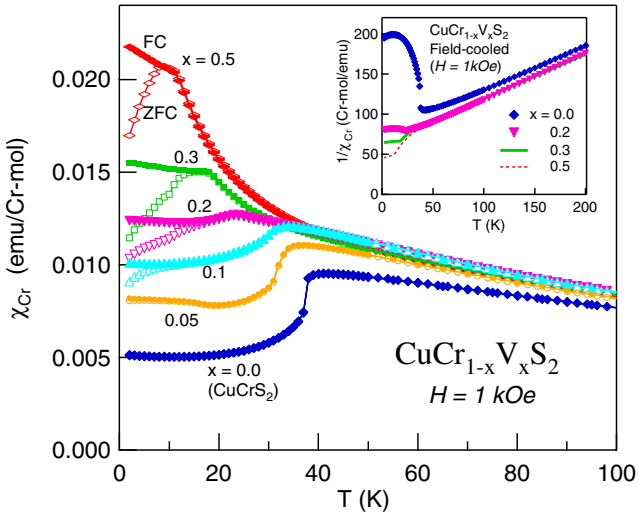

Figure 2. Temperature dependence of the magnetic susceptibility of $CuCr_{1-x}V_xS_2$. χ_{Cr} indicates that the susceptibility is normalized by the Cr concentration $(1 - x)$. Open and closed symbols represent the data of zero-field cooled measurements and those measured after cooling under $H = 1$ kOe, respectively. The inset shows the temperature dependence of $1/\chi_{Cr}$.

and temperature-independent susceptibility, respectively. We have fitted the data above 200 K by the Curie–Weiss function, and have estimated the effective Bohr magneton. Those values were 3.48–3.79 μ_B, almost consistent with the expected value for the Cr^{3+} ion ($S = 3/2$), 3.87 μ_B. This indicates that only the Cr ions have local magnetic moments, and the V ions are nonmagnetic. This is clearly seen from the inset of figure 2, the temperature dependence of the inverse of χ_{Cr}. For $x = 0$, 0.2, 0.3 and 0.5, the slopes in the Curie–Weiss region are in good agreement.

It is considered that both the Cr and V ions are trivalent. Since the V^{3+} ion can have local magnetic moment with $S = 1$, it seems curious that the V ions do not contribute to the Curie constants. Here, it should be noted that our previous study has shown that the electrical resistivities of these systems decrease rapidly with increasing x, and metallic conductivity appears in samples for $x \geqslant 0.8$ [7]. We hence suppose that the d electrons from the V ions behave as carrier electrons, which have temperature-independent Pauli paramagnetism.

In the main panel of figure 1, a magnetic transition is seen at low temperatures[1]. For $x = 0$, the sharp drop in χ is consistent with the antiferromagnetic transition at $T_N = 39$ K [1, 3]. For $x = 0.05$ and 0.1, a similar antiferromagnetic transition still remains, but T_N is reduced remarkably. Moreover, $x = 0.1$ shows a hysteresis behaviour at low temperature: χ measured after zero-field cooling (ZFC) and that after field-cooling under 1 kOe (FC) differs below $T_g = 12$ K. This behaviour is characteristic of short-range magnetic ordering, and for this case it most likely suggests the occurrence of a spin-glass transition. With increasing x, the spin-glass behaviour becomes dominant, and the antiferromagnetic transition disappears for $x \geqslant 0.2$.

[1] In our previous report [7], weak ferromagnetic-like behaviour was observed for $CuCr_{1-x}V_xS_2$ for $x \geqslant 0.1$ below 30 K. Such behaviour was not seen in the present data. The present measurements were carried out on new samples, which were prepared using different specimens. It is unclear whether the weak ferromagnetic behaviour was extrinsic. Neverthless, the electrical resistivity data of old samples, that show a gradual transition from insulator to metal with increasing x, is convincing.

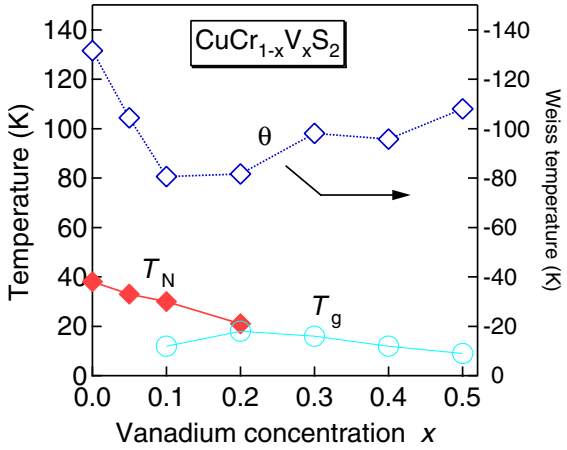

Figure 3. Magnetic phase diagram of $CuCr_{1-x}V_xS_2$. θ, T_N, and T_g represent the Weiss temperature, Néel temperature, and the temperature where spin-glass freezing occurs.

The origin of this spin-glass transition, on the one hand, would be the site disorder caused by the Cr–V substitution. On the other hand, the V ions do not have local moments, as was explained before; thereby a Néel-ordered state should still be the most stable ground state for those lightly substituted ($x \sim 0.2$) samples. Hence, the evolution of spin-glass state suggests the manifest geometrical-frustration effect in the Cr/V triangular-lattice structure. That effect of geometrical frustration is markedly seen in figure 3, in which the magnetic phase diagram of this system is shown. One can see that the Weiss temperature θ is around -100 K, almost one order of magnitude greater than the value of T_N or T_g. In general, geometrical frustration suppress the magnetic transition down to much lower temperatures than θ.

In figure 4, the specific heat of $CuCr_{1-x}V_xS_2$ is shown. For $x = 0$, an anomaly at T_N is clearly seen. This transition is hence a three-dimensional magnetic transition. For $x = 0.3$, the anomaly disappears, consistent with the spin-glass transition. We also have measured the specific heat under $H = 1$ kOe on heating after field-cooling. The results for the field-cooled sample were almost identical to that measured without field.

The most striking feature in figure 4 is the T^2-dependent C observed below about 8 K for $x = 0.3$. For conventional spin-glasses, C varies proportionally to T at $T < T_g$ [9]. The T^2-dependence is reminiscent of those of the kagome-lattice system $SrCr_8Ga_4O_{19}$ [10, 11], and of the triangular-lattice $NiGa_2S_4$ [12]. Both systems exhibit a spin-glass transition, but magnetic moments fluctuate dynamically even at very low temperatures [12, 13]. These systems are hence considered to be candidates of the spin-liquid system. The spin dynamics of $CuCr_{0.7}V_{0.3}S_2$ is also quite interesting.

For $x = 0.7$ ($CuCr_{0.3}V_{0.7}S_2$), the T-dependence of C is different from that when $x = 0.3$; $T^{1.5}$-dependence is seen below about 10 K. Although the origin of this behaviour is not yet clear, it should be noted that the electrical resistivity of $CuCr_{1-x}V_xS_2$ decreases with increasing x, and the system becomes metallic for $x \sim 0.8$ [7]. Since T-linear C is expected for metallic systems at low temperature, the $T^{1.5}$-dependent C for $x = 0.7$ may be due to a crossover from T^2 behaviour in $x = 0.3$ to T-linear C in the metallic state. In the present results, lattice contributions to the specific heat are not subtracted, thereby we could only discuss qualitatively using the low-temperature data. In order to discuss in more detail, more works should be performed.

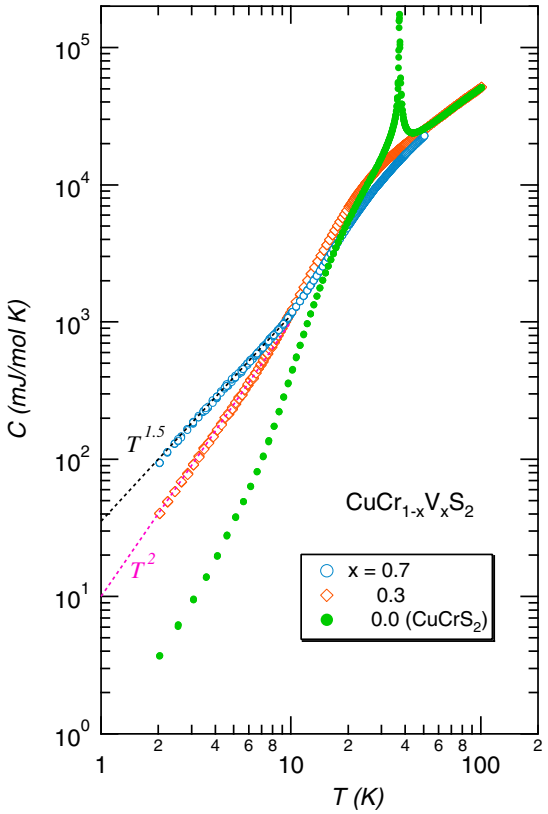

Figure 4. Log–log plot of the specific heat C and temperature T of $CuCr_{1-x}V_xS_2$.

4. Conclusion

Magnetic and thermal properties of the triangular-lattice system $CuCr_{1-x}V_xS_2$ have been studied. Magnetic susceptibility reveals that spin-glass behaviour develops at low temperatures for $x \geqslant 0.1$. Since the transition temperature and both T_N and T_g are much smaller than the Weiss temperature, it is suggested that geometrical frustration plays an important role in the magnetism of this system. Specific heat data reveal that C shows T^2 dependence at low temperatures for $x = 0.3$ instead of the T-linear C observed in conventional spin-glass systems. This quadratic temperature dependence is suggestive of dynamical spin fluctuation at low temperatures, similar to that in the frustrated compounds $SrCr_8Ga_4O_{19}$ and $NiGa_2S_4$.

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