Magnetic properties of V-jarosite $AV_3(SO_4)_2(OH)_6$ (A=Na, K) with *kagomé* lattice

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Abstract

We have newly synthesized V-jarosite, $NaV_3(SO_4)_2(OH)_6$ and $KV_3(SO_4)_2(OH)_6$, with *kagomé* lattice using the hydrothermal reaction method. Structural parameters were refined by powder X-ray diffraction. It was found that these compounds show a ferromagnetic behavior below 50 K and that the field dependence of magnetization has no hysteresis. Thus, it can be concluded that magnetic interactions of intralayer are ferromagnetic and those of interlayer are antiferromagnetic. Results of ^{23}Na NMR also will be presented in this report.

Key words: low-dimensional magnetism; *kagomé* lattice; jarosite; NMR

Low-dimensional magnetism on transition-metal compounds has been a focus of intensive research over the past decade. The jarosite family of compounds, $AM_3(SO_4)_2(OH)_6$, where A is Na, K, Rb, Ag, H_3O, NH_4 and M is Fe, Cr, or V, has a two-dimensional (2D) *kagomé* lattice as shown in Fig. 1. In this structure, a geometrical frustration should be expected when the exchange coupling between nearest neighbor magnetic atoms is antiferromagnetic as well as in 2D triangular lattice. Most of experimental efforts in *kagomé* has concentrated on $SrCr_xGa_{12-x}O_{19}$ (SCGO) [1,2]. Unusual dynamical magnetic properties were reported by neutron scattering and by μSR investigations, although SCGO does not provide a complete realization of the *kagomé* with antiferromagnetic couplings because of partial substitution of Ga atoms on Cr sites and of alternating planes with *kagomé* and triangular lattice. Cr-jarosites, on the other hand, shows a strong dynamic spin fluctuation even at 25 mK far below $T_g \sim 2$ K where the hysteresis appears in the magnetic susceptibility [3]. Recently, we also reported possible spin-singlet states in AV_6O_{11} (A=Na, Sr, Pb) compounds with *kagomé* lattice revealed by magnetic susceptibility and NMR measurements [4]. These compounds have, however, another V sites in the crystal structure. Thus, V-jarosite serves an ideal experimental stage to study *kagomé* lattice of $S = 1$ spins.

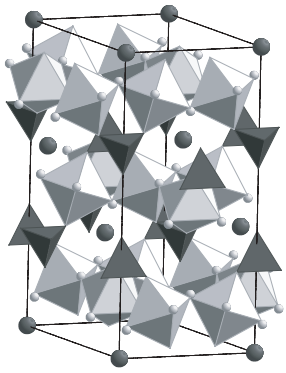

Fig. 1. Crystal structure of jarosite compounds. Blight and dark polyhedra represent VO_6 and SO_4, respectively. Black and white balls show Na and H atoms, respectively.

Recently, we succeeded in synthesizing new compounds of V-jarosite, $NaV_3(SO_4)2(OH)_6$ (Na-jarosite) and $KV_3(SO_4)2(OH)_6$ (K-jarosite). In this paper, we

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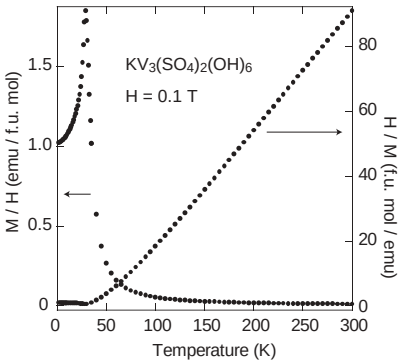

Fig. 2. Temperature dependence of magnetic susceptibility (M/H) for K-jarosite and its inverse.

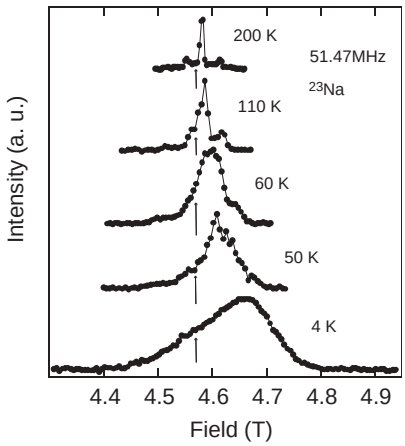

Fig. 3. ^{23}Na NMR spectra taken at various temperatures.

report magnetic properties of these V-jarosite compounds using magnetic susceptibility and NMR measurements.

Samples were prepared by a hydrothermal reaction. Procedures of synthesis in detail will be reported elsewhere. All the samples were characterized by powder X-ray diffraction (XRD) measurement. Chemical analysis is performed by energy-dispersion spectrometer (EDS) attached with scanning electron microscope. Magnetic susceptibilities were measured using SQUID magnetometer from 2 to 300 K under the field of 0.1T. NMR experiments were performed by the spin-echo pulse sequence mode using a homemade spectrometer.

Powder XRD patterns of Na- and K-jarosite were successfully refined by Rietveld method using structural parameters of $NaCr_3(SO_4)2(OH)_6$ as initial parameters. As a result of EDS analysis, chemical compositions of alkaline metals to vanadium were found to be almost 0.33. Initial Rietveld refinement gave Na and K contents in jarosite compounds to be 1.02 and 1.03, respectively. Thus the final result of the structural analysis was obtained on the condition that Na and K compositions were fixed to be 1. It is noted that values of R_{wp} were 8.09 % and 9.14 % for Na- and K-jarosite compounds, which show these refinements were sufficiently reliable in experimental errors.

In Fig. 2, we show temperature dependence of magnetic susceptibility (M/H) of K-jarosite. Ferromagnetic transition is clearly observed around 50 K. It was found that values of M for both compounds almost saturate to be 1.9 μ_B at $H \sim 20$ T. Above 150 K, the value of M/H was found to be well described by Curie-Weiss type behavior with Curie constant C = 2.894 emu/mol·K, Weiss temperature θ = 52.4 K. From the value of C, the effective moment ($\mu_{\rm eff}$) was calculated to be 2.778 μ_B. This value almost coincides with that of $S = 1$ spin (V^{3+} with d^2 state). Below 35 K, values of M/H rapidly decreases due to the possible development of the antiferromagnetic coupling between *kagomé* planes. Na-jarosite compound also showed a very similar result.

In order to clarify the low-dimensional magnetism from a microscopic viewpoint, we performed ^{23}Na NMR measurements for Na-jarosite compounds. Figure 3 shows ^{23}Na NMR spectra taken at various temperatures. The center peak around $4.5 \sim 4.7$ T shifts to higher field with decreasing temperature and broadens below 60 K due to the long-range magnetic order. $1/T_1$ above 60 K was almost constant, which means that $1/T_1T$ is proportional to the magnetic susceptibility. This value was found to be almost consistent with that of the high-temperature limit of localized Heisenberg model ($1/T_1 = (2\pi)^{1/2}(A/\hbar)^2 zS(S+1)/3\omega_{ex}$).

In summary, we have newly synthesized V-jarosite, $NaV_3(SO_4)_2(OH)_6$ and $KV_3(SO_4)_2(OH)_6$, with *kagomé* lattice using the hydrothermal reaction method. It was found that these compounds show a ferromagnetic behavior below 50 K. It can be concluded that magnetic interactions of intralayer are ferromagnetic and those of interlayer are antiferromagnetic.

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