

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

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A spinel related oxide, $\text{Na}_4\text{Ir}_3\text{O}_8$, was found to have a three dimensional network of corner shared Ir^{4+} (t_{2g}^5) 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 $\text{Na}_4\text{Ir}_3\text{O}_8$ is a three dimensional manifestation of a spin liquid.

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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 θ_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_2O_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 $\text{SrCr}_9\text{pGa}_{12-9\text{p}}\text{O}_{19}$ ($S = 3/2$) [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 glasslike 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 κ -(ET) $_2\text{Cu}_2(\text{CN})_3$ [7], an organic Mott insulator, and the $S = 1$ triangular magnet NiGa_2S_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 $\text{SrCr}_9\text{pGa}_{12-9\text{p}}\text{O}_{19}$ but the disorder effect appears to be much weaker.

Here we report on a three dimensional analogue of these two dimensional spin liquids. $\text{Na}_4\text{Ir}_3\text{O}_8$ was first reported as an unidentified phase in the Na-Ir-O ternary system by McDaniel [9]. We find that it is isostructural to $\text{Na}_4\text{Sn}_3\text{O}_8$ [10] and that a $S = 1/2$ hyperkagome system, consisting of low spin d^5 Ir^{4+} ions, is realized in $\text{Na}_4\text{Ir}_3\text{O}_8$. 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 $\text{Na}_4\text{Ir}_3\text{O}_8$ were prepared by a solid-state reaction. Stoichiometric amounts of Na_2CO_3 and IrO_2 were mixed, and the mixture was calcined at 750 °C for 18 h. We added 5% excess of Na_2CO_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 the 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 $\text{Na}_4\text{Sn}_3\text{O}_8$ structure ($P4_332$ or $P4_332$) [10]. The result of this refinement is summarized in Table I and Fig. 1(b). The structure of $\text{Na}_4\text{Ir}_3\text{O}_8$, shown in Fig. 1(a), is derived from those of spinel oxides ($AB_2\text{O}_4$), which can be intuitively demonstrated by rewriting the chemical formulae as $(\text{Na}_{1.5})_1(\text{Ir}_{3/4}, \text{Na}_{1/4})_2\text{O}_4$. The B -sublattice of spinel oxides forms the so-called pyrochlore lattice, a network of corner shared tetrahedra. In $\text{Na}_4\text{Ir}_3\text{O}_8$, each tetrahedron in the B -sublattice is occupied by three Ir and one Na (Na1). These Ir and Na atoms form an intriguing ordering pattern as shown in Fig. 1(c), giving rise to a network of corner shared Ir triangles, called a hyperkagome lattice [12]. All the Ir sites and Ir-Ir bonds are equivalent and, therefore, strong geometrical frustration is anticipated. The

TABLE I. Atomic parameters obtained by refining x-ray powder diffraction for $\text{Na}_4\text{Ir}_3\text{O}_8$ at room temperature with a space group $P4_132$. The cubic lattice constant is $a = 8.985 \text{ \AA}$. g of Na2 and Na3 are fixed to 0.75 according to Ref. [10].

		x	y	z	g	$B \text{ (\AA)}$
Ir	12d	0.61456(7)	$x + 1/4$	5/8	1.00	0.15
Na1	4b	7/8	7/8	7/8	1.00	2.6
Na2	4a	3/8	3/8	3/8	0.75	2.6
Na3	12d	0.3581(8)	$x + 1/4$	5/8	0.75	2.6
O1	8c	0.118(11)	x	x	1.00	0.6
O2	24e	0.1348(9)	0.8988(8)	0.908(11)	1.00	0.6

hyperkagome lattice is also realized in the A sublattice of the garnet $\text{A}_3\text{B}_5\text{O}_{12}$ but in these it is distorted. It might be interesting to infer here that there exists a chirality in this hyperkagome lattice and that the two structures $P4_132$ [Fig. 1(c)] and $P4_332$ [Fig. 1(d)] have different degenerate chiralities. Na_{1,5} in $\text{Na}_{1,5}(\text{Ir}_{3/4}, \text{Na}_{1/4})_2\text{O}_4$ occupies the octahedral A site rather than the tetrahedral A site normally occupied 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 Ir^{4+} to have a low spin (t_{2g}^5) state with $S = 1/2$. The electrical resistivity ρ of a ceramic sample at room temperature was $\sim 10 \text{ } \Omega \text{ cm}$, followed by a thermally activated increase

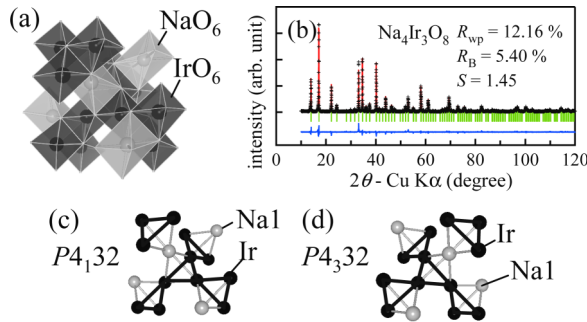


FIG. 1 (color online). (a) Crystal structure of $\text{Na}_4\text{Ir}_3\text{O}_8$ with the space group $P4_132$. Among the three Na sites, only Na1 site is shown for clarity. Black and gray octahedra represent IrO_6 and NaO_6 , respectively. The spheres inside the octahedra represent Ir and Na atoms and oxygens occupy all the corners. (b) The x-ray diffraction pattern of $\text{Na}_4\text{Ir}_3\text{O}_8$ at room temperature. The crosses indicate the raw data and the solid line indicates the spectrum calculated based on the refinement using $P4_132$. (c) and (d) Hyperkagome Ir and Na sublattice derived from the structure of $\text{Na}_4\text{Ir}_3\text{O}_8$ with the space group $P4_132$ (c) and $P4_332$ (d). These two structures with different chirality are indistinguishable by conventional x-ray diffraction, giving the identical result in refinement.

with an activation energy of 500 K with decreasing temperature. This, together with the magnetic properties described below, indicates that $\text{Na}_4\text{Ir}_3\text{O}_8$ is a $S = 1/2$ Mott insulator formed on a hyperkagome lattice.

The temperature dependent magnetic susceptibility $\chi(T)$, shown in Fig. 2(a), indicates that $\text{Na}_4\text{Ir}_3\text{O}_8$ 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 antiferromagnetic Curie-Weiss constant $\theta_W \sim 650 \text{ K}$ 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 θ_W . The observed Curie-Weiss behavior of $\chi(T)$ below θ_W is consistent with the presence of the $S = 1/2$ antiferromagnetic spins on a frustrated hyperkagome lattice. The large antiferromagnetic interaction inferred from θ_W is supported by

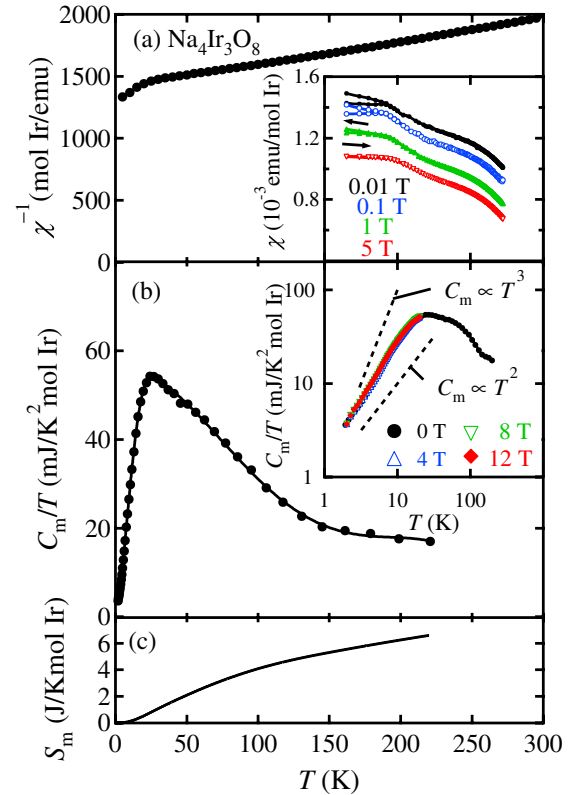


FIG. 2 (color online). Temperature dependence of the inverse magnetic susceptibility χ^{-1} under 1 T (a), magnetic specific heat C_m divided by temperature T (b) and magnetic entropy S_m (c) of polycrystalline $\text{Na}_4\text{Ir}_3\text{O}_8$. To estimate C_m , data for $\text{Na}_4\text{Sn}_3\text{O}_8$ is used as a reference of the lattice contribution. Inset: (a) Temperature dependence of magnetic susceptibility χ of $\text{Na}_4\text{Ir}_3\text{O}_8$ in various fields up to 5 T. For clarity, the curves are shifted by 3, 2, and $1 \times 10^{-4} \text{ emu/mol Ir}$ for 0.01, 0.1, and 1 T data, respectively. (b) C_m/T vs T of $\text{Na}_4\text{Ir}_3\text{O}_8$ in various fields up to 12 T. Broken lines indicate C_m proportional to T^2 and T^3 , respectively.

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 ordering in the susceptibility at least down to 2 K, which is 2 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 glasslike 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 likely represents the bulk, we see the susceptibility tend to saturate and approach a finite value as $T \rightarrow 0$. 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 $\text{Na}_4\text{Sn}_3\text{O}_8$ as a lattice contribution. Because of the subtraction, the data at high temperatures above ~ 100 K, where the lattice contribution dominates the specific heat, are subject to certain ambiguity. The T -dependent magnetic specific heat C_m of $\text{Na}_4\text{Ir}_3\text{O}_8$ is plotted as C_m/T in Fig. 2(b). We observe only a broad peak with its maximum around ~ 30 K and any anomaly indicative of long range ordering is absent. The magnetic entropy, estimated by integrating $C_m/T-T$ data shown in Fig. 2(c), is as large as ~ 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 θ_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 $S = 1$ NiGa_2S_4 [8] but less significant than in the two dimensional $S = 3/2$ kagome $\text{SrCr}_9\text{pGa}_{12-9\text{p}}\text{O}_{19}$ [6].

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 antiferromagnetically. This field independence is universally observed

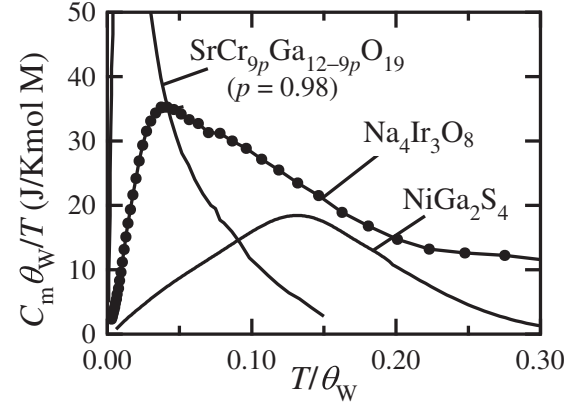


FIG. 3. Comparison of the normalized magnetic specific heat of $\text{Na}_4\text{Ir}_3\text{O}_8$ with those of other frustrated antiferromagnets $\text{SrCr}_{9\text{p}}\text{Ga}_{12-9\text{p}}\text{O}_{19}$ ($p = 0.98$) [6] and NiGa_2S_4 [8]. M in the unit of vertical axis denotes magnetic element Ir, Cr and Ni for $\text{Na}_4\text{Ir}_3\text{O}_8$, $\text{SrCr}_{9\text{p}}\text{Ga}_{12-9\text{p}}\text{O}_{19}$ and NiGa_2S_4 , respectively. Temperature T is normalized by the Curie-Weiss constant θ_w for comparison.

in geometrically frustrated magnets proposed to have a spin-liquid ground state [6,8], providing a further support for a similar state in $\text{Na}_4\text{Ir}_3\text{O}_8$.

We also found that nonmagnetic Ti^{4+} can be substituted partially for Ir^{4+} . As shown in Fig. 4, the introduction of “nonmagnetic” 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 $\text{Na}_4\text{Ir}_3\text{O}_8$. 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 $\text{Na}_4\text{Ir}_3\text{O}_8$ which should be tackled urgently. Firstly, the orbital state of Ir^{4+} should be clarified in understanding the spin-liquid state of $\text{Na}_4\text{Ir}_3\text{O}_8$, because orbital ordering often results in anisotropic spin coupling and hence suppresses frustration. Taking a close look at the atomic coordination in Table I, one notices that, because of chemical pressure from the large Na^+ ion in Ir_3Na tetrahedron, the IrO_6 octahedra are distorted and elongate towards

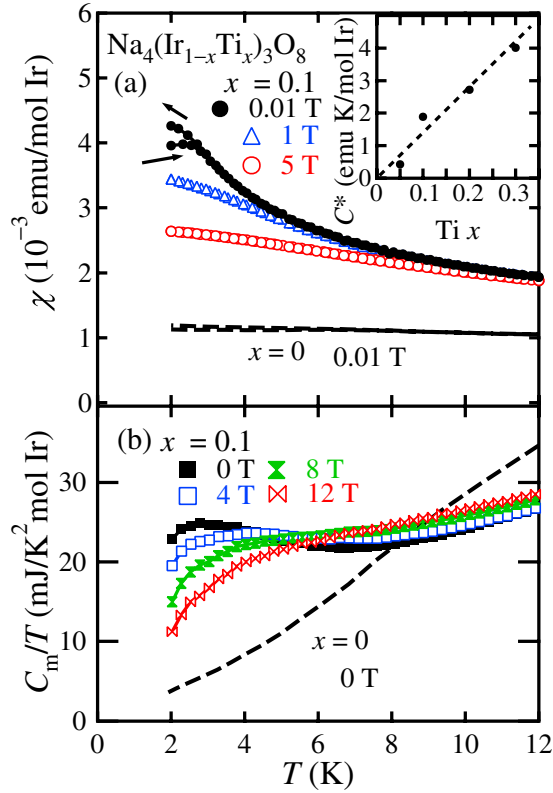


FIG. 4 (color online). (a) Temperature dependence of the magnetic susceptibility $\chi(T)$ of polycrystalline $\text{Na}_4(\text{Ir}_{1-x}\text{Ti}_x)_3\text{O}_8$ ($x = 0.1$) in magnetic fields up to 5 T, compared to the data of $x = 0$ under 0.01 T. (b) Magnetic specific heat C_m of the $x = 0.1$ sample 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 $\text{Na}_4(\text{Ir}_{1-x}\text{Ti}_x)_3\text{O}_8$ ($0 \leq x \leq 0.3$), defined by Schiffer and Daruka [15].

the center of the Ir_3Na tetrahedra. This destabilizes the a_{1g} orbital ($\{|xy\rangle + |yz\rangle + |zx\rangle\}/\sqrt{3}$) pointing towards the center of the Ir_3Na tetrahedra. We may speculate that the $S = 1/2$ on Ir^{4+} has primarily a_{1g} character. If this is the case, the interactions between the $S = 1/2$ spins originate from exchange coupling through the overlap of a_{1g} orbitals. All the nearest neighbor interactions then should be equivalent and Heisenberg-like, consistent with the presence of strong geometrical frustration.

Second, the effect of spin-orbit coupling should be considered. Since Ir is a $5d$ element, the spin-orbit coupling is likely to be much larger than in $3d$ and $4d$ 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_2S_4 [8] and the $S = 3/2$ kagome $\text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19}$ [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 magnonlike dispersion [6,8]. 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 spinel related oxide $\text{Na}_4\text{Ir}_3\text{O}_8$ 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.

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