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Neutron powder diffraction experiments on the layered triangular-lattice antiferromagnets $RbFe(MoO_4)_2$ and $CsFe(SO_4)_2$

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Abstract

Powder specimens of the layered triangular-lattice antiferromagnets $RbFe(MoO_4)_2$ and $CsFe(SO_4)_2$ were prepared and neutron powder diffraction experiments were carried out in order to determine the magnetic structure. The magnetic structure of both compounds is the so-called 120° structure in the triangular plane and is incommensurate between the planes. The ordered moments are confined in the basal *ab*-plane. It is also found that $RbFe(MoO_4)_2$ exhibits structural phase transition at around 190 K from $P\bar{3}m1$ to $P\bar{3}$.

Keywords: Triangular-lattice antiferromagnet; Powder neutron diffraction; One-third plateau

1. Introduction

Magnetic systems with geometrical frustration have attracted unremitting attention for more than three decades, because the systems remain disordered at low temperatures despite ordered regular lattices with simple short range interactions [1]. These systems of spins on triangle-based lattices are characterized by low-lying excited states, which prevent the systems from undergoing long range ordered states. In fact, for kagomé and pyrochlore lattices, liquid-like ground states are predicted [2] and observed [3]. In triangular lattices, although long range ordered states are realized, rich field–temperature ($H-T$) phase diagrams stem from almost degenerate ground states [4]. The quest for new geometrically frustrated magnets, hence, is continuing even recently, and such efforts have come to fruition as the rediscovery of, for instance, clinoatacamite [5] and volborthite [6].

A family of compounds $AM(XO_4)_2$ ($A = NH_4$, Tl, K, Rb, Cs; $M = M^{3+}$ and M^{5+}; $X =$ P, S, Se, Cr, Mo, W) crystallize into a layered structure [7]. The structure with the highest symmetry is the $KAl(MoO_4)_2$-type structure (space group $P\bar{3}m1$) shown in Fig. 1(a), which is composed of M cation layers well separated by non-magnetic XO_4 tetrahedra and A ions. Hence, pronounced two-dimensional magnetic properties are expected when the M ions are magnetic. All other structures are derivatives of this parent structure [7]. If all XO_4 tetrahedra rotate about the *c*-axis clockwise (or counter-clockwise), the space group becomes $P\bar{3}$. On the other hand, if tetrahedra in one layer rotate clockwise and tetrahedra in the adjacent layer rotate counter-clockwise, the space group is $P321$ as shown in Fig. 1(b). There are also rhombohedral structures (space groups $R32$ and $R\bar{3}$) with a different stacking sequence of A and $M(XO_4)_2$ layers along the *c*-axis.

These compounds with trigonal structure are a candidate for layered triangular-lattice antiferromagnets, and several investigations have already been performed in this respect [8–10]. An advantage of these compounds is that the magnitude of the exchange interactions J is suitable for investigating the entire H–T phase diagram; J is large enough that the transition temperatures are around tractable liquid ^{4}He temperature and J is not so large that the saturation field is below the maximum field of conventional pulsed magnets. In fact, a one-third magnetization plateau, which is a specific feature of quasi-two-dimensional triangular-lattice antiferromagnets, is first observed in two of these compounds $RbFe(MoO_4)_2$ and $CsFe(SO_4)_2$, among all the insulating triangular-lattice antiferromagnets [8].

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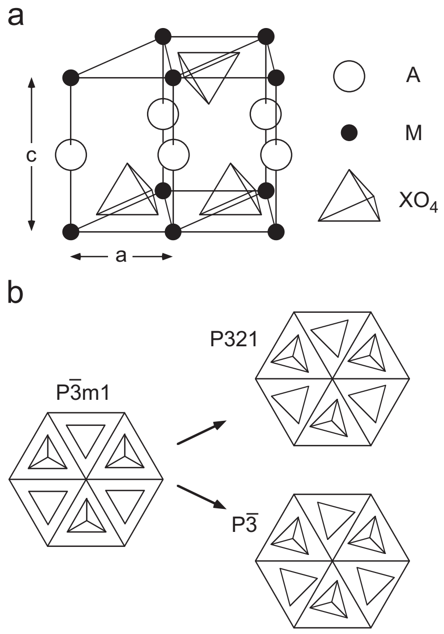

Fig. 1. (a) Crystal structure of $KAl(MoO_4)_2$ type structure, $P\bar{3}m1$. (b) Schematic [0 0 1] view of $P\bar{3}m1$, $P\bar{3}$ and $P321$.

Knowledge of the magnetic structure gives a fair insight into the dominant interactions in compounds and dimensionality of the magnetic moments. And then this insight may allow us to consider, for instance, what mechanism gives rise to the one-third magnetization plateau in above-mentioned two compounds and whether the $AM(XO_4)_2$ family of compounds is a good model of two-dimensional triangular-lattice antiferromagnets. In this paper, neutron powder diffraction experiments were carried out on the two compounds $RbFe(MoO_4)_2$ and $CsFe(SO_4)_2$ in order to determine the magnetic structures.

2. Experimental

A polycrystalline sample of $RbFe(MoO_4)_2$ was synthesized by solid-state reaction of stoichiometric quantities of Rb_2MoO_4 and $Fe_2(MoO_4)_3$. First a mixture of Fe_2O_3 and MoO_3 in the atom ratio $Fe:Mo = 2:3$ was heated at 650 °C. The obtained $Fe_2(MoO_4)_3$ was then mixed with Rb_2MoO_4 and was heated at 650 °C in air for 24 h. Finally, a green powder specimen was prepared.

A powder sample of $CsFe(SO_4)_2$ was prepared by dehydration of $CsFe(SO_4)_2{\cdot}nH_2O$. Stoichiometric quantities of Cs_2SO_4 and $Fe_2(SO_4)_3$ were dissolved in hot water with a small amount of H_2SO_4 and were cooled. The obtained $CsFe(SO_4)_2{\cdot}nH_2O$ was vacuum filtered, washed with water, and dried in vacuum. Dehydration of the alum was carried out at 250° in air and at 500° in vacuum for 10 h. White powder slightly colored pink was prepared.

Neutron powder diffraction data were collected on the triple axis spectrometer TAS-2 at the research reactor JRR-3M, JAEA (Tokai). Data were measured on TAS-2 operated in a two-axis mode at several temperatures using wavelengths of 2.3672 and 2.3541 Å. The powder samples of $RbFe(MoO_4)_2$ and $CsFe(SO_4)_2$ were placed in cylindrical vanadium cans of 10 and 8 mm in diameter, respectively, together with ^{4}He exchange gas, and were cooled using an ILL "orange" liquid helium cryostat. The diffraction patterns were analyzed by the Rietveld method using the programs RIETAN [11] and FullProf [12] for crystal structure and magnetic structure, respectively. In the refinements, the background was fitted with a 6-term polynomial and a pseudo-Voigt peak shape function was employed. Since only small wave number region was measured, isotropic thermal parameters were fixed at appropriate values and 0 at room temperature and low temperatures, respectively, and occupation factors were fixed at unity through the refinements.

3. Results and discussion

3.1. $RbFe(MoO_4)_2$

The neutron diffraction patterns of $RbFe(MoO_4)_2$ measured at room temperature, 15 and 1.5 K are shown in Fig. 2. The diffraction pattern at room temperature is well described by the reported space group $P\bar{3}m1$ [13]. However, the diffraction pattern at 15 K cannot be reproduced using this space group. The difference is prominent in the 111 reflection. The temperature dependence of the 111 reflection is displayed in Fig. 3. Peak intensity shown in the inset as a function of temperature indicates that a structural phase transition occurs at around 190 K and that the transition is very close to being of second order. This transition is also observed in electron spin resonance and Raman spectroscopy, and as the change of the lattice constants [14]. Space groups reported in $AM(XO_4)_2$ layered compounds so far are $P\bar{3}m1$, $C2/m$, $P321$, $R32$, $R\bar{3}$ and $P\bar{3}$ [7]. The observed diffraction patterns are not described by monoclinic or rhombohedral structures, and all reflections can be indexed with $P321$ and $P\bar{3}$. Hence, Rietveld refinements were carried out using these two space groups, and refinements with $P\bar{3}$ converged well to $R_{\mathrm{wp}} = 7.84\%$. Crystallographic data at 15 K and room temperature derived from the refinements are given in Table 1.

Magnetic Bragg reflections are visible in the diffraction patterns measured at 1.5 K. All magnetic peaks are indexed using the incommensurate (IC) propagation vector $\vec{Q}_{\mathrm{M}} = (\frac{1}{3}, \frac{1}{3}, 0.448)$. This magnetic structure in the *ab*-plane corresponds to the so-called 120° structure, in which a spin on the triangular lattice rotates by 120° clockwise or counter-clockwise when it moves to neighboring sites. Magnetic structure along the *c*-axis is IC and a spin rotates by about 160° when it moves up to the next triangular layer. This is the same model discussed in Ref. [9] as "incommensurate 1". Rietveld refinement using FullProf converged to $R_{\mathrm{wp}} = 8.23\%$ and ordered magnetic moment of $4.2(1)\mu_{\mathrm{B}}$ was obtained. Magnetic moments confined in the basal *ab*-plane show better agreement with the observed intensity than magnetic moments in the *ac*-plane. As a

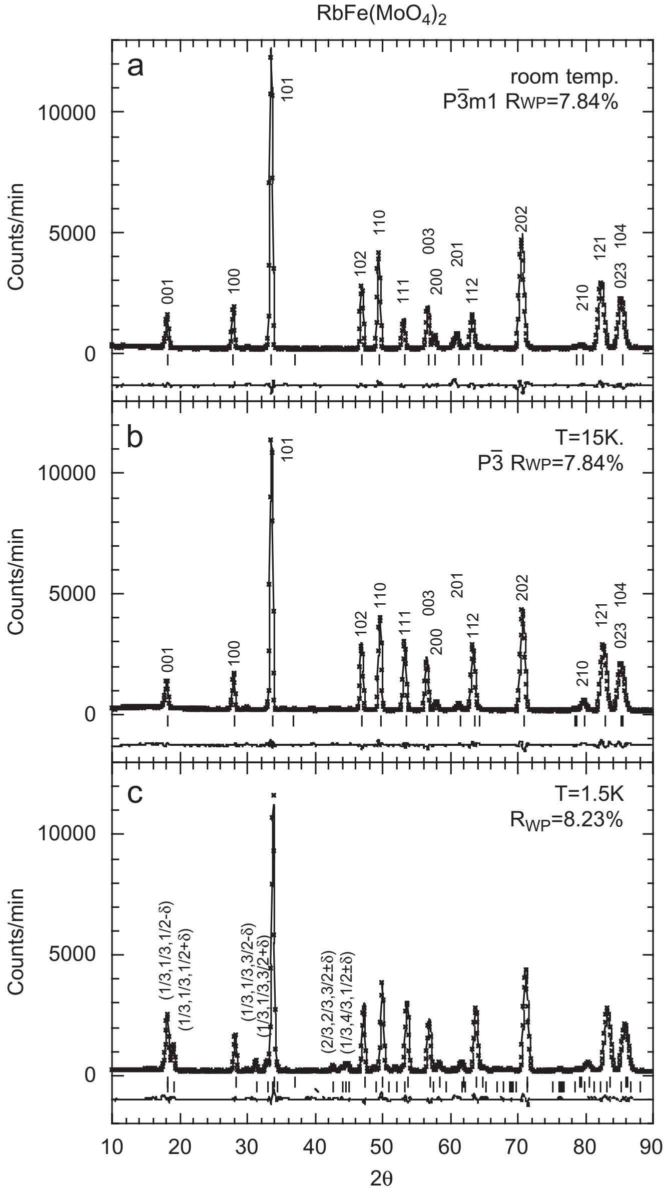

Fig. 2. Neutron diffraction patterns of $RbFe(MoO_4)_2$ (a) at room temperature, (b) at 15 K, and (c) at 1.5 K. Observed, calculated and difference diffraction patterns are shown. The tick marks indicate the position of the Bragg reflections. In (c), the tick marks at bottom indicate the position of the magnetic Bragg reflections.

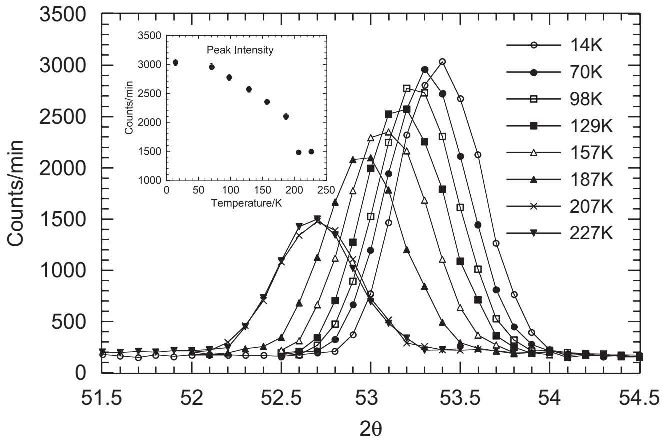

Fig. 3. Temperature evolution of the 111 reflection of $RbFe(MoO_4)_2$.

Table 1
Structure parameters of $RbFe(MoO_4)_2$ at room temperature (RT) and 15 K as derived from the Rietveld refinement

Atom	Site	x	y	z
RT		$a = 5.6717(7)$ Å	$c = 7.4911(7)$ Å	
		$R_{wp} = 7.84\%$	$R_{exp} = 4.27\%$	$R_F = 1.69\%$
Rb	1b	0.0	0.0	0.5
Fe	1a	0.0	0.0	0.0
Mo	2d	0.33333	0.66667	0.237(8)
O(1)	2d	0.33333	0.66667	0.47(1)
O(2)	6i	0.160(3)	−0.160(3)	0.155(5)
15 K		$a = 5.5955(6)$ Å	$c = 7.4377(7)$ Å	
		$R_{wp} = 7.84\%$	$R_{exp} = 4.43\%$	$R_F = 2.15\%$
Rb	1b	0.0	0.0	0.5
Fe	1a	0.0	0.0	0.0
Mo	2d	0.33333	0.66667	0.234(3)
O(1)	2d	0.33333	0.66667	0.463(6)
O(2)	6g	0.103(4)	−0.218(3)	0.158(4)

Standard deviations for refined values are given in parentheses. Space group is $P\bar{3}m1$ at RT and $P\bar{3}$ at 15 K.

result, it is found that $RbFe(MoO_4)_2$ is a classical Heisenberg triangular-lattice antiferromagnet with weak XY-type anisotropy.

This result corrects the type of the anisotropy inferred in a previous report [8]. Under magnetic fields, magnetization of $RbFe(MoO_4)_2$ shows a plateau between 5.2 and 7.6 T, at which the magnetization is just one-third of the saturated magnetization. In a classical Heisenberg triangular-lattice antiferromagnet, the field width of this one-third plateau is zero. Hence a perturbation is required to stabilize the one-third plateau, and weak Ising anisotropy is the best candidate [4]. Nevertheless, the experimental result shows that this is not the case for this compound. The one-third plateau of $RbFe(MoO_4)_2$ is stabilized by thermal and quantum fluctuations [10], through a mechanism known as "order by disorder".

The peak intensity of the magnetic Bragg peak at $\vec{Q} = (\frac{1}{3}, \frac{1}{3}, 0.552)$ is shown in Fig. 4 as a function of temperature. The transition temperature is estimated to be 3.7 K.

3.2. $CsFe(SO_4)_2$

The neutron diffraction pattern of $CsFe(SO_4)_2$ measured at room temperature is shown in Fig. 5(a). Broad peaks of impurity phases around $2\theta = 63°$ and $72°$ are omitted. The crystal structure of $CsFe(SO_4)_2$ was previously reported to be $P321$ [15]. However, the observed diffraction pattern cannot be reproduced using this space group. Instead, refinements using the space group $P\bar{3}$, which is the same as the low-temperature phase of $RbFe(MoO_4)_2$, result in fairly good convergence to $R_{wp} = 10.49\%$. This result

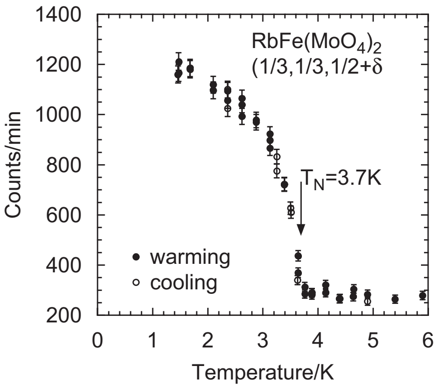

Fig. 4. Temperature dependence of the peak intensity of magnetic Bragg peak at $\vec{Q}=(\frac{1}{3},\frac{1}{3},\frac{1}{2}+\delta)$ ($\delta=0.052$).

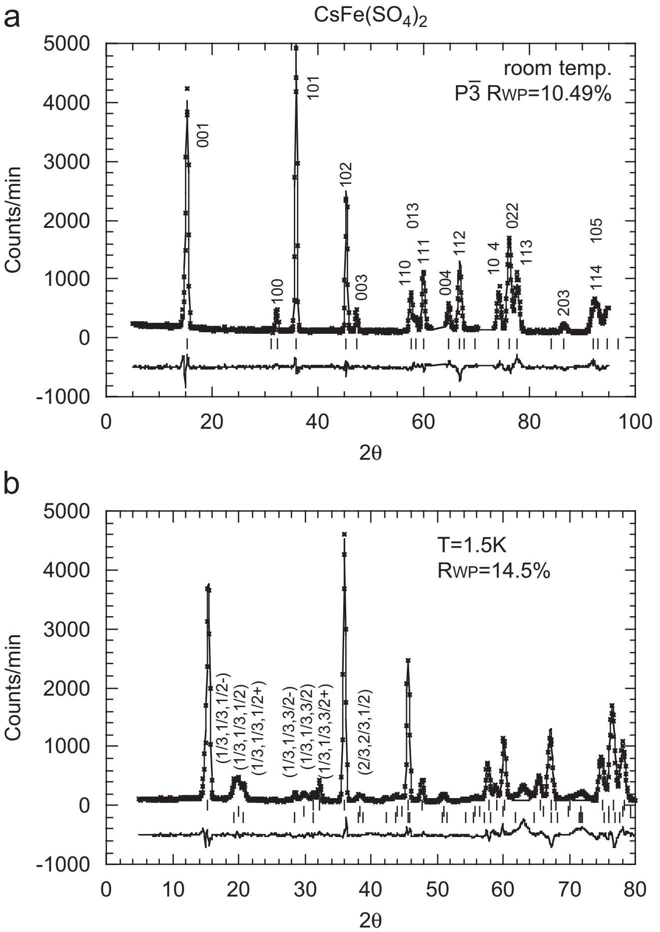

Fig. 5. Neutron diffraction patterns of $CsFe(SO_4)_2$: (a) at room temperature and (b) at 1.5 K. Observed, calculated and difference diffraction patterns are shown. The tick marks indicate the position of the Bragg reflections. In (b), the tick marks at top, middle, and bottom indicate the position of the nuclear, commensurate magnetic, and incommensurate magnetic Bragg reflections, respectively.

Table 2
Structure parameters of $CsFe(SO_4)_2$ at room temperature as derived from the Rietveld refinement

Atom	Site	x	y	z
		$a = 4.8912(6)$ Å	$c = 8.798(1)$ Å	
		$R_{wp} = 10.49\%$	$R_{exp} = 5.81\%$	$R_F = 1.86\%$
Cs	1b	0.0	0.0	0.5
Fe	1a	0.0	0.0	0.0
S	2d	0.33333	0.66667	0.18(1)
O(1)	2d	0.33333	0.66667	0.350(6)
O(2)	6g	0.100(4)	0.366(6)	0.133(3)

Standard deviations for refined values are given in parentheses. Space group is $P\bar{3}$.

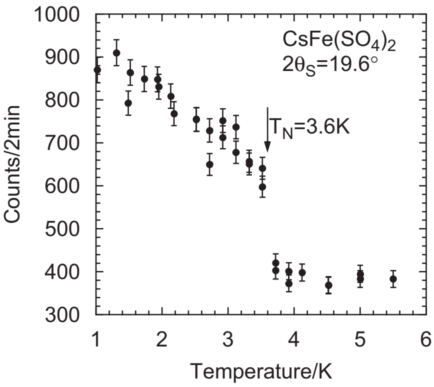

Fig. 6. Temperature dependence of the peak intensity at $2\theta = 19.6°$.

agrees with another report [9]. Crystallographic data derived from the refinements are given in Table 2.

The magnetically ordered phase of $CsFe(SO_4)_2$ is somewhat complicated. The diffraction pattern measured at 1.5 K is shown in Fig. 5(b). Both commensurate (C) and IC peaks are observed. The propagation vector of the C peaks is $\vec{Q}_M = (\frac{1}{3},\frac{1}{3},\frac{1}{2})$, while that of the IC peaks is $\vec{Q}_M = (\frac{1}{3},\frac{1}{3},0.387(1))$. The ordered moments are confined in the ab-plane. The magnitudes of the ordered moments are deduced to be $3.0(3)\mu_B$ and $2.4(3)\mu_B$ for C and IC phases, respectively. If the magnitudes of the ordered moments are the same for both phases, it becomes $3.8\mu_B$. The line width of peaks in the phases is broader than instrumental resolution. The lineshape is well modeled by incorporating particle size broadening of platelet coherent domains. Coherent lengths along the c-axis were estimated from the fit to be 110 ± 10 and 400 ± 80 Å for C and IC phases, respectively.

Since the domain size of the IC phase is much larger than that of the C phase, it is likely that the ground state of $CsFe(SO_4)_2$ is the IC phase. Probably a considerable number of stacking faults exist in this sample, and the C phase may be stabilized around such defects. The previous neutron diffraction experiment could not determine whether the magnetic structure is C or IC, probably due to poor sample quality [9]. In this work, it became very clear that the ordered magnetic structure of $CsFe(SO_4)_2$ is the IC phase, and probably this structure is the common ground state for $AM(XO_4)_2$ with $P\bar{3}$ space group. The temperature dependence of magnetic intensity at

$2\theta = 19.6^\circ$ is shown in Fig. 6. The transition temperature is 3.6 K and it seems that the magnetic phase transition is of first order.

4. Summary

Powder samples of the layered triangular-lattice antiferromagnets $RbFe(MoO_4)_2$ and $CsFe(SO_4)_2$ were prepared and neutron powder diffraction experiments were carried out in order to determine the ordered magnetic structures. In $RbFe(MoO_4)_2$, a structural phase transition at around 190 K from $P\bar{3}m1$ to $P\bar{3}$ was detected. The magnetic structure of both compounds is the 120° structure in the *ab*-plane and is basically IC along the *c*-axis, although the C phase coexists in $CsFe(SO_4)_2$. Magnetic moments are confined in the *ab*-plane, and thus it is found that these compounds are classical Heisenberg triangular-lattice antiferromagnets with small XY-type anisotropy.

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