Semimetal behavior and magnetic correlations in the doped hyper-kagome Na$_2$Ir$_3$O$_8$

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We present a microscopic study of a doped quantum spin liquid candidate, the hyperkagome Na$_2$Ir$_3$O$_8$ compound by using $^{25}$Na NMR. We determine the intrinsic behavior of the uniform $\mathbf{q} = 0$ susceptibility via shift measurements and the dynamical response by probing the spin-lattice relaxation rate. Throughout the studied temperature range, the susceptibility is consistent with a semimetal behavior. Remarkably, the antiferromagnetic fluctuations present in the insulating parent compound Na$_4$Ir$_7$O$_8$ survive in the studied compound. The dynamics are consistent with 120$^\circ$ excitations modes that are correlated over short ranges.

Geometrical frustration in insulating spin systems has long been recognized as a way to access novel quantum states such as spin liquids [1]. Following the proposal of Anderson that a spin liquid can act as a substrate for superconductivity, the holy grail of the field of frustrated magnetism is the possibility to dope spin liquids, with a promise of emergent new strongly correlated metallic states and possibly even superconductivity [2–4]. However, despite many attempts it has remained elusive. In particular, efforts to follow up the ab-initio predictions of doped herbertsmithite [4–6] have revealed that doping Zn-Cu hydroxyl halides leaves the electrons localized, possibly due to the formation of polaronic states together with lattice displacements [7]. Different model systems are therefore needed to tackle the challenge.

The discovery of spin-orbit coupling assisted Mott insulators in iridates has further opened many new possibilities in the study of magnetism [8]. In addition to their appeal in the context of metal-insulator transitions, they can harbor novel $J_{\text{eff}} = 1/2$ spin states and provide new forms of frustration, dependent on the bond orientation [9, 10]. A growing list of iridate compounds [11, 12] ranges from honeycomb lattices of the $A_2$Ir$_3$O$_3$ formula [13] to triangular systems showcased by Ba$_3$Ir$_2$Ti$_2$O$_9$ [14] to three-dimensional compounds such as $\beta$ and $\gamma$ polytypes of Li$_2$Ir$_3$O$_3$ [15, 16]. Since in many cases the electronic gap is of the order of a few hundred meV [17–20], strong changes of the accessible states can be expected with minor modifications in the compounds.

A particularly interesting case is the unique hyperkagome lattice in the form of Na$_4$Ir$_7$O$_8$ [21] which is an insulator and despite a large effective exchange interaction of $J \approx 300$ K, was found to only exhibit spin freezing at $\approx 7$ K [22, 23]. The geometric frustration is evident from the arrangement of the iridium ions in the crystal structure, where the triangular motives share the Ir corners in a three-dimensional network as shown in Figure 1. Moreover, since the exchange pathway between different iridium ions proceed through edge-sharing oxygen octahedron with different orientations, some component of bond-dependent anisotropic (Kitaev) interaction is expected to be present. Recent Raman experiments suggest that it could be up to ten times stronger than Heisenberg exchange [24].

Remarkably, this system can be modified by removing 1/4 of the sodium atoms, which results in Na$_2$Ir$_3$O$_8$. Structurally it maintains the same space group P4$_1$32 (213), but some of the sodium atoms are rearranged: instead of the partially occupied Wyckoff 4a and 12d sites there is a fully occupied 8c site. The sodium ions positioned in the 4b site retain their position. The oxygen and the iridium atoms remain in the same Wyckoff positions and are only slightly shifted. Importantly, the underlying hyperkagome arrangement of iridium ions is preserved [25]. The iridium valence in this system is 4.33+ and not 4+ like in the parent compound. In terms of charge balance, it can be thought of as a 1/3rd hole doped hyper-kagome spin system and indeed the measured resistivity exhibits metallic behavior. The situation is in fact more complex, calling for an interplay between intersite hopping, Coulomb repulsion, crystal field splitting and spin-orbit coupling, with a resulting state that appears to be a semi-metal based on Hall measurements and DFT calculations [25]. Although the initial expectation has been that application of pressure should lead to a metallic state [25], recent studies showed that instead, a semimetal-insulator transition takes place [26], further indicating that
the system is on the verge of a metal to insulator transition.

In order to proceed in understanding the complex interplay between the charges and magnetic moments in this material and doped spin liquids in general, two outstanding key questions have to be tackled: i) what are the intrinsic magnetic properties of such a system and ii) do the magnetic correlations of a quantum spin liquid persist in a doped material and what role do they play in Na$_3$Ir$_3$O$_8$? In the present study we set out to answer these questions.

It is extremely challenging to access the fundamental properties of the spin correlations in these systems. On one hand, since the intrinsic susceptibility is small, the bulk response is dominated by the small number of impurities [25]. On the other hand, the difficulty of producing large samples coupled to the fact that iridium is a strong neutron absorber, prevent from neutron scattering studies. In this respect, Nuclear Magnetic Resonance (NMR) offers a unique way to investigate both the intrinsic susceptibility through the spectral measurements as a function of temperature as well as access the spin dynamics through relaxation measurements.

In this paper, we present a local-probe $^{23}$Na NMR study of Na$_3$Ir$_3$O$_8$ and find that the intrinsic susceptibility has a strong temperature dependence at high temperatures but a much weaker dependence at lower temperatures. We can reproduce the main features using a semimetal model. The temperature dependence of the spin-lattice relaxation rate and its magnitude suggest that the ground state is neither clearly metallic, nor insulating, in general agreement with the semimetal proposal. Most importantly, by comparing the two $^{23}$Na nuclei located at different sites, we find that short-range antiferromagnetic fluctuations persist in the semimetallic phase.

The experiments were performed on a small sub-millimeter single-crystal sample of Na$_3$Ir$_3$O$_8$ (see the inset of Fig. 2) from the same growth batch as used in Ref. [25]. We used a cryo-free 14 T sweep magnet and a flow cryostat. An additional series of measurements were performed down to 1.5 K using a cold-bore magnet to check for any possible spin freezing. All the measurements were obtained using the $\pi/2-\pi$ spin echo sequence. For the determination of the spin-lattice relaxation rate, the same experiments were performed with a varying repetition rate to obtain the intensity as a function of the rate. All of the measurements were performed at a nominal applied field of 12 T, with a calibration run measuring the spectrum from copper in the coil taken for every measurement, to account for any drift in the field.

Since Na is reasonably close to the iridium atoms and $^{23}$Na has a large gyromagnetic ratio with a 100 % abundance, it is an efficient probe of the magnetism of the iridium hyperkagome structure. The two inequivalent sodium sites in the structure (Fig. 1) lead to two distinct signals as seen in Fig. 2. The Na 1 and Na 2 nuclei are positioned at respectively $\approx 3.3$ Å and $\approx 3.7$ Å away from the Ir, suggesting that the Na 1 is coupled more strongly and hence shifted more, corresponding to the right-hand-side peak in the spectrum. The ratio of $\approx 0.5$ between the integrated intensities of the two peaks corresponds to the ratio of the two sites in the structure and confirms this assignment. Since the sodium ions are not located in cubic sites and have a non-zero quadrupolar moment, it would be expected that $^{23}$Na spectra display both a peak from the central transition (1/2 to -1/2) as well as quadrupolar satellites (3/2 to 1/2 and -1/2 to -3/2). However, no satellites were observed in our experiments, likely because of the substantial mosaicity [25] which leads to a distribution of the electric field gradients at different sites.

The observed peaks stay well defined throughout the whole temperature range. The temperature dependence of the peak positions is shown in Fig. 3. There is no reconstruction of the spectrum and the width of the peaks remains the same throughout the studied temperature range meaning that no freezing takes place. As seen in Fig. 3 both peaks shift as a function of temperature at high temperatures, but have a much reduced temperature dependence below around 60 K. This yields the intrinsic susceptibility for this material, while the bulk susceptibility measurements are swamped by a Curie-like tail [23, 25, 26] (which in this case is attributed to a small amount of impurity phases) and do not allow the study as a function of temperature.

To access the dynamics of the system, relaxation experiments were performed. Series of spin-recovery curves (see in the inset of Fig. 4) were obtained at different temperatures to estimate the spin-lattice relaxation rate. The magnetization recovery was fitted to equation 1, corresponding to the central line of I = 3/2 nucleus [27]:

$$I(T)/I_{\text{Max}} = 1 - \frac{1}{10} \exp \left(-\frac{T_R}{T_1}\right) - \frac{9}{10} \exp \left(-6\frac{T_R}{T_1}\right),$$

where I is the integrated intensity of the signal for the corresponding peak as a function of the repetition time $T_R$ and $T_1$ is the spin-lattice relaxation time. The data is well described using a standard exponential function, without any stretching parameter, which suggests that only one relaxation rate is present, in line with the absence of
broadening of the spectrum. The inverse of the relaxation time, which corresponds to the momentum integrated dynamical structure factor at very low energy is shown in Fig. 4 as a function of temperature. Interestingly, it also appears to exhibit different behavior depending on the temperature: at high temperatures the relaxation rate changes significantly more than at low temperatures.

We now turn to the interpretation of our results. It is first important to acknowledge the unusual temperature dependence of the shift as a function of temperature. While in standard metals it is constant, in magnetic insulators at temperatures higher than the relevant interaction scales it decreases with temperature. An increase of susceptibility with temperature has been observed in the pseudogap study the spin-lattice relaxation rate and its temperature dependence. 

In the present case, the most probable reason for the observed temperature dependence of the susceptibility lies in the semimetal electronic structure, where the conduction and valence bands overlap in energy by $E_h$. The unusual behavior of the susceptibility comes about from two effects. First, the chemical potential has a temperature dependence, which cannot be ignored. Second, the density of states near the Fermi energy varies rapidly with energy. In particular, as the temperature is increased, the density of states $g(E)$ further away from the Fermi energy becomes more important and the susceptibility is expected to increase due to increase of carriers[30]. Starting with a general expression of $\chi = \mu^2 \int \frac{dE}{T^2} g(E)dE$, where $f$ is the Fermi function, we follow the model worked out in the context of iron-based superconductors [31]. We use the effective masses and the number of valleys determined by ab initio calculations [25]: 1.4, 2.3, 3.7 and 5.6 $m_0$ for hole bands and 1.8 $m_0$ for two electron bands. With these parameters, we can reproduce the intrinsic susceptibility data, just by fitting the overlap of the conduction and valence bands, which we assume to be the same for all the bands and find to be $E_h = 120(10)$ K. Note that the semimetal susceptibility, which is calculated without adjusting the scale, only accounts for the temperature-dependent part of the susceptibility. To reproduce the measured data, a temperature-independent contribution of $1.78 \times 10^{-4}$ emu/Ir-mol is added which is likely due to a Van Vleck-like contribution exceeding core diamagnetism, which comes in at $-0.67 \times 10^{-4}$ emu/Ir-mol. While we cannot expect a perfect agreement from such a simplified model, Fig. 3 demonstrates that the general behavior is captured and further strengthens the case for the semimetal behavior in this system. The fact that the obtained band overlap appears to be smaller than calculated by ab-initio calculations by almost a factor of 10 already hints at the presence of correlations - likely a reconstruction of band structure takes place, which is not accounted by the ab initio calculations.

We now turn to the dynamics in this system. While the shift gives access to the uniform $q= 0$ susceptibility, we study the spin-lattice relaxation rate and its temperature dependence to explore the nature and role of the spin excitations. The two Na nuclei have a very similar temperature dependence of the relaxation rate as well as having a crossover between two different behaviors at different temperature ranges. At low temperatures the relaxation rate varies approximately as $1/T_1 \propto T^{1/2}$, whereas the higher temperature region has $1/T_1 \propto T^2$. The crossover takes place at a similar temperature as the change in slope in shift measurements. This is consistent with the fact that both properties are influenced by the density of states.

The temperature dependence itself is far from trivial. These two regimes are neither reminiscent of an insulating state with a magnetic gap $1/T_1 \propto \exp(-\Delta/T)$ nor obey the Korringa law, where the ratio $1/T_1 KT^2$ would remain constant provided the correlations are weak. In this latter case, one would have $1/T_1 \propto T g(E_F)^2$ and $K \propto g(E_F)$. Experimentally, the shift appears linear in the high-temperature regime so one would expect that $1/T_1 \propto T^3$, which is a faster increase than the observed $T^2$ behavior. This implies that strong correlations are present in the system and requires further understanding.

An insight to the behavior of the low-temperature range can be found by comparing it to the case of the insulating organic spin-liquid candidate $\kappa-(ET)_2Cu_2(CN)_3$, where in a large temperature range, the spin-lattice relaxation rate behaves with a power law of $1/2$ [32]. Both the $\kappa-(ET)_2Cu_2(CN)_3$ compound as well as the Na$_2$IrO$_8$ system are identified as being close to a metal-insulator transition and such power law dependence appears to be an indication for it. In the case of $\kappa-(ET)_2Cu_2(CN)_3$, it was argued that the relaxation is due to fluctuations which involve both the charge and spin.

A related way to look at the two different regions ($1/T_1 \propto T^2$ and $\propto T^{1/2}$) is to consider that temperature and pressure have opposing roles, and to examine the recent results.
obtained from the high-pressure resistivity measurements [26]. As soon as the lowest pressures in that study were applied, the material becomes an insulator. This indicates that indeed Na$_4$Ir$_8$O$_9$ is at the verge of a metal-insulator transition, which could be either due to correlations (Mott insulator), to the transformation to a band insulator or as a precursor of the dimerized state. Hence, the observed low-temperature regime in the unstrained compound could be related to an insulator-like behavior, however more detailed studies of the low-pressure-induced insulating state are needed to draw stringent analogies.

Since there are two inequivalent Na atoms in the system, one can use the ratio of the properties of the two sites to characterise the correlations at play. First, by inspecting the shift displayed in Fig. 3 in the range where there is a change, one finds that the ratio of the hyperfine coupling for the two sites is $\Delta K(\text{Na}_2) / \Delta K(\text{Na}_1) \approx 1$. Essentially the same value is also obtained by analyzing the shift and bulk susceptibility using the Clogston-Jaccarino plot (see [33]). As the relaxation rate depends on the square of the hyperfine coupling and on the number of nearest neighbors, the difference in the relaxation rates in the absence of correlations is expected to be of the order of $1/54 \approx 1/54$ - much smaller than what is observed. The ratio itself is plotted for clarity in Fig. 5. This again indicates that the weak-correlation approach is insufficient to explain the behavior in this system.

A likely reason for the discrepancy in the relaxation rates for the two different nuclei is the presence of antiferromagnetic correlations revealed by the virtue of the different local environment for the two sites. As can be seen in Fig. 1 the Na 1 nucleus is located in between two iridium triangles. In case of antiferromagnetic correlations favoring the 120° motif, the fluctuations at the $^{23}$Na nucleus will be screened. The Na 2 nucleus appears not to be located in such a symmetric position: it is linked to one triangle, which will be filtered as for Na 1, but the other six Ir ions are from three different triangles. This can be formalized for both sites by considering the general expression for the relaxation rate:

$$\frac{1}{T_1} = \sum_q |A(q)|^2 \chi''(q, 0),$$

(2)

where $\chi''(q, 0)$ is the imaginary part of the dynamical spin susceptibility and $A(q)$ is the hyperfine form factor, which encapsulates the sensitivity of the fluctuations to different wavevectors. It depends on the geometrical arrangement of the probing nucleus and the magnetic ions. The expression in the reciprocal space is obtained by the following calculation:

$$A(q) = \sum_i A_i \exp(-iqr_i),$$

(3)

where the sum runs over the nearest Ir neighbors at a distance $r_i$. The $A_i$ is in principle different for every Ir, but in the case of Na 1, all Ir atoms have the same distance and linkage to the Na 1 nucleus. As an illustration, the 120° arrangement is given in one of the insets of Fig. 5. First we calculate the hyperfine form factor giving the $q$ dependence of the $A(q)$ in simplified coordinates - simply using one triangle with a lattice constant $a$. This is displayed in the other inset of Fig. 5 and corresponds locally to the exact situation for the Na 1 nucleus. Dark regions in the form factor show the modes that would be filtered, which correspond to the 120° motif. This explains the deviation from the expected ratio of the relaxation rates - these local modes are filtered by Na 1 nucleus.

We now ask further, whether there are long-range modes that satisfy such restrictions and turn to the comparison...
between the Na 1 and Na 2. Quite unexpectedly we find that simple modes based on the 120° motif with long range coherence will be filtered both for Na 1 and Na 2 [33]. In terms of form factor, this means that only very unusual locations of the q-space have strong difference in filtering long range modes. While some exotic dynamics cannot be strictly excluded, the most likely reason for strong filtering in the case of Na 1 and not in the Na 2 is the short-range character of the correlations. The 120° dynamic correlations are restricted to approximately one triangle only.

To summarize, our measurements position the frustrated hyperkagome compound Na3Ir3O8 as a semimetal with persistent magnetic correlations. Since the antiferromagnetic fluctuations persist even in the semimetal regime, it is a very attractive system to study the transformation of magnetism through the metal-insulator transition. We hope that our study will stimulate theoretical efforts to understand the effect of doping a spin liquid in the state under pressure certainly deserves additional attention as does the exciting possibility to apply a negative chemical impurities to probe the correlation length more precisely [34, 35]. The study of magnetic properties in the insulating state under pressure certainly deserves additional attention as does the exciting possibility to apply a negative chemical pressure in the search of transformation to a metallic phase. Finally, an open question stays what would happen if we dope this system further? To this end, gating the material would be illuminating.

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