A Possible Magnetic Structure of the Cluster-Based Haldane Compound Fedotovite $K_2Cu_3O(SO_4)_3$

Masashi Hase[1]*, Kirrily C. Rule[2], James R. Hester[2], Jaime A. Fernandez-Baca[3], Takatsugu Masuda[4], and Yukari Matsuo[5]

[1]*Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305-0047, Japan*

[2]*Australian Nuclear Science and Technology Organisation (ANSTO), Locked Bag 2001, Kirrawee DC NSW 2232, Australia*

[3]*Neutron Scattering Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee 37831-6393, USA*

[4]*The Institute for Solid State Physics (ISSP), The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan*

[5]*Department of Advanced Sciences, Hosei University, 3-7-2 Kajino-cho, Koganei-shi, Tokyo 184-8584, Japan*

We carried out neutron powder diffraction experiments on the cluster-based Haldane compound fedotovite $K_2Cu_3O(SO_4)_3$. Weak magnetic reflections caused by a magnetic long-range order appeared below an antiferromagnetic transition temperature T_N = 3.1 K. We propose a possible magnetic structure that is consistent with the magnetic properties reported in the literature.

1. Introduction

Fedotovite $K_2Cu_3O(SO_4)_3$ is attractive in the field of quantum spin systems.[1)] The spin system in $K_2Cu_3O(SO_4)_3$ consists of spin hexamers which can be described as follows. The lines in Figs. 1(a) and (b) show short Cu-Cu pairs and Cu-O-Cu paths, respectively. The Cu-Cu distances are 3.408 Å or shorter at room temperature. The other Cu-Cu distances are 4.234 Å or longer. From the configuration of Cu^{2+} and O^{2-} ions, Fujihala *et al.* considered that six spins ($S = \frac{1}{2}$) on Cu^{2+} ions form a spin cluster (hexamer). Figure 1(c) shows schematically the spin hexamer proposed by Furrer *et*

*HASE.Masashi@nims.go.jp

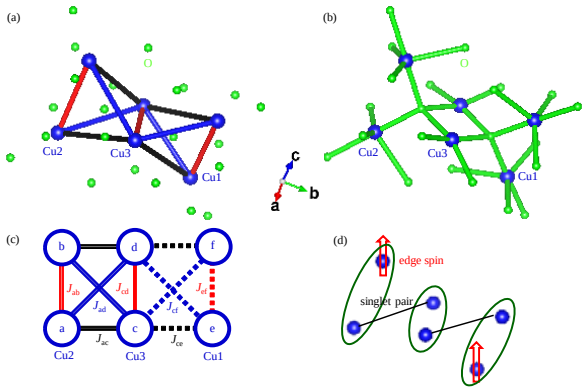

Fig. 1. (Color online) (a) Schematic picture of the Cu^{2+} hexamer (six-spin cluster) in $K_2Cu_3O(SO_4)_3$. There are three crystallographic Cu sites (Cu1, Cu2, and Cu3) having spin-$\frac{1}{2}$. The lines show short Cu-Cu pairs. (b) Schematic picture showing Cu-O-Cu paths. The configurations of Cu and O in (a) and (b) are the same. Details of the Cu-O-Cu paths and expected exchange interactions are described in the Supplemental Material of the literature.[1] (c) Exchange interactions expected in the spin hexamer. Furrer *et al.* evaluated the exchange interactions as follows; $J_{\rm ab} = -3.4$, $J_{\rm cd} = -8$, $J_{\rm ef} = -3.8$, $J_{\rm ac} = 7.4$, $J_{\rm ce} = 8.0$, $J_{\rm ad} = 19.0$, and $J_{\rm cf} = 17.0$ meV.[2] Fujihala *et al.* evaluated the exchange interactions as follows; $J_{\rm ab} = J_{\rm cd} = J_{\rm ef} = -3.0$, $J_{\rm ac} = J_{\rm ce} = 10.8$, and $J_{\rm ad} = J_{\rm cf} = 10.8$ meV.[1] Here, the exchange interactions are defined in the Hamiltonian $\mathcal{H} = \sum_{ij} J_{ij} S_i \cdot S_j$. (d) Schematic spin configuration of the triple states in the hexamer.[1] Two blue circles in a green oval means two Cu sites connected by one of the ferromagnetic interactions. The edge spins are denoted by a red arrow. The line indicates a singlet pair.

al.[2] As shown in Fig. 1(b) in the literature,[2] the ground states (GSs) of each hexamer in zero magnetic field are triplet states ($S = 1$) and are well separated from the excited states (by more than 12 meV). Therefore, it is enough that we consider only the triplet GSs in the energy range of a few meV or less. As shown in Fig. 1(d), it was considered that edge spins appeared on Cu1 and Cu2 sites and that spins on Cu3 and Cu1 (or Cu2) sites formed singlet pairs.[1]

A one-dimensional array of the hexamers was considered to be formed by weak antiferromagnetic (AF) intercluster exchange interactions along the b direction.[1] The hexamer corresponds to a Ni^{2+} ion in Ni-based Haldane compounds and a Haldane system of the hexamers can be expected. Fujihala *et al.* considered that gapped spectra at 1.5 K obtained in the inelastic neutron scattering experiments originate from the Haldane gap. The temperature (T) dependence of the magnetic excitations, however, is slightly different from that of other Haldane compounds. In $K_2Cu_3O(SO_4)_3$ where the value of the gap (Δ) at low temperature is 7.1 K, the magnetic excitations seem gapless

at 4.0 K.[1)] On the other hand, magnetic excitations are gapped even at high T in other Haldane compounds, for example, at 80 K in Y_2BaNiO_5 ($\Delta = 99$ K)[3)] and at 30 K in $Ni(C_3H_{10}N_2)_2N_3(ClO_4)$ (NINAZ) ($\Delta = 42$ K).[4)] In addition, the energy at which the intensity of the magnetic excitations is maximum is smaller at 4.0 K than that at 1.5 K in $K_2Cu_3O(SO_4)_3$, whereas the energy increases on heating in Y_2BaNiO_5 and NINAZ.

Fujihala *et al.* considered that the magnetic behavior above 4.0 K is determined by the single hexamer (not by the chain of hexamers) and therefore that the spin gap is closed at 4.0 K.[1)] To understand the T dependence of the magnetic excitations, it is important to investigate further differences in the magnetism below and above 4.0 K. The specific heat divided by T shows a maximum around 3 K in zero magnetic field.[1)] Fujihala *et al.* considered that the maximum indicates the existence of the spin gap. We infer, on the other hand, that the maximum suggests the occurrence of a magnetic long-range order (LRO) around 3 K. Fujihala *et al.* observed no magnetic reflections in the neutron powder diffraction measurement at 1.5 K.[1)] However, we think that it is important to reinvestigate whether a magnetic LRO exists or not using a neutron spectrometer with low background to understand properly the magnetism of $K_2Cu_3O(SO_4)_3$. Accordingly, we performed neutron powder diffraction experiments on $K_2Cu_3O(SO_4)_3$ using cold-neutron triple-axis spectrometers.

2. Experimental Methods

Crystalline $K_2Cu_3O(SO_4)_3$ powder was synthesized by a solid-state reaction. The starting materials were K_2SO_4 (purity 99 %), $CuSO_4$ (99.9 %), and CuO (99.99 %) powder. A stoichiometric mixture of powder was sintered at 783 K in air for 10 h in total. An X-ray powder diffraction pattern was measured at room temperature using an X-ray diffractometer (RINT-TTR III, Rigaku). We detected only the allowed reflections of $K_2Cu_3O(SO_4)_3$[5)] which leads us to believe that our sample is a single phase of $K_2Cu_3O(SO_4)_3$ within experimental accuracy.

We performed magnetization measurements using a superconducting quantum interference device magnetometer (magnetic property measurement system, Quantum Design). Preliminary neutron powder diffraction experiments were performed using the cold-neutron triple-axis spectrometer CTAX at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). Follow-up measurements were performed using the cold-neutron triple-axis spectrometer, SIKA, at the Open Pool Australian Lightwater (OPAL) reactor at ANSTO. We carried out Rietveld refinements of the

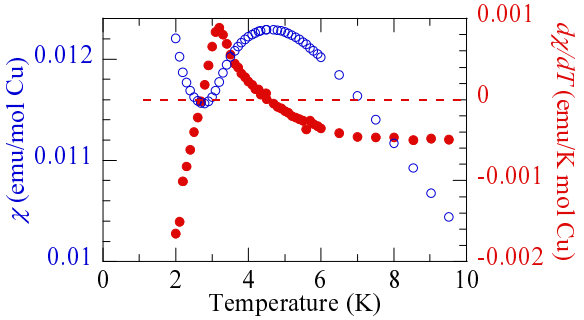

Fig. 2. (Color online) Temperature (T) dependence of the magnetic susceptibility [$\chi(T)$] of $K_2Cu_3O(SO_4)_3$ in a magnetic field of $H = 0.1$ T (blue open circles) and T derivative of the magnetic susceptibility [$d\chi(T)/dT$] (red solid circles).

crystal and magnetic structures using the FULLPROF SUITE program package[6] with its internal tables for scattering lengths and magnetic form factors.

3. Results

The blue open circles in Fig. 2 show the T dependence of the magnetic susceptibility [$\chi(T)$] of $K_2Cu_3O(SO_4)_3$ powder in a magnetic field of $H = 0.1$ T. The broad maximum of $\chi(T)$ around 4.6 K indicates the low-dimensional AF spin system with short-range correlations. The susceptibility obtained in this result is slightly different from that reported by Fujihala *et al.*[1] Probably the Curie-Weiss term is larger in our sample than in their sample although we cannot evaluate the Curie constant because of lack of $\chi(T)$ below 2 K. The red solid circles show the T derivative of $\chi(T)$ [$d\chi(T)/dT$]. A λ-type peak typical of the second order phase transition was observed in $d\chi(T)/dT$ at around 3.1 K. The peak suggests an AF transition at $T_N = 3.1$ K.

We performed preliminary neutron powder diffraction experiments on $K_2Cu_3O(SO_4)_3$ using the CTAX spectrometer at ORNL. Diffraction patterns at 1.6 K and 4.2 K suggest the appearance of magnetic reflections.[7]

We performed follow-up neutron powder diffraction experiments using the SIKA spectrometer at ANSTO. The horizontal collimator sequence was open-20'-sample-20'-60'. The red circles with error bars in Fig. 3(a) indicate a neutron powder diffraction pattern of $K_2Cu_3O(SO_4)_3$ at 2.2 K. The blue line on the experimental pattern portrays the result of Rietveld refinements and agrees well with the experimental pattern. We evaluated the scale coefficient for refinements of the magnetic structure from the results of the refinements of the crystal structure.

The red circles with error bars in Fig. 3(b) indicate a difference pattern of $K_2Cu_3O(SO_4)_3$ made by subtracting a neutron powder diffraction pattern at 5 K from that at 1.7 K obtained using the SIKA spectrometer. From the results of the CTAX measurements,[7] we inferred that magnetic reflections were observable in the three Q ranges in Fig. 3(b). We measured high-statistics data at 1.7 and 5 K only in the three Q ranges. We observed a magnetic reflection at $Q = 1.41$ Å^{-1} as in the CTAX results.[7] The magnetic reflection is weak but well-defined within experimental accuracy and is as sharp as the nuclear reflection at $Q = 1.37$ Å^{-1}. Therefore, the magnetic reflection is resolution-limited and indicates the appearance of a magnetic LRO. In addition, other weak magnetic reflections may exist around $Q = 0.75$ and 1.0 Å^{-1}.

4. Discussion

We looked for magnetic structures that were consistent with the magnetic properties reported in the literature such as an absence of magnetic frustration, an absence of spontaneous magnetization, and the signs of the exchange interactions in the hexamer.[1,2] From the positions of the magnetic reflections, we inferred that the propagation vector of the magnetic structures was $\mathbf{k} = (0, 0, 0)$. This propagation vector implies that magnetic frustration, which can generate incommensurate magnetic structures, does not exist. We simply considered a common irreducible representation for all the Cu sites due to the absence of magnetic frustration. We have four possible Shubnikov groups as listed in Table I.[8] Spontaneous magnetizations [ferromagnetic (F) components] were not observed. If the Shubnikov group for $K_2Cu_3O(SO_4)_3$ is $C2/c$, the v component should be negligible. If the Shubnikov group is $C2'/c'$, both the u and w components should be negligible. Here, u, v, and w are components of an ordered magnetic moment in the a, b, and c coordinates, respectively. As shown in Fig. 1, the J_{ab}, J_{cd}, and J_{ef} interactions are ferromagnetic. Magnetic moments of sites (1) and (2) in Table I are coupled by these interactions. Therefore, the signs of dominant components of magnetic moments of sites (1) and (2) should be the same. In $C2/c$, the signs of the u and w components of site (1) are opposite those of site (2). In $C2'/c'$, the sign of the v component of site (1) is opposite that of site (2). Consequently, magnetic structures based on $C2/c$ and $C2'/c'$ are not consistent with the reported magnetic properties.[1,2]

Let us consider $C2/c'$ and $C2'/c$. As described, the signs of dominant components of magnetic moments of sites (1) and (2) should be the same. The v component is probably dominant in $C2/c'$. Similarly, the u and w components are probably dominant in $C2'/c$.

Table I. Four possible Shubnikov groups (first row) in monoclinic $C2/c$ for the magnetic structure with the propagation vector $\mathbf{k} = (0, 0, 0)$. The most left line shows symmetry operations of $8f$ sites. Components of an ordered magnetic moment in the a, b, and c coordinates are indicated by u, v, and w, respectively.

	$C2/c$	$C2'/c$	$C2/c'$	$C2'/c'$
(1) x, y, z	u, v, w	u, v, w	u, v, w	u, v, w
(2) $\bar{x}, y, \bar{z}+1/2$	$\bar{u}, v, \bar{w}$	$u, \bar{v}, w$	$\bar{u}, v, \bar{w}$	$u, \bar{v}, w$
(3) $\bar{x}, \bar{y}, \bar{z}$	u, v, w	$\bar{u}, \bar{v}, \bar{w}$	$\bar{u}, \bar{v}, \bar{w}$	u, v, w
(4) $x, \bar{y}, z+1/2$	$\bar{u}, v, \bar{w}$	$\bar{u}, v, \bar{w}$	$u, \bar{v}, w$	$u, \bar{v}, w$
(5) $x+1/2, y+1/2, z$	u, v, w	u, v, w	u, v, w	u, v, w
(6) $\bar{x}+1/2, y+1/2, \bar{z}+1/2$	$\bar{u}, v, \bar{w}$	$u, \bar{v}, w$	$\bar{u}, v, \bar{w}$	$u, \bar{v}, w$
(7) $\bar{x}+1/2, \bar{y}+1/2, \bar{z}$	u, v, w	$\bar{u}, \bar{v}, \bar{w}$	$\bar{u}, \bar{v}, \bar{w}$	u, v, w
(8) $x+1/2, \bar{y}+1/2, z+1/2$	$\bar{u}, v, \bar{w}$	$\bar{u}, v, \bar{w}$	$u, \bar{v}, w$	$u, \bar{v}, w$

As shown in Fig. 1(d), spins on the Cu3 sites are nearly zero.[1)] Therefore, we take the moments on Cu1 and Cu2 sites into account. In $C2/c'$, when the v components of Cu1 and Cu2 sites are refined, the calculated magnetic reflection around $Q = 1.41$ Å^{-1} is not largest in all the calculated ones. We consider that $C2/c'$ is not applicable to the magnetic structure of $K_2Cu_3O(SO_4)_3$.

In $C2'/c$, when the u and w components of the Cu1 and Cu2 sites are refined simultaneously, values of these components do not converge which is probably due to the limited number of magnetic reflections. When only the w components of Cu1 and Cu2 sites are refined, the calculated magnetic reflection around $Q = 1.41$ Å^{-1} is not largest in all the calculated ones. When only the u components of Cu1 and Cu2 sites are refined, the calculated magnetic reflection around $Q = 1.41$ Å^{-1} is largest in all the calculated ones as indicated by the blue line in Fig. 3 (b). Consequently, we infer that $C2'/c$ is most applicable to describe the magnetic structure of $K_2Cu_3O(SO_4)_3$.

We consider the reason why only the magnetic reflection at 021 around $Q = 1.41$ Å^{-1} is statistically relevant. Table II shows calculated intensities of major magnetic reflections and nuclear reflections near the magnetic reflections. The intensities of the magnetic reflections at 110, 111, -203, and 003 are smaller by one order of magnitude than the intensity of the magnetic reflection at 021. Large nuclear reflections overlap with the magnetic reflections at -201, 111, 201, and -203. Therefore, it is difficult to extract properly the magnetic reflections at these indices. Accordingly, only the magnetic reflection at 021 was clearly observed. Intensities of magnetic reflections were calculated

Table II. Calculated intensities of major magnetic reflections and nuclear reflections near the magnetic reflections. The symbol "F" means a forbidden reflection. We consider only the u components. Therefore, the intensities of several allowed magnetic reflections are 0.

Q (Å^{-1})	Index	$I_{\rm magn}$ (arb. unit)	$I_{\rm nucl}$ (arb. unit)
0.701	-201	101	F
0.709	200	0	85,224
0.752	110	41	16
0.950	002	0	8,988
0.954	111	34	4,994
0.965	-202	0	9,710
0.982	201	223	F
1.350	-203	34	F
1.370	202	0	13,380
1.402	-402	0	11,232
1.409	021	409	466
1.425	003	47	F

from $Q = 0.70$ to 1.45 Å^{-1} in the Rietveld refinements. The maximum intensity between the three Q ranges in Fig. 3(b) is 8. Therefore, we think that we were not able to detect magnetic reflections between the three Q ranges in the CTAX measurements.[7)]

Figure 4 shows the "possible" magnetic structure. The values of u are $0.5(2)\mu_{\rm B}$ and $-1.0(2)\mu_{\rm B}$ at 1.7 K on the site (1) of Cu1 and that of Cu2, respectively. The w components of Cu1 and Cu2 sites may not be negligible. As described, however, we were not able to evaluate them in Rietveld refinements. The ratio of the Cu1 and Cu2 atoms to the total atoms is 2 : 21. Since the concentration of Cu sites having the ordered moments is small, the magnetic reflections are very weak as the magnitudes of the ordered moments. The ordered moments are parallel to one another in each hexamer. This alignment is consistent with the signs of the intracluster interactions. The magnetic structure indicates that intercluster interactions are F, F, and AF in the a, b, and c directions, respectively, whereas the AF chains were considered to be formed parallel to the b direction.[1)] We have to reconsider the direction of the AF chains.

The results reported in the literature[1,2)] and our results indicate totally that the spin gap remains even when the magnetic LRO appears in a unique state. Similar results have been reported in impurity-doped spin-Peierls $CuGeO_3$[9)] and AF spin-cluster compounds such as $Cu_2CdB_2O_6$[10)] and $CrVMoO_7$.[11,12)] The GS of the spin system in $CuGeO_3$ is spin singlet.[13–15)] In the AF spin-cluster compounds, if each cluster were isolated, the

GS of each cluster would be spin singlet. The GS can be magnetic in impurity-doped $CuGeO_3$ due to the appearance of unpaired spins and in the AF spin-cluster compounds due to intercluster interactions.[10] Therefore, the magnetic LRO is possible by interchain or intercluster interactions. The origin of the spin gap is essentially singlet pairs that can remain in the above-mentioned magnetic GS. Therefore, the spin-gap excitations are observable even in the ordered state. As shown in Fig. 1 (d), two edge spins were considered to appear in each hexamer of $K_2Cu_3O(SO_4)_3$ like two $S = \frac{1}{2}$ spins on a Ni^{2+} ion in the valence bond solid picture.[16] Therefore, the origin of the spin gap is singlet pairs formed by AF intercluster interactions. If interactions between chains of hexamers also exist, the magnetic LRO is possible like in $CsNiCl_3$.[17]

Nambu-Goldstone (NG) mode excitations must exist in the ordered state but were not observed in $K_2Cu_3O(SO_4)_3$. We consider the reasons as follows. The magnetic reflections are very weak. Therefore, NG mode excitations are also very weak. In addition, nuclear reflections seem generate signals up to 0.5 meV in Fig. 3(a) of the literature.[1] The signals may hide NG mode excitations.

5. Summary

We performed neutron powder diffraction experiments on the cluster-based Haldane compound fedotovite $K_2Cu_3O(SO_4)_3$ of which space group is monoclinic $C2/c$ (No. 15). We observed weak magnetic reflections caused by a magnetic long-range order below $T_N = 3.1$ K. We looked for magnetic structures that were consistent with the magnetic properties reported in the literature. Probably, the Shubnikov group $C2'/c$ with the propagation vector $\mathbf{k} = (0, 0, 0)$ is applicable to describe the magnetic structure of $K_2Cu_3O(SO_4)_3$. Among the three crystallographic Cu sites (Cu1, Cu2, and Cu3) having spin-$\frac{1}{2}$, the edge sites (Cu1 and Cu2) in the hexamer have ordered magnetic moments. The a components of the magnetic moments are dominant.

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Facility operated by the Oak Ridge National Laboratory (ORNL), USA (proposal ID. 2018-06). Follow-up neutron powder diffraction experiments were performed by using the SIKA spectrometer at Australian Nuclear Science and Technology Organisation (ANSTO), Australia (proposal ID. P6939). Business travel expense for the CTAX experiments was supported by the US-Japan cooperative program for neutron scattering. We are grateful to T. Hong, M. Matsuda, H. Mamiya, M. Nishino, N. Terada, N. Tsujii, M. Fujihala, and T. Sugimoto for fruitful discussion and to S. Matsumoto for the sample syntheses and X-ray diffraction measurements.

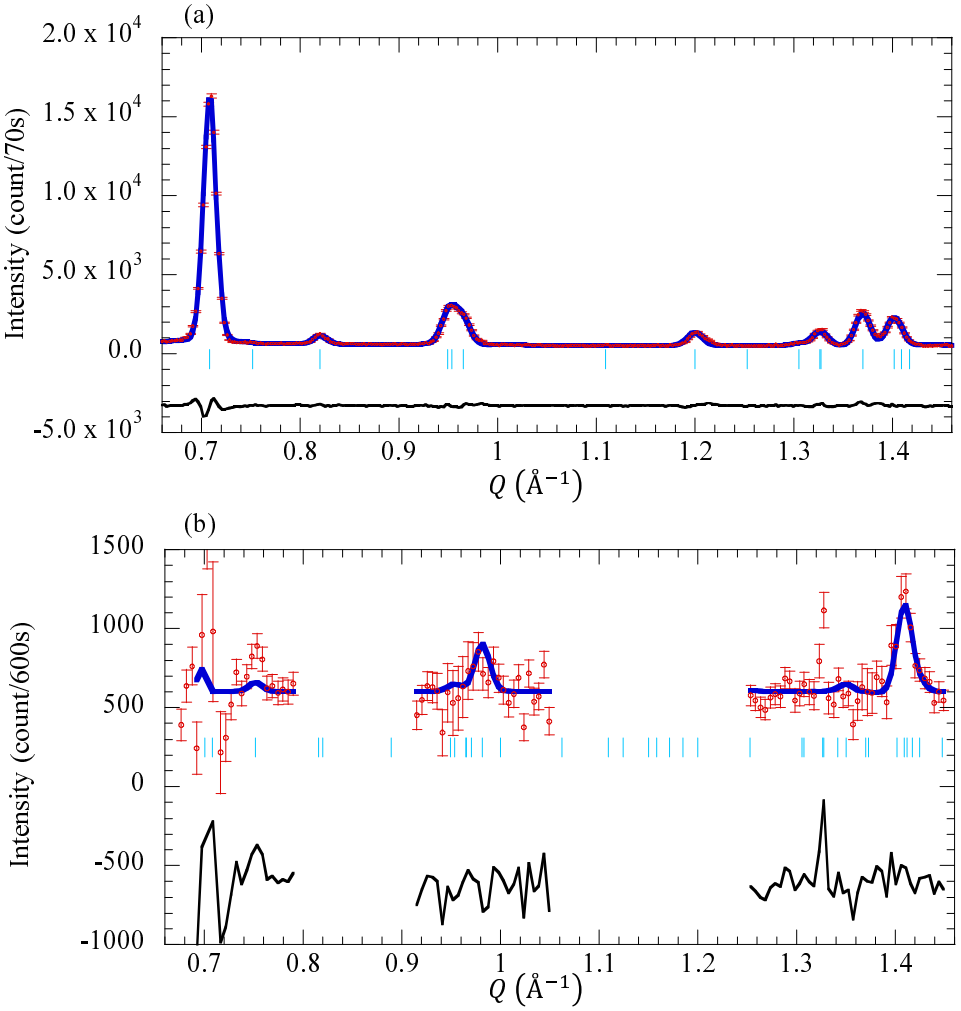

Fig. 3. (Color online) Neutron powder diffraction patterns of $K_2Cu_3O(SO_4)_3$ obtained using the SIKA spectrometer. The wavelength is 4.04 Å. (a) A neutron powder diffraction pattern at 2.2 K (red circles with error bars). A blue line on the measured pattern indicates a Rietveld refined pattern obtained using the crystal structure with monoclinic $C2/c$ (No. 15). In the refinements, we used the fractional atomic coordinates and isotropic displacement factor listed in the Supplemental Material for the paper.[2)] The lattice constants were evaluated as $a = 18.944(6)$ Å, $b = 9.472(3)$ Å, $c = 14.131(2)$ Å, and $\beta = 110.56(1)^\circ$. A black line at the bottom indicates the difference between the measured and the Rietveld refined patterns. Hash marks show positions of nuclear reflections. (b) A difference pattern made by subtracting a neutron powder diffraction pattern at 5 K from that at 1.7 K (red circles with error bars). A blue line on the measured pattern indicates a Rietveld refined pattern of the magnetic structure only. The measured and refined patterns are shifted 600 in the vertical direction to decrease overlap with the black line, indicating the difference between the measured and the Rietveld refined patterns. Hash marks show positions of magnetic reflections.

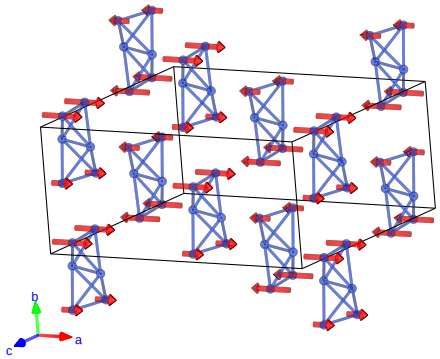

Fig. 4. (Color online) The possible magnetic structure of $K_2Cu_3O(SO_4)_3$. Blue lines indicate short Cu-Cu pairs in the hexamer. The gray-line box represents a unit cell.

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