Charge fluctuation in $S = 1/2$ triangular lattice cluster antiferromagnets $\text{Li}_2\text{ScMo}_3\text{O}_8$ and $\text{Li}_2\text{InMo}_3\text{O}_8$

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Abstract. We investigated macroscopic and microscopic physical properties of $S = 1/2$ Mo$_3$ cluster magnets $\text{Li}_2\text{ScMo}_3\text{O}_8$ and $\text{Li}_2\text{InMo}_3\text{O}_8$. $\text{Li}_2\text{InMo}_3\text{O}_8$ shows magnetic ordering at $T_N \approx 12$ K, while no magnetic ordering is observed down to 0.5 K in $\text{Li}_2\text{ScMo}_3\text{O}_8$ in spite of the strong antiferromagnetic interaction among clusters probed by the Weiss temperature. $^{115}\text{In}$ and $^{45}\text{Sc}$ NMR measurements demonstrate that there should be difference in charge fluctuation in clusters between $\text{Li}_2\text{InMo}_3\text{O}_8$ and $\text{Li}_2\text{ScMo}_3\text{O}_8$. Our result suggests that the origin of different ground states realized in $\text{Li}_2\text{InMo}_3\text{O}_8$ and $\text{Li}_2\text{ScMo}_3\text{O}_8$ is different condition in charge and local structure as one of characteristics of the cluster magnet.

1. Introduction

In condensed matter physics, spin frustrated magnets have attracted much interest for their ground states and low energy excitations[1, 2, 3]. In theoretical predictions, the spin frustration effect leads to the emergence of an exotic ground state such as a resonating valence bond state, a spin liquid state, and so on. A strong spin frustration is realized in a characteristic lattice like triangular, kagome (in 2D), face-centered cubic and pyrochlore lattice (in 3D). With this kind of background, many challenges of searching model compounds to study spin frustration have been accomplished.

Recently, we newly discovered $S = 1/2$ triangular lattice cluster antiferromagnet $\text{Li}_2\text{ScMo}_3\text{O}_8$ which has the isostructure of $\text{Li}_2\text{InMo}_3\text{O}_8$ [4]. Their ground states are completely different from each other; while $\text{Li}_2\text{InMo}_3\text{O}_8$ exhibits a conventional magnetic ordering with $120^\circ$ structure, $\text{Li}_2\text{ScMo}_3\text{O}_8$ show a spin liquid like condensation [4]. In the theoretical predictions, charge and lattice fluctuation as characteristics of the cluster based triangular lattice compound would lead their ground state to spin liquid state [5, 6]. Therefore, it is necessary to perform their microscopic structural studies to reveal the origin of different ground states of $\text{Li}_2\text{ScMo}_3\text{O}_8$ and $\text{Li}_2\text{InMo}_3\text{O}_8$.

In this work, we report on $^{45}\text{Sc}/^{115}\text{In}$ nuclear magnetic resonance (NMR) measurements for $\text{Li}_2\text{ScMo}_3\text{O}_8$ and $\text{Li}_2\text{InMo}_3\text{O}_8$. From the $^{45}\text{Sc}/^{115}\text{In}$-NMR studies, charge fluctuations are found to play a key role for suppression of a magnetic ordering in $\text{Li}_2\text{ScMo}_3\text{O}_8$. $\text{Li}_2\text{ScMo}_3\text{O}_8$ is found to be a novel spin liquid candidate produced in the cooperating system between spin and charge fluctuations.
Figure 1. (Color online) (a) [Mo$_3$]$^{11+}$ trimers forming the triangular lattice. (b) Schematic 4$d$ orbital energy level of the Mo$_3$ trimer with the electron configurations expected in Li$_2$AMo$_3$O$_8$ ($A =$ In or Sc). (c) Coordination of Mo$_3$ clusters around In/Sc ion.

Figure 2. (Color online) Temperature dependence of the magnetic heat capacity divided by temperature $C_M/T$ in Li$_2$InMo$_3$O$_8$ and Li$_2$ScMo$_3$O$_8$ reproduced from ref. [4]. The dashed line is fit to the power law ($C_M \propto T^\alpha$) with $\alpha = 1.5$ for Li$_2$ScMo$_3$O$_8$.

2. Experimental Methods
Polycrystalline samples of Li$_2$ScMo$_3$O$_8$ and Li$_2$InMo$_3$O$_8$ were prepared using conventional solid-state reactions as describe in a previous report [4]. The thermodynamic properties were measured by using a conventional relaxation method with a physical property measurement system (PPMS; Quantum Design). NMR measurements were performed by the spin-echo method by using a standard phase coherent pulse spectrometer. The $^{115}$In and $^{45}$Sc nuclei have nuclear spins $I = \frac{9}{2}$ and $\frac{7}{2}$ and gyromagnetic ratios $^{115}\gamma = 9.3301$ MHz/kOe and $^{45}\gamma = 10.343$ MHz/kOe, respectively.

3. Results and Discussion
As shown in the inset of Fig. 2, the temperature derivative $d\chi/dT$ for Li$_2$InMo$_3$O$_8$ decreases discontinuously at $\sim 12$ K indicating the presence of long-range ordering, which is also suggested by the result of heat capacity measurement as mentioned below. In contrast, $d\chi/dT$ for Li$_2$ScMo$_3$O$_8$ does not show any discontinuous changes down to 2 K. The specific heat data provides further evidence of the formation of the spin-liquid state. The magnetic specific heat $C_M$ is estimated by subtracting the specific heat of isomorphic nonmagnetic compound Li$_2$SnMo$_3$O$_8$ as a lattice contribution. Figure 2 shows the temperature dependence of the
Figure 3. (Color online) Magnetic field-swept $^{115}$In and $^{45}$Sc NMR spectra at 20 K for (a) Li$_2$InMo$_3$O$_8$ and (b) Li$_2$ScMo$_3$O$_8$ with constant frequencies $\nu$ of 59.79 and 70.84 MHz for Li$_2$InMo$_3$O$_8$ and Li$_2$ScMo$_3$O$_8$, respectively. Simulated powder-pattern spectra are also presented by solid lines for comparison. The simulated conditions of the isotropic and anisotropic shifts $K_{iso}$ and $K_{ax}$, and the pure nuclear quadrupole frequency $\nu_Q$ are written in the figure for each nuclei.

magnetic specific heat divided by temperature ($C_M/T$) for Li$_2$InMo$_3$O$_8$ and Li$_2$ScMo$_3$O$_8$. In the case of Li$_2$InMo$_3$O$_8$, the $\lambda$-shaped peak was observed at the same temperature, suggesting the existence of long-range ordering. In the case of Li$_2$ScMo$_3$O$_8$, we observed no $\lambda$-typed anomaly in $C_M/T$ down to 0.5 K but only a broad hump near 10 K, indicating the absence of any magnetic orderings. The $C_M$ of Li$_2$ScMo$_3$O$_8$ between 0.5 and 4 K are well fitted by the power-law $C_M \simeq T^{1.5}$. Such power low behavior of $C_M$ suggests the presence of gapless excitations in low temperatures.

In the theoretical predictions, the ground state of the cluster-based triangular lattice systems is ruled by the charge and lattice fluctuations within a cluster [5, 6]. Thus, the origin of the different ground states between Li$_2$ScMo$_3$O$_8$ and Li$_2$InMo$_3$O$_8$ could be the difference in the local structure around a Mo$_3$O$_3$ cluster. To clarify the difference of the local structure, we have measured the $^{45}$Sc and $^{115}$In NMR spectra for Li$_2$ScMo$_3$O$_8$ and Li$_2$InMo$_3$O$_8$, respectively at 20 K sweeping a magnetic field at constant frequencies described in the figure. These results are plotted in Fig. 4. The observed spectra are well reproduced by powder-pattern simulations with second-order quadrupole effects using the three parameters listed in the figure, suggesting that In and Sc ions occupy only single site in both compounds. The electric field gradient at Sc and In sites can be estimated with using the values of pure nuclear quadrupole frequency $\nu_Q$ derived from the following function,

$$\nu_Q = \frac{3eQ \cdot (eq)}{2hI(2I-1)},$$

where $e$ is the elementary charge, $h$ is the Planck’s constant, $q$ is the electric quadrupole moment, $Q$ is the nuclear electric quadrupole moment ($Q = -0.22 \times 10^{-24}\text{cm}^2$ for Sc and $1.66 \times 10^{-24}\text{cm}^2$ for In), and $I$ is the nuclear spin quantum number ($I = 7/2$ for Sc and $9/2$ for In). Estimated values of $eq$ are $3.89 \times 10^{-17}$ and $1.47 \times 10^{-17}$ J.C.$^{-1}$cm.$^{-2}$ for In of Li$_2$InMo$_3$O$_8$ and Sc of Li$_2$ScMo$_3$O$_8$, respectively. The quadrupole asymmetry parameter $\eta$ is zero because that the In/Sc site is on a hexagonal axis. The value of the electric field gradient $eq$ is expected to be
contributed only by environmental ions owing to the closed-shelled In\(^{3+}\) and Sc\(^{3+}\) ions. In and Sc sites occupy almost the same environmental site; hence, the relation of \(eq(\text{In}^{3+}) \approx eq(\text{Sc}^{3+})\) can be expected. However, \(eq\) for In\(^{3+}\) is 2.6 times larger than that for Sc\(^{3+}\), indicating a strong suppression of \(eq\) at Sc site. The difference of \(eq\) is difficult to be explained by a simple point charge model because of the similar environmental In and Sc sites.

The shielding effect derived from the charge fluctuations in the clusters can explain the origin of large difference in \(eq\) for In\(^{3+}\) of Li\(_2\)InMo\(_3\)O\(_8\) and Sc\(^{3+}\) of Li\(_2\)ScMo\(_3\)O\(_8\). As shown in Fig. 1(c), Sc/In ions surrounded by the Mo\(_3\) cluster. Thus, Sc/In sites are thought to be susceptible to the charge fluctuation within the cluster. Chen et al. expressed the occurrence in the spin-disordered ground state of Mo\(_3\) cluster magnet by using an extend Hubbard model taking into account of electron transfers of intra- and inter-cluster [6]. When both inter- and intra-cluster transfers are effective, the electron charge should fluctuate without strong localization. Such the charge fluctuation explaining the shielding effect of \(eq\) possibly suppresses the magnetic ordering. There is a possibility that spins in the intermediate charge glass state undergo a dynamical slowing down.

In the scenario to explain the difference of \(eq\), the charge fluctuations suppress the magnetic ordering in Li\(_9\)ScMo\(_3\)O\(_8\), which is in contrast to the case of Li\(_2\)InMo\(_3\)O\(_8\) with 120\(^0\) structural magnetic ordering. In Li\(_9\)ScMo\(_3\)O\(_8\), the observed power law behavior of \(C_m \approx T^{1.5}\) suggests a gapless quantum spin liquid in the low temperatures. In a similar case of \(S = 1/2\) triangular lattice cluster compound, \(\kappa\)-(BEDT-TTF)\(_2\)Cu\(_2\)(CN)\(_3\) exhibits power law behavior in the temperature dependence of the nuclear spin-lattice relaxation rate \((1/T_1)\) [8, 9]. On the other hand, the result of thermal-transport measurement supports the existence of a gapped quantum spin liquid phase[10]. In other cases, spin liquid candidates of triangular lattice Heisenberg antiferromagnets NiGa\(_3\)S\(_4\)[11, 12] and Ba\(_3\)Ir\(_2\)O\(_9\)[13] exhibit the power law behaviors as the power index \(\alpha \simeq 2\) in \(C_m = T^\alpha\). In the spin liquid ground state on the triangular lattice Heisenberg antiferromagnet, the presence/absence of the spin gap in the low energy spin excitations have been of great interest. Our results of Li\(_2\)ScMo\(_3\)O\(_8\) indicate that there is gapless excitations in the low temperature regime, although the observed power index is somewhat different from the above mentioned gapless spin liquid candidates.

### 4. Summary

We studied the microscopic physical properties of Li\(_2\)ScMo\(_3\)O\(_8\) and Li\(_2\)InMo\(_3\)O\(_8\). These compounds are categorized in the triangular lattice antiferromagnetic cluster magnet. Li\(_9\)InMo\(_3\)O\(_8\) shows the magnetic ordering at \(T_N \simeq 12\) K, while Li\(_2\)ScMo\(_3\)O\(_8\) shows no magnetic ordering down to 0.5 K with gapless excitations in the low temperature regime. From \(^{115}\)In and \(^{45}\)Sc NMR measurements, it has been revealed that there is the difference in \(eq\) at crystallographically equivalent In and Sc sites. This fact suggests the effective charge fluctuation stabilize the spin liquid state rather than the magnetic ordering state. Such fluctuations as a characteristic of cluster magnets are regarded as an important factor in these compounds.

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