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# $S = 1/2$ Kagomé antiferromagnets $\text{Cs}_2\text{Cu}_3\text{MF}_{12}$ with $\text{M} = \text{Zr}$ and $\text{Hf}$

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Received 8 September 2006

Published 23 March 2007

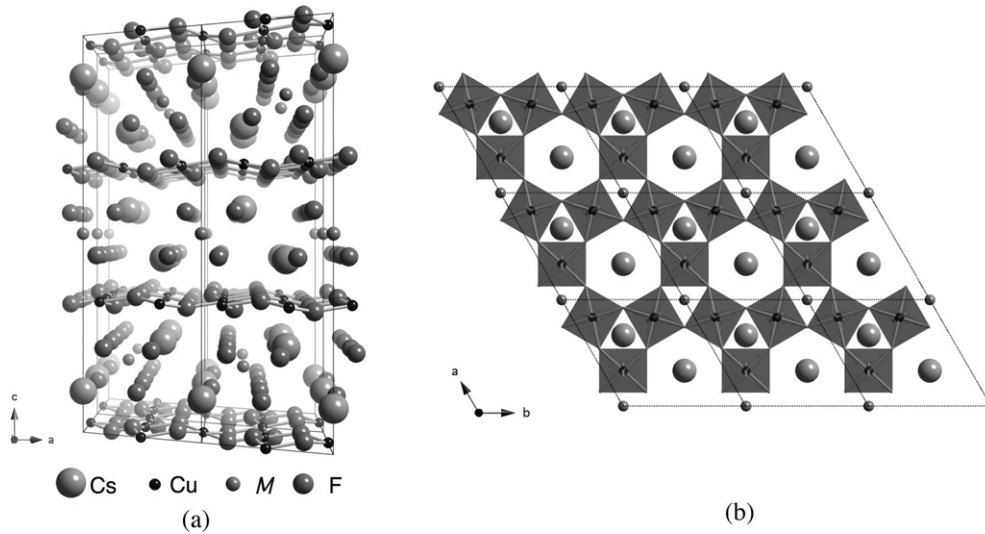
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## Abstract

Magnetization and specific heat measurements have been carried out on  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$  single crystals, in which  $\text{Cu}^{2+}$  ions with spin- $1/2$  form a regular Kagomé lattice. The antiferromagnetic exchange interaction between neighbouring  $\text{Cu}^{2+}$  spins is  $J/k_B \simeq 360$  and  $540$  K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. Structural phase transitions were observed at  $T_t \simeq 210$  and  $175$  K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. The specific heat shows a small bend anomaly indicative of magnetic ordering at  $T_N = 23.5$  and  $24.5$  K in  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. Weak ferromagnetic behaviour was observed below  $T_N$ . This weak ferromagnetism should be ascribed to the antisymmetric interaction of the Dzyaloshinsky–Moriya type that are generally allowed in the Kagomé lattice.

## 1. Introduction

Antiferromagnets with strong geometrical frustration are fascinating systems which can display a variety of exotic magnetic phases different from conventional Néel ordering [1, 2]. Recently, frustrated systems with strong quantum fluctuation have been attracting much attention from a viewpoint of the interplay of quantum fluctuation and spin frustration. The  $S = 1/2$  Kagomé antiferromagnet (KAF) is a typical example of such systems. There are many theoretical works on the  $S = 1/2$  KAF. By virtue of careful analyses and numerical simulation, it has been predicted that the ground state of the  $S = 1/2$  KAF is quantum spin liquid as the resonating valence bond state (RVB), and that there are a huge number of singlet excitations which fill up the triplet excitation gap [3–5]. However, this intriguing prediction has not been demonstrated experimentally. The experimental study of the  $S = 1/2$  KAF is limited because of few model substances. Three compounds,  $[\text{Cu}_3(\text{titmb})_2(\text{CH}_3\text{CO}_2)_6] \cdot \text{H}_2\text{O}$  [6],  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  [7], and  $\beta\text{-Cu}_3\text{V}_2\text{O}_8$  [8], are known to have Kagomé lattice or closely related lattices. However, the Kagomé net is distorted into an orthorhombic form in  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , and buckled like a staircase in  $\beta\text{-Cu}_3\text{V}_2\text{O}_8$ , so that the exchange network is anisotropic. For



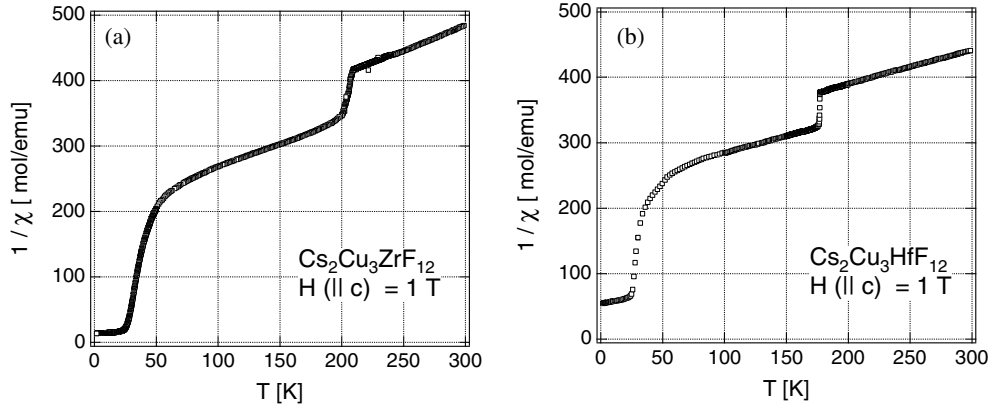
**Figure 1.** (a) The crystal structure of  $\text{Cs}_2\text{Cu}_3\text{MF}_{12}$  ( $M = \text{Zr}, \text{Hf}$ ) and (b) its projection onto the  $c$ -plane.  $\text{CuF}_6$  octahedra are shaded in (b).

$[\text{Cu}_3(\text{timb})_2(\text{CH}_3\text{CO}_2)_6]\cdot\text{H}_2\text{O}$ , the nearest-neighbour exchange interaction is ferromagnetic. Recently, Shores *et al* introduced the basic magnetic properties of  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  [9]. Taking into account the crystal structure and the results of  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , this compound should be a strong candidate of the ideal KAF, and several experimental studies are ongoing.

$\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  is a new  $S = 1/2$  KAF candidate [10]. In this paper, we will report the magnetic properties in  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$  in addition to those in  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$ , both of which were originally synthesized by Müller *et al* [11]. Figure 1 shows the room-temperature crystal structure of  $\text{Cs}_2\text{Cu}_3\text{MF}_{12}$  ( $M = \text{Zr}, \text{Hf}$ ) and its projection onto the  $c$ -plane. These compounds crystallize in trigonal structures (space group  $R\bar{3}m$ ) [11].  $\text{CuF}_6$  octahedra are connected in the  $c$ -plane, sharing corners. Magnetic  $\text{Cu}^{2+}$  ions with  $S = 1/2$  form a regular Kagomé lattice in the  $c$ -plane, and all of the nearest-neighbour exchange interactions are equivalent.  $\text{CuF}_6$  octahedra are elongated along the principal axes which are almost parallel to the  $c$ -axis, so that the hole orbitals  $d(x^2 - y^2)$  of  $\text{Cu}^{2+}$  spread in the Kagomé layer. Since the bond angle of superexchange  $\text{Cu}^{2+}-\text{F}^{-}-\text{Cu}^{2+}$  in the  $c$ -plane is about  $140^\circ$ , the nearest-neighbour superexchange interaction  $J$  through  $\text{F}^{-}$  ion in the Kagomé layer should be antiferromagnetic and strong. The interlayer exchange interaction  $J'$  should be much smaller than  $J$ , because magnetic  $\text{Cu}^{2+}$  layers are sufficiently separated by nonmagnetic  $\text{Cs}^+$ ,  $\text{Zr}^{4+}$  ( $\text{Hf}^{4+}$ ) and  $\text{F}^{-}$  layers. Thus, the present systems can be described as a quasi-two-dimensional (2D)  $S = 1/2$  KAF.

## 2. Experiments

$\text{Cs}_2\text{Cu}_3\text{MF}_{12}$  with  $M = \text{Zr}$  and  $\text{Hf}$  crystals were synthesized according to the chemical reaction  $2\text{CsF} + 3\text{CuF}_2 + \text{MF}_4 \rightarrow \text{Cs}_2\text{Cu}_3\text{MF}_{12}$ .  $\text{CsF}$ ,  $\text{CuF}_2$  and  $\text{ZrF}_4$  were dehydrated by heating in vacuum at  $\sim 150^\circ\text{C}$ . The materials were packed into a Pt tube in the ratio of 2:3:1. Single crystals of  $\text{Cs}_2\text{Cu}_3\text{MF}_{12}$  were grown by both vertical and horizontal Bridgman methods. The temperature at the centre of the furnace was set at  $700^\circ\text{C}$ . Transparent colorless crystals were obtained. The crystals obtained were identified to be  $\text{Cs}_2\text{Cu}_3\text{MF}_{12}$  by x-ray powder and



**Figure 2.** Temperature dependences of inverse magnetic susceptibilities in (a)  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and (b)  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$  measured at  $H = 0.1$  T for  $H \parallel c$ .

**Table 1.** Structural phase transition temperature  $T_t$ , Weiss constants  $\Theta$  and spontaneous magnetization  $M_{\text{sp}}$  at 1.8 K in  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , where  $T_t$  and  $\Theta$  are in units of K and  $M_{\text{sp}}$  is in units of  $\mu_{\text{B}}/\text{Cu}^{2+}$ .  $\Theta$  is obtained for  $H \parallel c$ .

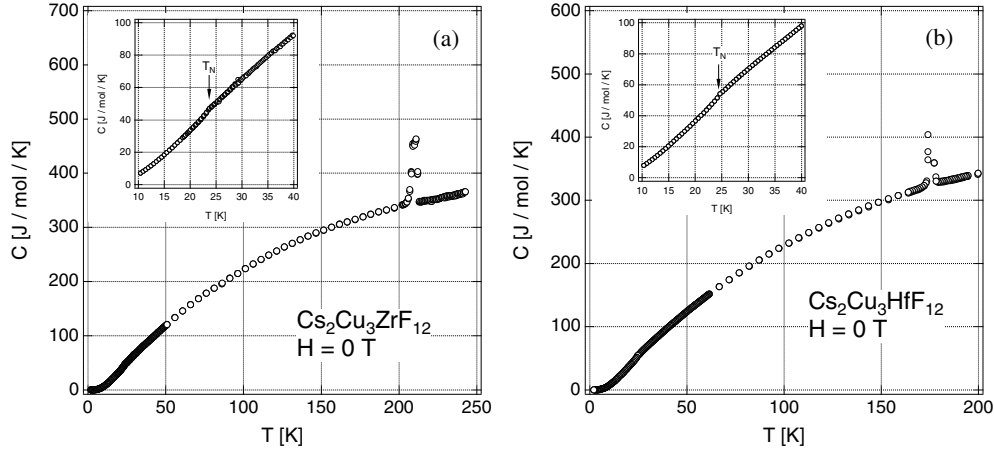
Substance	$T_t$	$\Theta (>T_t)$	$\Theta (<T_t)$	$M_{\text{sp}} (H \parallel c)$	$M_{\text{sp}} (H \perp c)$
$\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$	210	-360	-300	$\simeq 0.015$	$\simeq 0.071$
$\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$	175	-540	-450	$\simeq 0.010$	$\simeq 0.048$

single-crystal diffraction. The crystals were cleaved parallel to the  $c$ -plane. Magnetization was measured down to 1.8 K in magnetic fields up to 7 T, using a SQUID magnetometer (Quantum Design MPMS XL). The specific heat was measured down to 1.8 K, using a physical property measurement system (Quantum Design PPMS) by the relaxation method.

### 3. Results and discussion

Figure 2 shows the inverse magnetic susceptibilities of  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$  as functions of temperature measured for external field parallel to the  $c$ -axis. With decreasing temperature, the susceptibilities increase, obeying the Curie–Weiss law with large negative Weiss constants, which is indicative of strong antiferromagnetic exchange interaction. The Weiss constants obtained for  $H \parallel c$  are listed in table 1. The susceptibilities exhibit sudden jumps at  $T_t \simeq 210$  and 175 K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. In both systems, the phase transition at  $T_t$  has small hysteresis, which is indicative of the first-order transition. The susceptibilities obey the Curie–Weiss law also below  $T_t$ . These results indicate that the phase transition at  $T_t$  is not of magnetic but of structural origin. We tried to analyse the crystal structure below  $T_t$  by x-ray diffraction but did not succeed because of multidomain structures.

With further decrease of temperature, the magnetic susceptibilities increase rapidly below 40 K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and below 50 K for  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ . The spontaneous magnetizations were observed at  $T = 1.8$  K, as listed in table 1. The weak ferromagnetic moment for  $H \parallel c$  is much smaller than that for  $H \perp c$ . The weak ferromagnetic moment is intrinsic to the present system, because its magnitude is strongly dependent on field direction and independent of sample. Therefore, the rapid increase in the magnetic susceptibility at low temperatures is originated from magnetic ordering with the weak ferromagnetic moment.



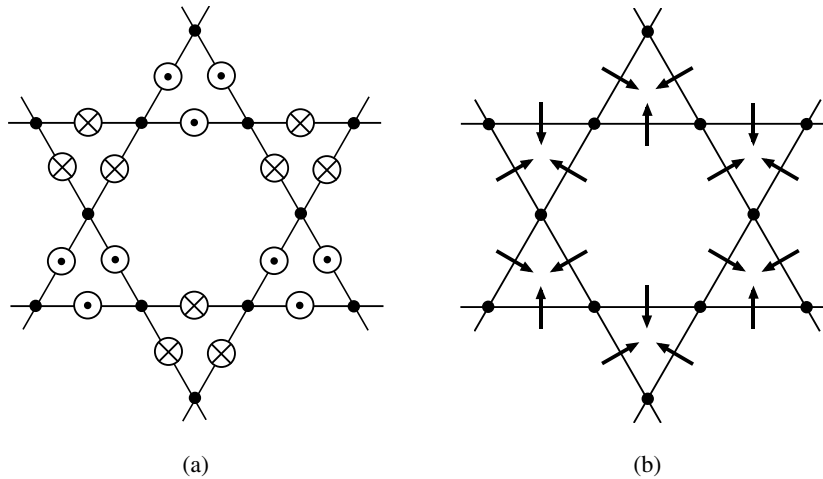
**Figure 3.** Temperature dependences of specific heat in (a)  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and (b)  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$  measured at zero magnetic field. The insets show the enlargements of low-temperature specific heat in both systems.

Within the mean-field theory, the Weiss constant for the Kagomé lattice is related to the nearest-neighbour exchange interaction as  $\Theta = -J/k_B$ , where  $J$  is defined as  $\mathcal{H} = \sum_{(i,j)} J(\mathbf{S}_i \cdot \mathbf{S}_j)$ . From the Weiss constants listed in table 1, we obtain  $J_H/k_B \simeq 360$  K and  $J_L/k_B \simeq 300$  K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$ , and  $J_H/k_B \simeq 540$  K and  $J_L/k_B \simeq 450$  K for  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , where  $J_H$  and  $J_L$  are exchange interactions above and below  $T_t$ , respectively. In both systems, the exchange interactions are antiferromagnetic and strong. This is attributed to the facts that the hole orbitals  $d(x^2 - y^2)$  of  $\text{Cu}^{2+}$  spread in the Kagomé layer, and that the bond angle  $\text{Cu}^{2+}-\text{F}^{-}-\text{Cu}^{2+}$  of about  $140^\circ$  is much larger than  $90^\circ$  and rather close to  $180^\circ$  for which strong antiferromagnetic superexchange interaction can be produced [12].

Figure 3 shows the temperature dependences of total specific heat in  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ . Sharp peaks are observed at the structural phase transition temperature  $T_t \simeq 210$  and 175 K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. Peaks at  $T_t$  are not  $\lambda$ -like due to the first-order transitions.

As shown in the insets of figure 3, the specific heat exhibits a small bend anomaly at  $T_N = 23.5$  and 24.5 K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. This anomaly is different from  $\lambda$ -like and cusplike anomalies which are characteristic of a phase transition of the second order. The small specific heat anomaly is indicative of a small change in the entropy at  $T_N$ .  $T_N$  increases with increasing applied field; for example, for  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ ,  $T_N = 28.8$  K at  $H = 9$  T. At present, the spin structure below  $T_N$  is unclear. The ratio of  $|\Theta|$  to  $T_N$  is approximately 10 for both systems. The large  $|\Theta|/T_N$  value implies good two-dimensionality and strong frustration in the present systems.

Next, we discuss the origin of the weak ferromagnetic moment. There is no inversion centre at the middle point of two neighbouring magnetic ions in the Kagomé lattice. This situation differs from that in the triangular lattice. Thus, in general, antisymmetric interaction of the Dzyaloshinsky–Moriya (DM) type,  $\mathcal{H}_{\text{DM}} = \sum_{(i,j)} \mathbf{D}_{ij} \cdot [\mathbf{S}_i \times \mathbf{S}_j]$ , is allowed, and DM interaction should be taken into account at low temperature [13]. For the high symmetric crystal structure above  $T_t$  in which the regular Kagomé lattice is realized, there are mirror planes that are parallel to the  $c$ -axis, cross the middle points of neighbouring  $\text{Cu}^{2+}$  ions and are perpendicular to the lines connecting these ions. Therefore, the  $\mathbf{D}$  vectors should be parallel to the mirror planes. Since there are two-fold screw axes along the [100], [010] and [110]



**Figure 4.** Arrangement of the  $D$  vectors for  $T > T_l$  in  $\text{Cs}_2\text{Cu}_3\text{MF}_{12}$  systems, (a) the  $c$ -axis component and (b) the  $c$ -plane component.

directions, the  $D$  vectors become antiparallel along these directions. Thus, arrangement of the  $D$  vectors should be as shown in figure 4. In this case, if the Néel ordering occurs, the DM interaction acts to stabilize the so-called  $q = 0$  structure and also gives rise to the weak ferromagnetic moment due to the canting of ordered moments. If the ground state is a spin liquid as the RVB state, the DM interaction acts to mix the excited triplet state into the ground singlet state, which leads to the magnetic ground state with finite susceptibility. Although the details of the crystal structure below  $T_l$  are not clear at present, we infer that the weak ferromagnetic moment observed below  $T_N$  is attributed to the DM interaction, because the low-temperature crystal structure is expected to be closely related to the high-temperature crystal structure.

#### 4. Conclusion

We have presented the results of magnetization and specific heat measurements on single crystals of  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$  which are described as quasi-2D  $S = 1/2$  Kagomé antiferromagnets. Both systems undergo structural phase transitions, at  $T_l \simeq 210$  and 175 K, respectively. Magnetic orderings accompanied with the weak ferromagnetic moment occur at  $T_N = 23.5$  and 24.5 K for  $\text{Cs}_2\text{Cu}_3\text{ZrF}_{12}$  and  $\text{Cs}_2\text{Cu}_3\text{HfF}_{12}$ , respectively. At present, the spin structure in the ground state is not clear. The Dzyaloshinsky–Moriya interaction that is generally allowed in the Kagomé lattice should be responsible for the weak ferromagnetic moment. For further discussion on the magnetic ground state, we need detailed data of the crystal structure below  $T_l$ . The present systems are characterized as  $S = 1/2$  Kagomé antiferromagnets with strong exchange interactions,  $J/k_B = 360$ –540 K. Therefore, novel magnetic excitations predicted by recent theory [3–5] may be examined by neutron inelastic scattering just above  $T_l$  where the regular Kagomé lattice is realized.

#### Acknowledgments

The authors would like to thank I Yamada for useful suggestions on the sample preparation. This work was supported by a Grant-in-Aid for Scientific Research and the 21st Century

COE Program at Tokyo Tech ‘Nanometer-Scale Quantum Physics’, both from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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