Spin-Liquid State in the $S = 1/2$ Hyperkagome Antiferromagnet Na$_4$Ir$_3$O$_8$

Yoshihiko Okamoto$^{1, *}$, Minoru Nohara$^2$, Hiroko Aruga-Katori$^1$, and Hidenori Takagi$^{1, 2}$

$^1$RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
$^2$Department of Advanced Materials, University of Tokyo and CREST-JST, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

(Dated: February 1, 2008)

A spinel related oxide, Na$_4$Ir$_3$O$_8$, was found to have a three dimensional network of corner shared Ir$^{4+}$ ($4_{2d}$) triangles. This gives rise to an antiferromagnetically coupled $S = 1/2$ spin system formed on a geometrically frustrated hyperkagome lattice. Magnetization $M$ and magnetic specific heat $C_m$ data showed the absence of long range magnetic ordering at least down to 2 K. The large $C_m$ at low temperatures is independent of applied magnetic field up to 12 T, in striking parallel to the behavior seen in triangular and kagome antiferromagnets reported to have a spin-liquid ground state. These results strongly suggest that the ground state of Na$_4$Ir$_3$O$_8$ is a three dimensional manifestation of a spin liquid.

PACS numbers: Valid PACS appear here

The experimental realization of a quantum spin liquid in geometrically frustrated magnets has been one of the biggest challenges in the field of magnetism since Anderson proposed resonating valence bond theory [1] for antiferromagnetically coupled $S = 1/2$ spins on a triangular lattice. Geometrical frustration in magnets arises from the incompatibility of local spin-spin interactions, which gives rise to macroscopic degeneracy of the ground state. Possible playgrounds for this include triangular, kagome, pyrochlore and garnet lattices essentially consisting of networks of triangles. In real materials, however, it is not easy to prevent spin ordering at substantially lower temperatures than the Curie-Weiss temperature $\theta_W$. This is because the spin degeneracy can be lifted by coupling with the other degrees of freedom such as the orbitals, lattice and charges. Such an interplay between the frustrated spins, orbitals and lattice, for example, can be realized in the trimer singlet formation in the $S = 1$ triangular LiVO$_2$ [2, 3] with orbital ordering or the spin-Jahn-Teller transition in the $S = 3/2$ pyrochlore ZnCr$_2$O$_4$ [4]. In addition, only a minute amount of disorder can strongly influence the spin-liquid state in geometrically frustrated magnets and may give rise to the formation of a glassy state of spins.

The most likely candidate for the realization of a spin-liquid ground state has been the two dimensional kagome antiferromagnet SrCr$_9$Ga$_{12-9p}$O$_{19}$ ($S = 3/2$) [5, 6]. It does not show any evidence for long range ordering down to 100 mK, and a large and field independent magnetic specific heat was observed which was ascribed to spin-liquid contributions. Nevertheless, the strong spin glass-like behavior at low temperatures instills a certain ambiguity in identifying the spin-liquid state. Recently, a new generation of spin-liquid compounds has emerged, the $S = 1/2$ triangular magnet $k$-(ET)$_2$Cu$_2$C(N)$_3$ [7], an organic Mott insulator, and the $S = 1$ triangular magnet NiGa$_2$S$_4$ [8]. They were reported to have a spin-liquid ground state or at least a robust liquid phase down to 100 mK. Their magnetic and thermal properties are in striking parallel to those of SrCr$_9$Ga$_{12-9p}$O$_{19}$ but the disorder effect appears to be much weaker.

Here we report on a three dimensional analogue of these two dimensional spin liquids. Na$_4$Ir$_3$O$_8$ was first reported as an unidentified phase in the Na-Ir-O ternary system by McDaniel [9]. We find that it is isostructural to Na$_4$Sn$_3$O$_8$ [10] and that a $S = 1/2$ hyperkagome system, consisting of low spin $d^5$ Ir$^{4+}$ ions, is realized in Na$_4$Ir$_3$O$_8$. The magnetization and specific heat measurements on the ceramic samples indicate that $S = 1/2$ spins are highly frustrated and remain in a liquid state down to the lowest temperature measured.

Polycrystalline samples of Na$_4$Ir$_3$O$_8$ were prepared by a solid-state reaction. Stoichiometric amounts of Na$_2$CO$_3$ and IrO$_2$ were mixed, and the mixture was calcined at 750°C for 18 h. We added 5% excess of Na$_2$CO$_3$ to compensate the loss of Na during the calcination. The product was finely ground, pressed into a pellet, sintered at 1020°C for 22 h on gold foil, and then quenched in air. Powder x-ray diffraction (XRD) data showed that the powders were single phase. The crystal structure was determined by performing Rietveld analysis on the powder XRD data using RIETAN-2000 program [11]. Thermodynamic and magnetic properties were measured by a Physical Properties Measurement System (Quantum Design) and a Magnetic Properties Measurement System (Quantum Design).

We were able to refine the powder XRD pattern with the cubic Na$_4$Sn$_3$O$_8$ structure ($P_{4_{1}}3$2 or $P_{4_{3}}3$2) [10]. The result of this refinement is summarized in Table I and Fig. 1 (b). The structure of Na$_4$Ir$_3$O$_8$, shown in Fig. 1 (a), is derived from those of spinel oxides ($AB_2$O$_4$), which can be intuitively demonstrated by rewriting the
A site rather than the tetrahedral one in a conventional spinel structure [10]. We refined the structure by assuming two Na positions, Na2 and Na3, in the octahedral A-site with 75 % occupation following Ref. [10].

Ir in this compound is tetravalent with five electrons in 5d orbitals. Because of the octahedral coordination with the oxygens and the large crystal field splitting effect expected for 5d orbitals, it is natural for Ir⁴⁺ to have a low spin (t₂g⁵) state with S = 1/2. The electrical resistivity ρ of a ceramic sample at room temperature was ~10 Ωcm, followed by a thermally activated increase with an activation energy of 500 K with decreasing temperature. Inset: (a) Temperature dependence of magnetic susceptibility χ of Na₄Ir₃O₈ in various fields up to 5 T. For clarity, the curves are shifted by 3, 2 and 1 × 10⁻⁴ emu/mol Ir for 0.01, 0.1 and 1 T data respectively. (b) Cₘ/T vs T of Na₄Ir₃O₈ in various fields up to 12 T. Broken lines indicate Cₘ proportional to T² and T³ respectively.

The temperature dependent magnetic susceptibility χ(T), shown in Fig. 2 (a), indicates that Na₄Ir₃O₈ is indeed a frustrated S = 1/2 system with a strong antiferromagnetic interaction. In the χ⁻¹ vs T plot in Fig. 2 (a), Curie-Weiss like behavior can be seen. The Curie-Weiss fit around room temperature yields a large anti-
ferromagnetic Curie-Weiss constant $\theta_W \sim 650$ K and an
effective moment $p_{\text{eff}} = 1.96 \mu_B$, which is slightly larger
than those expected for $S = 1/2$ spins. In geometrically
frustrated antiferromagnets, it is known that the Curie-
Weiss behavior expected above $T = \theta_W$ persists even
below $\theta_W$. The observed Curie-Weiss behavior of $\chi(T)$
below $\theta_W$ is consistent with the presence of $S = 1/2$ anti-
ferromagnetic spins on a frustrated hyperkagome lattice.
The large antiferromagnetic interaction inferred from $\theta_W$
is supported by the observation of a magnetization linear
with magnetic field at least up to 40 T without any sign
of saturation at 4.2 K [13].

The geometrical frustration in the $S = 1/2$ hyperkagome antiferromagnet is extremely strong and, indeed, we do not find any anomaly indicative of long range order in the susceptibility at least down to 2 K, which is two orders of magnitude lower than $\theta_W \sim 650$ K. We also note that a neutron diffraction measurement at 10 K did not detect any signature of ordering [14]. These strongly suggest that a spin-liquid state is indeed realized in this three dimensional $S = 1/2$ frustrated magnet. As shown in the inset of Fig. 2 (a), a trace of spin glass like contribution with $T_g = 6$ K is observed. The difference between zero-field cooling and field cooling magnetization, however, is less than 10 % of the total magnetization. This hysteresis does not represent a contribution from the majority of spins. The glassy component becomes negligibly small at high fields above 1 T, relative to the other contributions. In the high field susceptibility data that most
represents the bulk, we see the susceptibility tend to saturate and approach a finite value as $T \to 0$. This strongly suggests that the majority of the system remains a paramagnetic spin liquid at least down to 2 K.

The specific heat data provides further evidence for
a spin-liquid state. The magnetic specific heat was
estimated by subtracting the specific heat of nonmagnetic Na$_4$Sn$_3$O$_8$ as a lattice contribution. Because of

the subtraction, the data at high temperatures above
$\sim 100$ K, where the lattice contribution dominates the
specific heat, are subject to certain ambiguity. The $T$-
dependent magnetic specific heat $C_m$ of Na$_4$Ir$_3$O$_8$ is plotted as $C_m/T$ in Fig. 2 (b). We observe only a broad peak with its maximum around $\sim 30$ K and any anomaly indicative of long range ordering is absent. The magnetic entropy, estimated by integrating $C_m/T$ data shown in Fig. 2 (c), is as large as $\sim 4.5$ J/molK per Ir at 100 K ($\ll \theta_W = 650$ K), which is 70-80 % of the total spin entropy $R\ln 2 = 5.7$ J/molK. The quenching of spin entropy at lower temperature than the Weiss temperature $\theta_W$ is a hallmark of frustrated systems, often referred to as a downshift of entropy. Comparing with other frustrated systems in Fig. 3, the downshift with respect to the Curie-Weiss temperature is much more significant than in the two dimensional $S = 1/2$ frustrated magnet Na$_4$Ir$_3$O$_8$ but less significant than in the two dimensional $S = 3/2$ kagome SrCr$_{9p}$Ga$_{12-9p}$O$_{19}$ [13].

As seen in the inset of Fig. 2 (b), the magnetic specific heat was found to be surprisingly independent of applied magnetic fields up to $H = 12$ T, which corresponds to $\mu_B H/k_B \sim 8$ K. This suggests that the low energy spin excitation, seen as a large magnetic specific heat at low temperature, has nothing to do with the glassy contribution with the characteristic energy scale of $T_g \sim 6$ K but derives from frustrated spins strongly coupled anti-

FIG. 3: Comparison of the normalized magnetic specific heat of Na$_4$Ir$_3$O$_8$ with those of other frustrated antiferromagnets SrCr$_{9p}$Ga$_{12-9p}$O$_{19}$ ($p = 0.98$) and NiGa$_2$S$_4$. M in the unit of vertical axis denotes magnetic element Ir, Cr and Ni for Na$_4$Ir$_3$O$_8$, SrCr$_{9p}$Ga$_{12-9p}$O$_{19}$ and NiGa$_2$S$_4$ respectively. Temperature $T$ is normalized by the Curie-Weiss constant $\theta_W$ for comparison.

FIG. 4: (a) Temperature dependence of the magnetic susceptibility $\chi(T)$ of polycrystalline Na$_4$(Ir$_{1-x}$Ti$_x$)$_3$O$_8$ ($x = 0.1$) in magnetic fields up to 5 T, compared to the data of $x = 0$ under 0.01 T. (b) Magnetic specific heat $C_m$ of the $x = 0$ sample plotted as $C_m/T$ vs $T$. The broken line indicates $C_m/T$ of $x = 0$ under zero field. inset: Orphan spin Curie constant $C^*$ of Na$_4$(Ir$_{1-x}$Ti$_x$)$_3$O$_8$ ($0 \leq x \leq 0.3$), defined by Schiffer and Daruka [13].
ferromagnetically. This field independence is universally observed in geometrically frustrated magnets proposed to have a spin-liquid ground state [4], providing a further support for a similar state in Na$_4$Ir$_3$O$_8$.

We also found that nonmagnetic Ti$^{4+}$ can be substituted partially for Ir$^{4+}$. As shown in Fig. 4, the introduction of “non-magnetic” Ti$^{4+}$ impurities gives rise to a localized magnetic moment, which manifests itself as a Curie-like contribution in the susceptibility, roughly scaled by the number of Ti$^{4+}$ ($S = 1/2$ per 3Ti$^{4+}$). This is induced by the so-called orphan spin, and is again analogous to the other spin-liquid systems [15]. These localized magnetic moments simultaneously give rise to a drastic shift of the magnetic specific heat to even lower temperatures as shown in Fig. 4 (b). This low-temperature specific heat in Ti$^{4+}$ doped samples, however, is strongly magnetic field dependent [Fig. 4 (b)], indicating that it has a physically distinct origin from those of the nominally pure compound. Incidentally, the Curie-like contribution induced by Ti$^{4+}$ is accompanied by an enhanced hysteresis at low temperatures [Fig. 4 (a)], which may support the idea that the glassy contribution seen in the nominally pure compound originates from a small amount of impurity or disorder.

These experimental results all point to a spin-liquid ground state in Na$_4$Ir$_3$O$_8$. Recent theoretical calculations using the large $N$ mean field theory indeed support spin-liquid formation on a hyperkagome lattice [16]. However, there remain many issues and puzzles on the novel spin-liquid state of Na$_4$Ir$_3$O$_8$ which should be tackled urgently. Firstly, the orbital state of Ir$^{4+}$ should be clarified in understanding the spin-liquid state completely. Secondly, the effect of spin-orbit coupling should be considered. Since Ir is a 5$d$ element, the spin-orbit coupling is likely to be much larger than in 3$d$ and 4$d$ elements. The large spin-orbit coupling will give rise to a spin anisotropy and can reduce the frustration to a certain extent. It is likely from the experimental observation here, however, that this effect is not sufficient to suppress the spin-liquid state completely.

Finally, the origin of the unusual temperature dependence of the magnetic specific heat $C_m$ is worthy of further exploration. $C_m$ at low temperatures shows a weaker temperature dependence than $T^3$ at least down to 2 K [see the inset of Fig. 2 (b)]. This approximately $T^2$-behavior is in striking parallel with the behavior found in the $S = 1$ triangular NiGa$_2$S$_4$ [8] and the $S = 3/2$ kagome SrCr$_9$Ga$_{12-9}$O$_{19}$ [6]. In those two dimensional frustrated magnets, the $T^2$-dependence of $C_m(T)$ at low temperatures may be interpreted as the presence of a 2D magnon-like dispersion [4, 5]. The hyperkagome lattice, however, is a three dimensional system and it is not obvious at all why low temperature specific heat shows such a peculiar temperature dependence.

In conclusion, we have demonstrated that a spin related oxide Na$_4$Ir$_3$O$_8$ has an intriguing Ir-sublattice, due to ordering of Na and Ir in the spinel B-site and that a $S = 1/2$ hyperkagome antiferromagnet is realized in this oxide. The magnetization and specific heat data collectively suggest that the ground state is a spin liquid state due to strong geometrical frustration. This is the first demonstration of a $S = 1/2$ spin-liquid ground state in a three dimensional magnet and, we believe, provides a new, and fascinating playground for quantum magnetism.

We thank D. I. Khomskii, N. E. Hussey, T. Arima, S. Onoda, S. Shamoto and H. Mitamura for stimulating discussion. This work was partly supported by a Giant-in-Aid for Scientific Research, from the ministry of Education, Culture, Sports, Science, and Technology.

[1] P. W. Anderson, Mat. Res. Bull. 8, 153 (1973).
[2] K. Kobayashi, K. Kosuge, and S. Kachi, Mat. Res. Bull. 4, 95 (1969).
[3] H. F. Pen et al., Phys. Rev. Lett. 78, 1323 (1997).
[4] S.-H. Lee et al., Phys. Rev. Lett. 84, 3718 (2000).
[5] X. Obradors et al., Solid State Commun. 65, 189 (1988).
[6] A. P. Ramirez, B. Hessen, and M. Winklemann, Phys. Rev. Lett. 84, 2957 (2000).
[7] Y. Shimizu et al., Phys. Rev. Lett. 91, 107001 (2003).
[8] S. Nakatsuji et al., Science 309, 1697 (2005).
[9] C. L. McDaniel, J. Solid State Chem. 9, 139 (1974).
[10] M. Iwasaki et al., J. Mater. Chem. 12, 1068 (2002).
[11] F. Izumi and T. Ikeda, Mater. Sci. Forum 321-324, 198 (2000).
[12] A. P. Ramirez, in Handbook on Magnetic Materials, edited by K. J. H. Busch (Elsevier Science, Amsterdam, 2001), Vol. 13, p. 423.
[13] H. Mitamura (private communication).
[14] S. Shamoto (private communication).
[15] P. Schiffer and I. Duruk, Phys. Rev. B 56, 13712 (1997).
[16] J. M. Hopkinson et al., Phys. Rev. Lett. 99, 037201 (2007); M. J. Lawler et al., arXiv:0705.0990.

* Present address: Institute for Solid State Physics, University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan.