Robust Spin Liquid State in Na\textsubscript{4-x}Ir\textsubscript{3}O\textsubscript{8}

Ashwini Balodi,\textsuperscript{1} A. Thamizhavel,\textsuperscript{2} and Yogesh Singh\textsuperscript{1}

\textsuperscript{1}Indian Institute of Science Education and Research (IISER) Mohali, Knowledge city, Sector 81, Mohali 140306, India
\textsuperscript{2}Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India

(Dated: December 2, 2014)

The hyper-kagome material Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8} is a three-dimensional spin-liquid candidate proximate to a quantum critical point (QCP). We present a comprehensive study of the structure, magnetic susceptibility $\chi$, heat capacity $C$, and electrical transport on polycrystalline samples of the doped hyper-kagome material Na\textsubscript{4-x}Ir\textsubscript{3}O\textsubscript{8} ($x \approx 0, 0.1, 0.3, 0.7$). Materials with $x \leq 0.3$ are found to be Mott (local-moment) insulators with strong antiferromagnetic interactions. No magnetic ordering down to $T = 2$ K demonstrates that the Mott insulating spin-liquid state seen in $x = 0$ material is robust against large hole doping. The $x = 0.7$ sample shows $\rho(T)$ which weakly increases with decreasing temperature $T$, nearly $T$ independent $\chi$, a linear in $T$ contribution to the low temperature $C$, and a Wilson ratio $R_{\text{W}} \approx 7$ suggesting anomalous semi-metallic behavior.

Intense reasearch on geometrically frustrated magnets has led to a plethora of exciting new physics in the recent past (see \cite{12,13} for recent reviews). The spin-ice phase in pyrochlore magnets\textsuperscript{14,15}, quantum spin-liquid (QSL) in triangular lattice organic compounds $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$\textsuperscript{17,18} and EtMe$_3$Sb[Pd(dmit)$_2$]\textsuperscript{19}, and in 2D kagome lattice inorganic materials ZnCu$_3$(OH)$_2$Cl$_6$\textsuperscript{20,21} and BaCu$_2$V$_2$O$_6$(OH)$_2$\textsuperscript{22}, the possibility of magnetic monopoles as excitations of the spin-ice state\textsuperscript{12-15}, and heavy fermion behavior in the itinerant frustrated magnet LiV$_2$O$_4$\textsuperscript{23} are just a few examples.

There is growing evidence that Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8}, with effective spins $S = \frac{1}{2}$ on a frustrated hyperkagome lattice, may be the first candidate QSL with a 3-dimensional (3D) structure\textsuperscript{22,23}. Heat capacity measurements down to $T = 0.5$ K have shown an absence of long-range magnetic ordering\textsuperscript{18} even though magnetic susceptibility provides evidence for strong antiferromagnetic interactions as evidenced by a Weiss temperature of $\theta \sim -600$ K\textsuperscript{17,18}. Several anomalous features, apparently associated with the spin-liquid state, have been observed in thermodynamic measurements on Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8}. These include an anomaly around $T \sim 30$ K in the magnetic heat capacity, a $T^6$ dependence of the heat capacity at low temperatures with an exponent $n$ between 2 and 3, and a large Wilson ratio $R_{\text{W}} \approx 30$\textsuperscript{17,18}. Recently microscopic muSR and neutron scattering measurements down to $T = 20$ mK have shown absence of long-range magnetic order on polycrystalline samples. It has been suggested that Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8} goes into a short-range frozen state with quasi-static moments below $T = 6$ K which is either disorder driven or is stabilized by quantum fluctuations\textsuperscript{26}.

Tuning a spin-liquid away from the Mott insulating state is expected to lead to anomalous metallic properties and even unconventional superconductivity. The high-$T_c$ cuprates and the organic Mott insulators are such examples where carrier doping and/or modest pressures can tune the system from antiferromagnetic or spin-liquid insulators to superconductors (see \cite{24,25} for reviews). It is known that the charge gap in Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8} is small ($\sim 500 - 1000$ K) and that it is close to a metal-insulator transition\textsuperscript{17,18}. There is also recent experimental evidence that Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8} may be situated close to a quantum-critical-point (QCP)\textsuperscript{18}.

Recently, attempts to hole-dope Na\textsubscript{4}Ir\textsubscript{3}O\textsubscript{8} have led to the discovery of a new material Na$_3$Ir$_3$O$_8$ having the same hyper-kagome Ir sublattice.\textsuperscript{27} Na$_3$Ir$_3$O$_8$ is found to be a semi-metal with a small density of states.\textsuperscript{27} A recent study of the thermal conductivity of weakly insulating Na$_4$Ir$_3$O$_8$ and semi-metallic Na$_3$Ir$_3$O$_8$ have been reported showing anomalously low thermal-conductivity for the insulating sample compared to the metallic sample.\textsuperscript{28} The new Na$_3$Ir$_3$O$_8$ material however, crystallizes in a different structure to Na$_4$Ir$_3$O$_8$ and hence one cannot continuously go from one structure to the other.\textsuperscript{27} Therefore, what happens on doping the original hyper-kagome Na$_4$Ir$_3$O$_8$ structure is still unknown.

To explore the possibility of a nearby metallic (superconducting!) or magnetically ordered state we have tried to tune Na$_4$Ir$_3$O$_8$ away from its Mott insulating spin-liquid state by creating Na deficient samples while keeping the original structure intact. To this end we have synthesized hole-doped materials Na$_{4-x}$Ir$_3$O$_8$ ($x = 0, 0.1, 0.3, 0.7$) and studied their structural, magnetic and thermal properties.

Specifically we track the evolution of the Weiss temperature, the anomaly in the magnetic heat capacity, the power-law heat capacity at low temperatures, and the Wilson ratio as increasing amounts of Na are removed from the parent spin-liquid Na$_4$Ir$_3$O$_8$. Rather surprisingly we find that the insulating behavior, the local moment magnetism with strong antiferromagnetic interactions, and indeed the spin-liquid state persists in the Na deficient samples. Only in the largest doping $x = 0.7$ do we see a conventional $T^3$ low temperature heat capacity and a much reduced Wilson ratio $R_{\text{W}} \approx 7$. These results demonstrate that the spin-liquid state in Na$_4$Ir$_3$O$_8$ is robust under large hole dopings and that most likely a fully metallic state is not attained if the original structure is retained.

Polycrystalline samples of Na$_{4-x}$Ir$_3$O$_8$ ($x = 0 - 0.7$) and Na$_4$Sn$_3$O$_8$ were synthesized using high-purity starting materials Na$_2$CO$_3$ (5N Alfa Aesar) and Ir metal powder (4N, Alfa Aesar) or SnO$_2$ (5N, Alfa Aesar). Starting materials were mixed in amounts appropriate for a given $x$ and heated in air inside covered alumina crucibles at 750 °C for 24 hrs for calcination. The resulting black powders were thoroughly ground and mixed in an agate mortar and pestle, pressed into pellets, and given two heat treatments at 985 °C and 1000 °C for 16 hrs each with an intermediate grinding and pelletizing.
step. The material was finally quenched in air after the final treatment. All materials were then stored and handled in an inert gas glove-box (MBraun, Argon, $H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm). Magnetic susceptibility, heat capacity, and electrical transport measurements down to $T = 2$ K were measured using a Quantum Design PPMS. The low temperature specific heat for the $x = 0$ sample were measured using the dilution refrigerator option of the PPMS.

Powder X-ray diffraction patterns for three representative samples $\text{Na}_{1-x}\text{Ir}_3\text{O}_8$ ($x = 0, 0.3, 0.7$) are shown in Fig. 1. The solid (red) curves through the data are the results obtained from Rietveld refinement of the data. The parameters obtained from the refinements are listed in Table I. The quoted values of $x$ are those obtained from the refinements. All samples were found to have the correct majority phase. The only impurity phase found in the samples was a small amount of $\text{Ir}_2\text{O}_5$. The position of the most intense $\text{Ir}_2\text{O}_5$ reflection is marked with a * in the patterns shown in Fig. 1. From the Table I it can be seen that the lattice parameter does not change with Na deficiency. The major change is in the occupation of the Na2 and Na3 sites which reduces for the Na deficient samples as expected. Between the two sites, the occupancy of Na2 site reduces more in comparison to Na3. In the diffraction pattern, the only major change with increasing Na deficiency is the intensity of the (311) reflection which increases relative to the other reflections as indicated by an arrow in the Fig. 1.

The resistance $R(T)$ divided by the $T = 300$ K value is shown in Fig. 2 for the $x = 0$ and $x = 0.7$ samples. The $T = 300$ K resistivity values for the two samples are 41 m$\Omega$ cm and 16 m$\Omega$ cm, respectively. Since the samples were pressed sintered pellets, the errors on these absolute values could be upto 50% due to uncertainty in determining the true dimensions, specially for the $x = 0.7$ sample pellet which were porous. However, the values and temperature dependence suggest that the conductivity for the $x = 0.7$ sample is slightly enhanced compared to the parent $x = 0$ material. The temperature dependence and room temperature value of the resistivity for our samples are similar to those recently reported for $\text{Na}_{3.4}\text{Ir}_3\text{O}_8$ single crystals. For the $x = 0.7$ sample $R(2K)/R(300K) \approx 3.5$ suggesting that this sample is close to being (semi-)metallic. Both the magnetic susceptibility $\chi$ and heat capacity $C$ for this sample support this.

Figure 3 shows the magnetic susceptibility $\chi$ versus temperature $T$ between $T = 1.8$ K and $400$ K for $\text{Na}_{1-x}\text{Ir}_3\text{O}_8$ ($x \approx 0, 0.1, 0.3, 0.7$). Data for two samples with $x \approx 0$ are shown and are marked with arrows in Fig. 3. Although the temperature dependence of these two samples are similar, one can already see a slight difference in the absolute magnitude of $\chi(T)$ for two samples with apparently same Na content. When Na is intentionally removed the magnetic susceptibility drops in magnitude although the local moment behavior persists up to at least $x \approx 0.3$. The high temperature ($T \geq 200$ K) data were fit by the Curie-Weiss expression $\chi = \chi_0 + \frac{C}{T - \theta}$. The parameters obtained from fits to the data for the samples $\text{Na}_{1-x}\text{Ir}_3\text{O}_8$ ($x = 0, 0.1, 0.3$) are given in Table II. We see that the Curie constant $C$ monotonically decreases with increasing $x$ suggesting a decrease in the effective moment per Iridium in the Na deficient sample. The Weiss temperature $\theta$

![Figure 1: (Color online) Powder X-ray diffraction pattern for $\text{Na}_{1-x}\text{Ir}_3\text{O}_8$ ($x = 0, 0.3, 0.7$) materials (open symbols). The solid (red) curves through the data are the results obtained from Rietveld refinement of the data. The parameters obtained from the refinements are listed in Table I. The quoted values of $x$ are those obtained from the refinements. All samples were found to have the correct majority phase. The only impurity phase found in the samples was a small amount of $\text{Ir}_2\text{O}_5$. The position of the most intense $\text{Ir}_2\text{O}_5$ reflection is marked with a * in the patterns shown in Fig. 1. From the Table I it can be seen that the lattice parameter does not change with Na deficiency. The major change is in the occupation of the Na2 and Na3 sites which reduces for the Na deficient samples as expected. Between the two sites, the occupancy of Na2 site reduces more in comparison to Na3. In the diffraction pattern, the only major change with increasing Na deficiency is the intensity of the (311) reflection which increases relative to the other reflections as indicated by an arrow in the Fig. 1.](image-url)

---

**TABLE I: Structural parameters obtained from a Rietveld refinement of room temperature powder X-ray patterns shown in Fig. 1 with space group #213, $P4_132$. We have used the standardized structural parameters. The unit cell co-ordinates in this notation are related to the earlier published unit cell by an origin shift of $(1/2, 1/2, 1/2)$.**

| Na$_{1-x}$Ir$_3$O$_8$ | $a = 8.981(2)$ Å |
|----------------------|-------------------|
| **atom**             | **Wyck**          |
| Na                   | 12d               |
| Na1                  | 4a                |
| Na2                  | 4b                |
| Na3                  | 12d               |
| O1                   | 8c                |
| O2                   | 24e               |

| Na$_{3.7}$Ir$_3$O$_8$ | $a = 8.979(7)$ Å |
|----------------------|------------------|
| **atom**             | **Wyck**          |
| Ir                   | 12d               |
| Na1                  | 4a                |
| Na2                  | 4b                |
| Na3                  | 12d               |
| O1                   | 8c                |
| O2                   | 24e               |

---

**FIG. 1:** The temperature dependence and room temperature value of the resistivity for our samples are similar to those recently reported for $\text{Na}_{3.4}\text{Ir}_3\text{O}_8$ single crystals. For the $x = 0.7$ sample $R(2K)/R(300K) \approx 3.5$ suggesting that this sample is close to being (semi-)metallic. Both the magnetic susceptibility $\chi$ and heat capacity $C$ for this sample support this.

**FIG. 2:** The resistance $R(T)$ divided by the $T = 300$ K value is shown in Fig. 2 for the $x = 0$ and $x = 0.7$ samples. The $T = 300$ K resistivity values for the two samples are 41 m$\Omega$ cm and 16 m$\Omega$ cm, respectively. Since the samples were pressed sintered pellets, the errors on these absolute values could be upto 50% due to uncertainty in determining the true dimensions, specially for the $x = 0.7$ sample pellet which were porous. However, the values and temperature dependence suggest that the conductivity for the $x = 0.7$ sample is slightly enhanced compared to the parent $x = 0$ material. The temperature dependence and room temperature value of the resistivity for our samples are similar to those recently reported for $\text{Na}_{3.4}\text{Ir}_3\text{O}_8$ single crystals. For the $x = 0.7$ sample $R(2K)/R(300K) \approx 3.5$ suggesting that this sample is close to being (semi-)metallic. Both the magnetic susceptibility $\chi$ and heat capacity $C$ for this sample support this.

**FIG. 3:** The magnetic susceptibility $\chi$ versus temperature $T$ between $T = 1.8$ K and $400$ K for $\text{Na}_{1-x}\text{Ir}_3\text{O}_8$ ($x \approx 0, 0.1, 0.3, 0.7$). Data for two samples with $x \approx 0$ are shown and are marked with arrows in Fig. 3. Although the temperature dependence of these two samples are similar, one can already see a slight difference in the absolute magnitude of $\chi(T)$ for two samples with apparently same Na content. When Na is intentionally removed the magnetic susceptibility drops in magnitude although the local moment behavior persists up to at least $x \approx 0.3$. The high temperature ($T \geq 200$ K) data were fit by the Curie-Weiss expression $\chi = \chi_0 + \frac{C}{T - \theta}$. The parameters obtained from fits to the data for the samples $\text{Na}_{1-x}\text{Ir}_3\text{O}_8$ ($x = 0, 0.1, 0.3$) are given in Table II. We see that the Curie constant $C$ monotonically decreases with increasing $x$ suggesting a decrease in the effective moment per Iridium in the Na deficient sample. The Weiss temperature $\theta$
FIG. 2: (Color online) Resistance divided by the $T = 300$ K value $R(T)/R(300K)$ versus $T$ of Na$_{4-x}$Ir$_3$O$_8$ ($x = 0, 0.7$).

TABLE II: Parameters obtained from fits to the magnetic susceptibility data by the Curie-Weiss expression $\chi = \chi_0 + \frac{C}{T-\theta}$.

| $x$ | $\chi_0$ ($10^{-4}$ cm$^3$/Ir mol) | $C$ (cm$^3$ K/Ir mol) | $\theta$ (K) |
|-----|---------------------------------|----------------------|------------|
| 0   | 1.2(1)                          | 0.39(1)              | -568(9)    |
| 0.1 | 1.4(1)                          | 0.33(2)              | -512(6)    |
| 0.3 | 1.8(6)                          | 0.28(3)              | -509(7)    |
| 0.7 |                                 |                      |            |

decreases slightly but stays large and negative indicating that strong antiferomagnetic interactions persist between the surviving local magnetic moments.

The $\chi(T)$ behavior for the $x = 0.7$ sample shows qualitatively different behavior. The $\chi(T)$ is almost $T$ independent except the low temperature upturn which is seen for all samples. The $T$ independent $\chi$ is similar to the behavior expected for a Pauli paramagnetic metal. It must be noted however, that $\chi$ actually shows a weak increase with $T$ and thus is not the behavior of a simple metal.

To confirm absence of any ordering, we have performed heat capacity measurements on Na$_4$Ir$_3$O$_8$ down to $T = 100$ mK. In Fig. 4 we show the low temperature magnetic heat capacity $C_{mag}$ versus $T$ for Na$_4$Ir$_3$O$_8$ measured at various magnetic fields $H = 0, 5, 14$ T between $T = 100$ mK and 2 K. The magnetic contribution $C_{mag}$ was obtained by subtracting the $C(T)$ data of Na$_3$Sn$_3$O$_8$ (corrected for the molar mass difference) from the data of Na$_4$Ir$_3$O$_8$. We do not see any evidence for magnetic ordering down to the lowest temperatures measured. The $C_{mag}$ is also insensitive to applied magnetic fields up to $H = 14$ T as shown in Fig. 4. The Fig. 4 inset shows the zero field $C_{mag}/T$ vs $T$ between $T = 100$ mK and $T = 4$ K. The data above $T = 0.75$ K were fit by the expression $C = \gamma T + \beta T^n$. We were able to obtain an excellent fit, shown as the solid curve through the data in the inset of Fig. 4 with the values $\gamma = 2.8(4)$ mJ/K$^2$ mol Ir, $\beta = 3.4(2)$ mJ/mol K$^3$, and $n = 2.38(3)$. The value of $\gamma \approx 2$ mJ/K$^2$ mol Ir and an exponent $n$ between 2 and 3 is consistent with previous reports.$^{17,18}$

Below about 0.6 K we see an upturn in $C_{mag}/T$. Although nuclear Schottky anomalies are common at these low temperatures, the low temperature upturn does not follow the expected $1/T^2$ behavior for the high temperature tail of a Schottky anomaly. The upturn is also only weakly dependent on the applied field. Thus a low temperature magnetic transition can also be probably ruled out. A recent measurement on metallic single crystals of Na$_3$Ir$_3$O$_8$ has seen a similar upturn in the heat capacity below $T = 1$ K and it has been suggested to arise from a small impurity contribution.$^{28}$ Paramagnetic impurities would also be expected to show Schottky like anomalies due to a splitting of their magnetic ground state by the crystalline electric field. However, these anomalies would be

FIG. 3: (Color online) Magnetic susceptibility $\chi$ versus $T$ of Na$_{4-x}$Ir$_3$O$_8$ ($x = 0, 0.1, 0.3, 0.7$) between $T = 2$ K and 400 K.

FIG. 4: (Color online) Low temperature magnetic heat capacity $C_{mag}$ versus temperature $T$ for the spin-liquid Na$_4$Ir$_3$O$_8$ between $T = 100$ mK and 2 K in magnetic fields $H = 0, 5, 14$ T. The inset shows the $H = 0$ data plotted as $C_{mag}/T$ versus $T$. The data above $T = 0.75$ K were fit (shown as the solid red curve through the data) by the expression $C = \gamma T + \beta T^n$ (see text for details).
magnetic field dependent, moving up in temperature with increasing field. Since we do not observe such a behavior, the origin of this upturn is unknown at present.

We now present the evolution with doping of another notable feature of the undoped spin-liquid material: the broad anomaly in the magnetic contribution to the heat capacity at around \( T \sim 30 \, K \) \cite{17,18}. Figure 5 shows the zero-field \( C_{\text{mag}}/T \) vs \( T \) for \( \text{Na}_{1-x}\text{Ir}_8 \text{O}_8 \) \((x = 0, 0.3, 0.7)\) between \( T = 2 \, K \) and \( T = 50 \, K \). The broad anomaly observed earlier for the undoped sample persists in the Na-deficient samples as well. Although the magnitude of the anomaly decreases slightly, the maximum of the anomaly only reduces from \( \approx 55 \, mJ/mol \, K^2 \) to about \( \approx 42 \, mJ/mol \, K^2 \). The position of the peak also doesn’t change. These observations suggest that the mechanism leading to the anomaly in \( \text{Na}_3\text{Ir}_8 \text{O}_8 \) is also at work in the Na deficient samples.

Figure 5 inset, shows the zero-field \( C_{\text{mag}}/T \) vs \( T^2 \) for \( \text{Na}_{1-x}\text{Ir}_8 \text{O}_8 \) \((x = 0, 0.3, 0.7)\) between \( T = 2 \, K \) and \( T = 10 \, K \). The downward curvature of the data for \( \text{Na}_3\text{Ir}_8 \text{O}_8 \) in this plot highlights the power-law dependence of \( C_{\text{mag}}(T) \) with an exponent between 2 and 3. This exponent increases for the Na deficient samples with the data at the lowest temperatures \( (T < 5 \, K) \) for the \( x = 0.7 \) sample \( \text{Na}_{3.3}\text{Ir}_8 \text{O}_8 \) showing a more conventional \( T^3 \) behavior. It is also evident that \( C_{\text{mag}}/T \) for all samples extrapolate to similar \( T = 0 \) values of \( \gamma \approx 2.5 \, mJ/\text{Ir mol} \, K^2 \).

**Summary and Discussion:** We have successfully synthesized Na deficient samples \( \text{Na}_{1-x}\text{Ir}_8 \text{O}_8 \) \((x = 0, 0.1, 0.3, 0.7)\) having the hyperkagome structure and performed thermodynamic measurements of the magnetic susceptibility \( \chi(T) \), and heat capacity \( C(T) \). We have extended heat capacity measurements on the \( x = 0 \) parent compound down to \( T = 100 \, mK \) to look for any magnetic transition and have found none. This firmly establishes \( \text{Na}_3\text{Ir}_8 \text{O}_8 \) as a strong spin-liquid candidate material. For the Na deficient samples we find, rather surprisingly, that the basic behavior of the parent \( x = 0 \) compound persists even on removing large amounts of Na. Specifically, the local moment magnetism with large antiferromagnetic interactions is seen up to \( x = 0.3 \). Additionally the broad anomaly in the magnetic heat capacity seen in the parent \( x = 0 \) material around \( T = 30 \, K \) is still seen even for the \( x = 0.7 \) sample although its magnitude decreases a bit. Thus, our results show that both the insulating state as well as the spin-liquid state is robust even under large hole doping. Additionally, we can estimate the Wilson ratio \( R_W = \frac{\pi^2 k_B^2}{3} \frac{\chi_P}{\gamma} \), which is the ratio of the density of states probed by \( \chi \) (\( \chi_P \) is the Pauli paramagnetic susceptibility as \( T \to 0 \)) to the density of states probed by heat capacity (\( \gamma \) is the Sommerfeld coefficient) and is expected to be 1 for a free-electron Fermi-gas. For \( \text{Na}_3\text{Ir}_8 \text{O}_8 \), using \( \chi_P = 9.4 \times 10^{-4} \, cm^3/mol \, \text{Ir} \) and \( \gamma = 2.5 \, mJ/mol \, \text{Ir} \, K^2 \) from our recent measurements\cite{12}, we find a quite large \( R_W \approx 30 \) suggesting strong magnetic correlations which enhance \( \chi_P \) compared to \( \gamma \). Since the \( \chi_P \) progressively decreases and \( \gamma \) stays approximately the same as Na is removed, the \( R_W \) progressively decreases for the Na deficient samples. For the \( x = 0.7 \) sample, using \( \chi_P \approx 2.2 \times 10^{-4} \, cm^3/mol \, \text{Ir} \) and \( \gamma = 2.5 \, mJ/mol \, \text{Ir} \, K^2 \) from Figs. 3 and 5 inset respectively, we obtain \( R_W \approx 7 \). The reduced value of \( R_W \) for the Na deficient samples is consistent with a recent theoretical work where it was shown that the susceptibility in the spin-liquid state is enhanced over the heat capacity due to strong spin-orbit coupling and correlations which are reduced in the metallic state leading to a smaller \( R_W \) for the metallic sample\cite{22}.

Refinements of the powder diffraction patterns have shown that with increasing \( x \), Na is progressively removed from the lattice. Additionally we have found that Na is preferentially removed from the Na2 (4b) site. This site is not on the Ir tetrahedra and hence deficiency in this site is not expected to lead to disorder in the magnetic Ir sub-lattice. Therefore, the frustrated hyperkagome lattice of Ir moments is not disturbed with Na deficiency. This is probably why the spin-liquid state is robust under removal of fairly large amounts of Na. Na deficiency is however, expected to lead to hole doping of the system. It is therefore surprising that local-moment behavior and insulating behavior survives under hole doping. This is consistent with recent experiments on single crystals of \( \text{Na}_3\text{Ir}_7 \text{O}_8 \) where it was found that for \( x = 0.6 \) (this would be \( x = 0.4 \) for our samples) the material was insulating and spin-liquid\cite{22}. A metallic state is obtained only for \( \text{Na}_3\text{Ir}_7 \text{O}_8 \) where a different crystal structure is obtained\cite{7}. These observations are surprising given that \( \text{Na}_3\text{Ir}_7 \text{O}_8 \) is regarded as sitting close to a metal-Insulator transition and possibly close to a quantum critical point (QCP)\cite{22}.

In summary we have shown that the Mott insulating spin-liquid state in \( \text{Na}_3\text{Ir}_7 \text{O}_8 \) is quite robust against large removal of Na from the lattice. The anomalous properties like the peak in \( C_{\text{mag}} \) at \( T \approx 30 \, K \), the power-law heat capacity, and the large Wilson ratio persist for the doped samples. Any theory for the parent material should thus also be able to explain the above surprising behaviors.

**Acknowledgments:** We thank the X-ray facility at IIEST Mohali for powder XRD measurements. YS acknowledges DST, India for support through Ramanujan Grant #SR/S2/RJN-
76/2010 and through DST grant #SB/S2/CMP-001/2013.

1. F. Mila, Eur. J. Phys. 21, 499 (2000).
2. A. P. Ramirez, Nature Physics 4, 442 (2008).
3. L. Balents, Nature 464, 199 (2010).
4. M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske, and K. W. Godfrey, Phys. Rev. Lett., 79, 2554 (1997).
5. S. T. Bramwell and Michel J. P. Gingras, Science 294, 1495 (2001).
6. S. Yamashita, Y. Nakazawa, M. Ogumi, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, Nature Physics 4, 459 (2008).
7. M. Yamashita, N. Nakata, Y. Kasahara, T. Sasaki, N. Yoneyama, N. Kobayashi, S. Fujimoto, T. Shibauchi, and Y. Matsuda, Nature 464, 199 (2010).
8. M. J. Lawler, A. Paramekanti, Y. B. Kim, and L. Balents, Phys. Rev. Lett. 101, 197201 (2008).
9. M. J. Lawler, A. Paramekanti, Y. B. Kim, and L. Balents, Phys. Rev. Lett. 100, 227201 (2008).
10. Y. Zhou, P. A. Lee, T-K. Ng, and F-C Zhang, Phys. Rev. Lett. 101, 197201 (2008).
11. S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, Phys. Rev. Lett. 78, 3729 (1997).
12. Y. Okamoto, M. Nohara, H. Aruga-Katori, and H. Takagi, Phys. Rev. Lett. 99, 137207 (2007).
13. Y. Singh, Y. Tokiwa, J. Dong, and P. Gegenwart, Phys. Rev. B 88, 202413(R) (2013).
14. J. M. Hopkinson, S. V. Isakov, H-Y. Kee, and Y. B. Kim, Phys. Rev. Lett. 99, 037201 (2007).
15. J. M. Lawler, H-Y. Kee, Y. B. Kim, and A. Vishwanath, Phys. Rev. Lett. 100, 227201 (2008).
16. S. T. Bramwell, S. R. Giblin, S. Calder, R. Aldus, D. Prabhakaran, and T. Fennell, Nature 464, 199 (2010).
17. S. Yamashita, Y. Nakazawa, M. Ogumi, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, Nature Physics 4, 459 (2008).
18. M. Yamashita, N. Nakata, Y. Senshu, M. Nagata, H. M. Yamamoto, R. Kato, T. Shibauchi, Y. Matsuda, Science 328, 1246 (2010).
19. J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, Phys. Rev. Lett. 98, 107204 (2007).
20. T. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, and Y. S. Lee, Nature 492, 406 (2012) and references therein.
21. Y. Okamoto, H. Yoshida, and Z. Hiroi, J. Phys. Soc. Jpn. 78, 033701 (2009).
22. C. Castelnovo, R. Moessner, and S. Somdhi, Nature 451, 42 (2008).
23. D. J. P. Morris, D. A. Tennant, S. A. Grigera, B. Klemke, C. Castelnovo, R. Moessner, C. Czternasty, M. Meissner, K. C. Rule, J.-U. Hoffmann, K. Kiefer, S. Gerischer, S. D. Krinsky, and R. S. Perry, Science 326, 411 (2009).
24. T. Fennell, P. P. Deen, A. R. Wildes, K. Schmalzl, D. Prabhakaran, A. T. Boothroyd, R. J. Aldus, D. F. McMorrow, and S. T. Bramwell, Science 326, 415 (2009).
25. S. T. Bramwell, S. R. Giblin, S. Calder, R. Aldus, D. Prabhakaran, and T. Fennell, Nature 461, 956 (2009).
26. S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, Phys. Rev. Lett. 78, 3729 (1997).
27. Y. Okamoto, M. Nohara, H. Aruga-Katori, and H. Takagi, Phys. Rev. Lett. 99, 137207 (2007).
28. Y. Singh, Y. Tokiwa, J. Dong, and P. Gegenwart, Phys. Rev. B 88, 202413(R) (2013).
29. J. M. Hopkinson, S. V. Isakov, H-Y. Kee, and Y. B. Kim, Phys. Rev. Lett. 99, 037201 (2007).
30. M. J. Lawler, H-Y. Kee, Y. B. Kim, and A. Vishwanath, Phys. Rev. Lett. 100, 227201 (2008).
31. Y. Zhou, P. A. Lee, T-K. Ng, and F-C Zhang, Phys. Rev. Lett. 101, 197201 (2008).
32. M. J. Lawler, A. Paramekanti, Y. B. Kim, and L. Balents, Phys. Rev. Lett. 101, 197202 (2008).
33. D. Podolsky, A. Paramekanti, Y. B. Kim, and T. Senthil, Phys. Rev. Lett. 102, 186401 (2009).
34. D. C. Johnston, in Handbook of Magnetic Materials, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1997), Vol. 10, Chap. 1, pp. 1237.
35. J. M._hopkinson, S. V. Isakov, H-Y. Kee, and Y. B. Kim, Phys. Rev. Lett. 99, 037201 (2007).
36. M. J. Lawler, A. Paramekanti, Y. B. Kim, and L. Balents, Phys. Rev. Lett. 101, 197202 (2008).
37. D. Podolsky, A. Paramekanti, Y. B. Kim, and T. Senthil, Phys. Rev. Lett. 102, 186401 (2009).
38. D. C. Johnston, in Handbook of Magnetic Materials, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1997), Vol. 10, Chap. 1, pp. 1237.
39. B. J. Powell, Ross H. McKenzie, Rep. Prog. Phys. 74, 056501 (2011).
40. R. Dally, T. Hogan, A. Amato, H. Luetkens, C. Baines, J. Rodriguez-Rivera, M. J. Graf, S. D. Wilson, arXiv:1410.7072 (2014).
41. T. Takayama, Akiyo Matsumoto, J. Nuss, A. Yaresko, K. Ishii, M. Yoshida, J. Mizuki, and H. Takagi, SCIENTIFIC REPORTS, 4, 6818 (2014).
42. B. Fauque, Xiaofeng Xu, A. F. Bangura, E. C. Hunter, A. Yamamoto, K. Behnia, A. Carrington, H. Takagi, N. E. Hussey, and R. S. Perry, arXiv:1410.8792 (2014).
43. G. Chen and Y. B. Kim, Phys. Rev. B 87, 165120 (2013).