Novel Phases in Iridates

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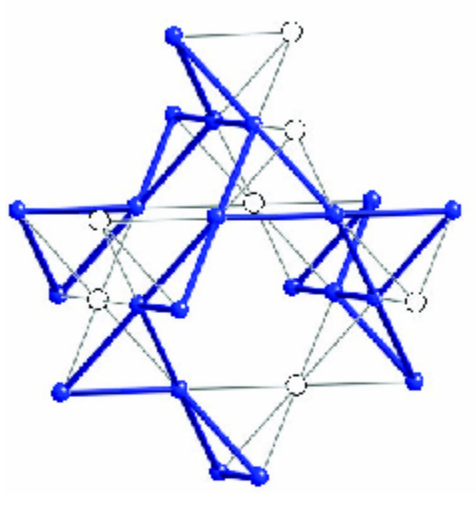

Outline

- The Hyper-Kagome material $Na_4Ir_3O_8$

- The Honeycomb lattice iridates A_2IrO_3 (A = Na, Li)

The Hyper-Kagome material $Na_4Ir_3O_8$

Collaborators

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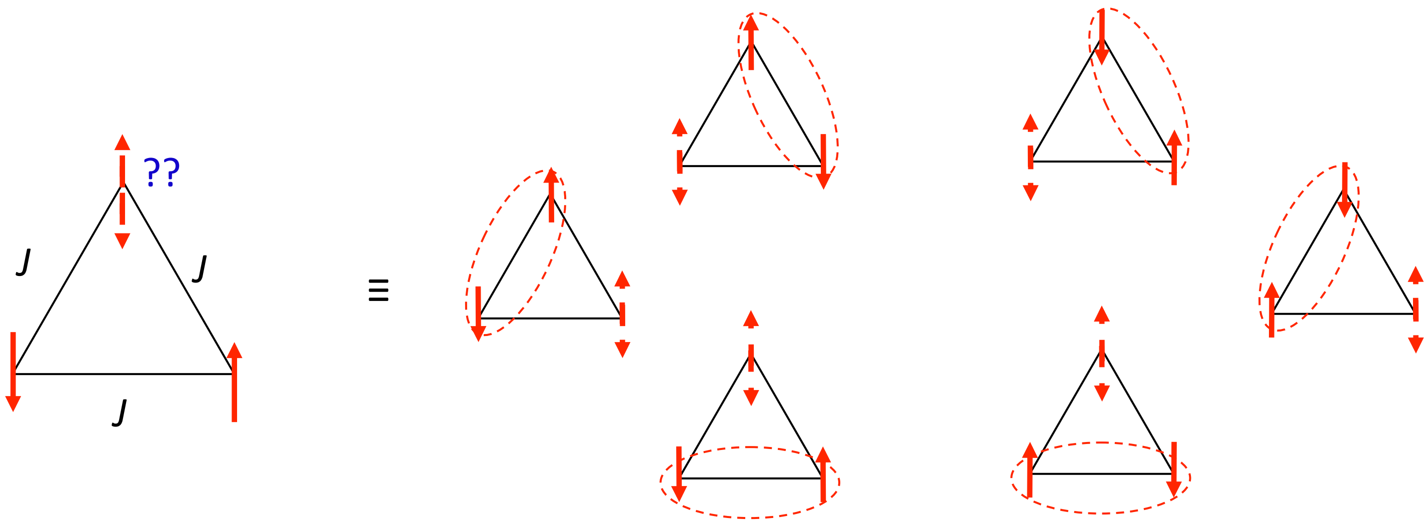
Spin Liquids in Geometrically Frustrated Magnets

Huge degeneracy



Spin–liquid: Quantum Disordered State of Strongly Interacting Spins

Recipe for Quantum Fluctuations

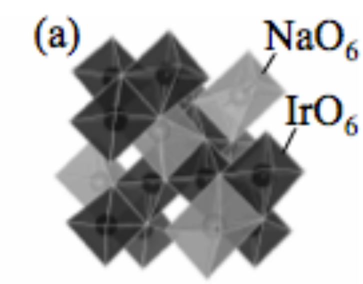
- Small spin S = ½
- Low-Dimensionality and/or co-ordination
- Geometric Frustration

Most Candidate Spin Liquids are S = ½ Quasi-Low-Dimensional Magnets

$Na_4Ir_3O_8$: Possible 3D Spin Liquid?

Spin-Liquid State in the $S = 1/2$ Hyperkagome Antiferromagnet $Na_4Ir_3O_8$

Y. Okamoto *et al.* , PRL **99,** 137207 (2007)



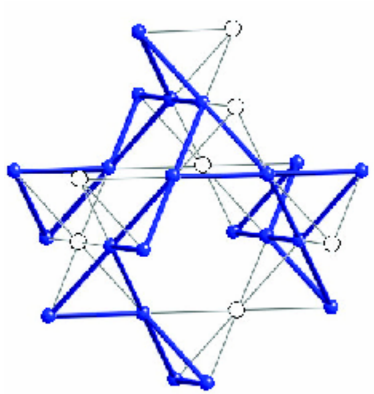
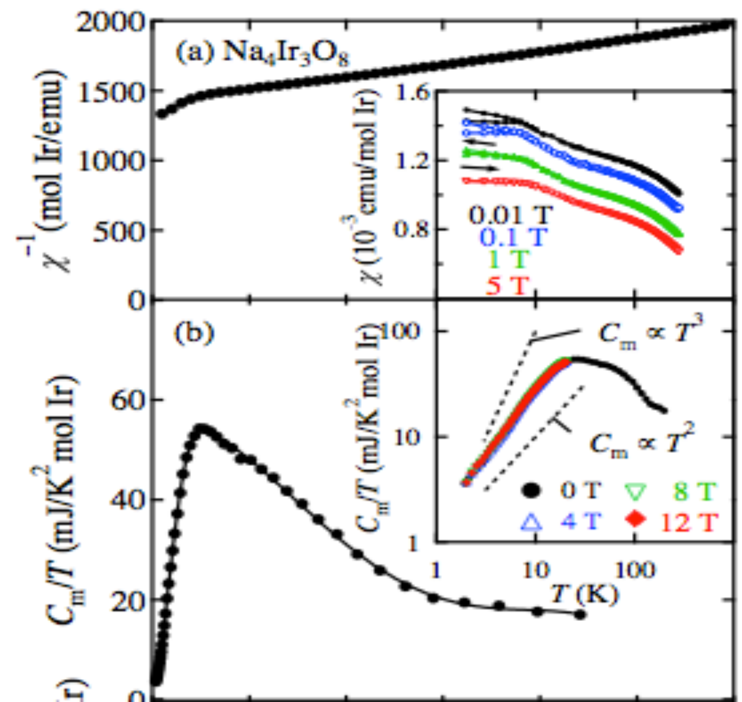


TABLE I: Atomic parameters obtained by refining x-ray powder diffraction for $Na_4Ir_3O_8$ at room temperature with a space group $P4_132$. The cubic lattice constant is $a = 8.985$ Å. g of Na2 and Na3 are fixed to 0.75 according to Ref. [10].

		x	y	z	g	B (Å)
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

Hyper-Kagome

Magnetic frustration expected and seen



Predictions for $Na_4Ir_3O_8$

- J. M. Hopkinson,…, Phys. Rev. Lett. **99**, 037201 (2007).

A classical Heisenberg model on the hyperkagome lattice predicts a spin nematic order with long range dipolar spin correlations is chosen at T ≈ 1 K by an order-by-disorder mechanism

- M. J. Lawler… Phys. Rev. Lett. **100**, 227201 (2008).

Semi-classical spin-model of Heisenberg spins predicts a 120^{o} coplanar magnetically ordered state. This was found to give way, through a quntum phase transition, to a gapped topological Z2 ’bosonic’ spin liquid phase when quantum fluctuations are turned on.

- Y. Zhou…. Phys. Rev. Lett. **101**, 197201 (2008).
- M. J. Lawler…. Phys. Rev. Lett. 101, 197202 (2008).

Predicted gapless spin liquids with a Fermi surface of chargeless spinons which at low temperatures was found to be unstable to the formation of paired states with line nodes

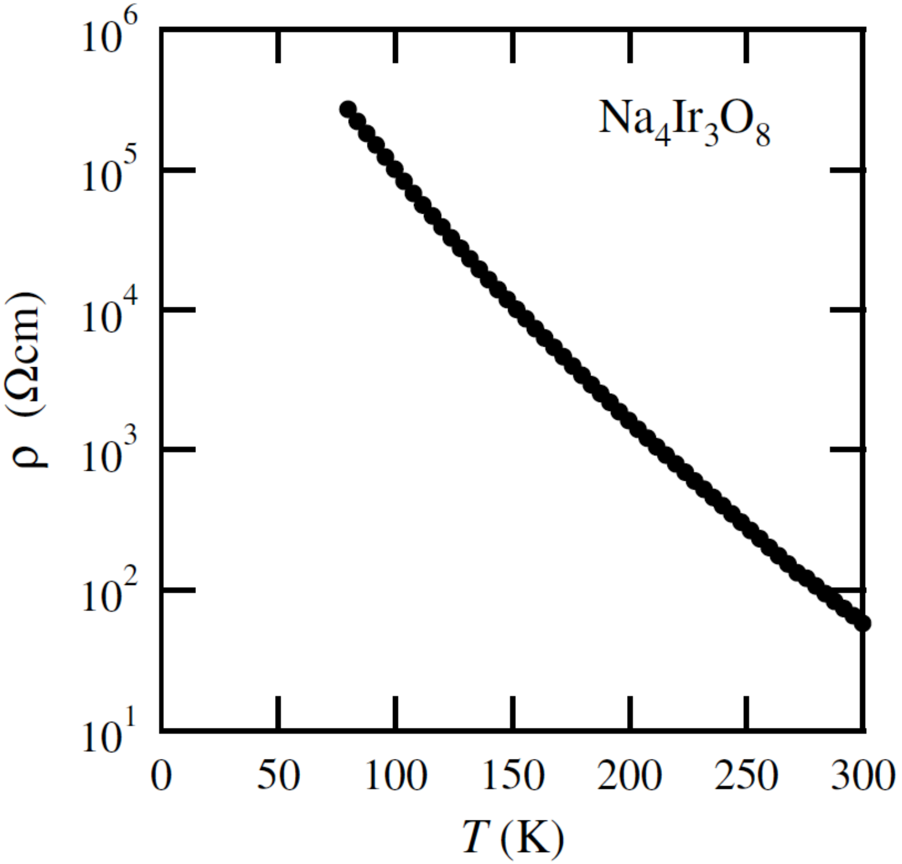
- G. Chen and L. Balents, Phys. Rev. B **78**, 094403 (2008).

Inclusion of spin- orbit coupling was shown to relieve the frustration in some regions of parameter space and might lead to ordering at low temperatures

$Na_4Ir_3O_8$: Resistivity

Insulator but near MIT

$\Delta \approx 500 - 900$ K



Magnetic Susceptibility

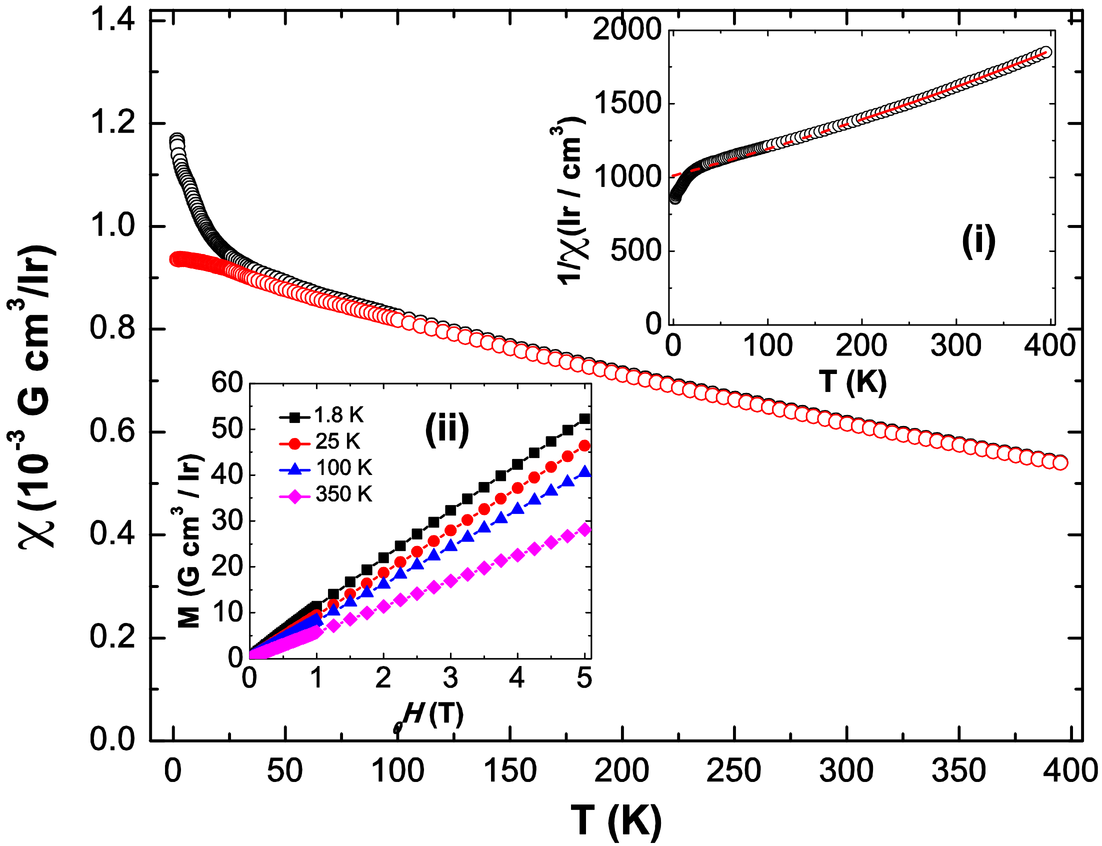
- Curie-Weiss fit to inverse susceptibility gives

S_{eff} = ½, θ ≈ - 600 K

- No transition down to 1.8 K

- Intrinsic susceptibility 'saturates' below 20 K

χ_0 ~ const. as in metal

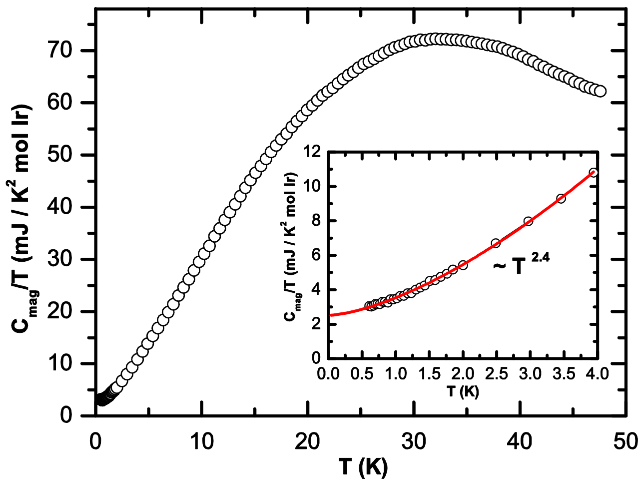


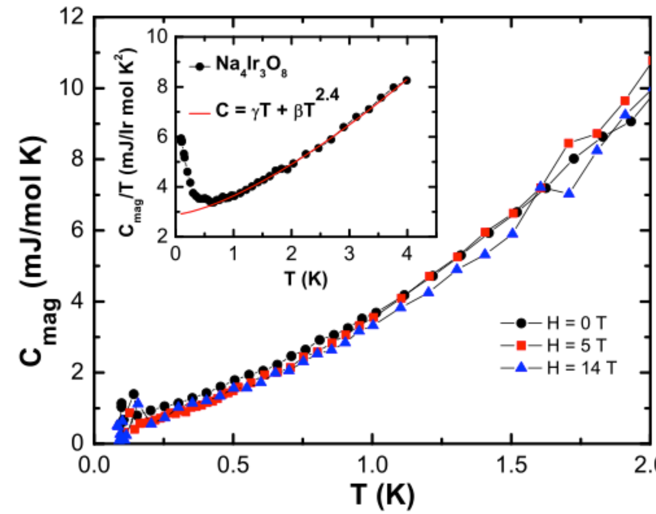
Gapless Spin Liquid !!

Heat Capacity and Thermal Conductivity

- No transition down to 100 mK
- Broad peak at around 30 K
- $C_{mag} \sim T^n$ ($2 < n < 3$)
- Finite $\gamma \sim$ 2-3 mJ/mol K^2 as in a metal

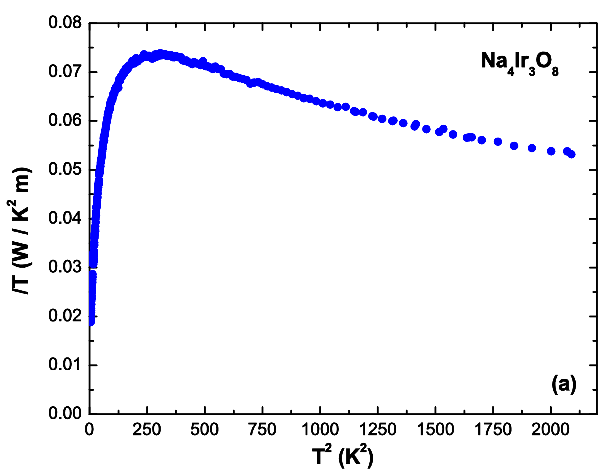
Heat Capacity

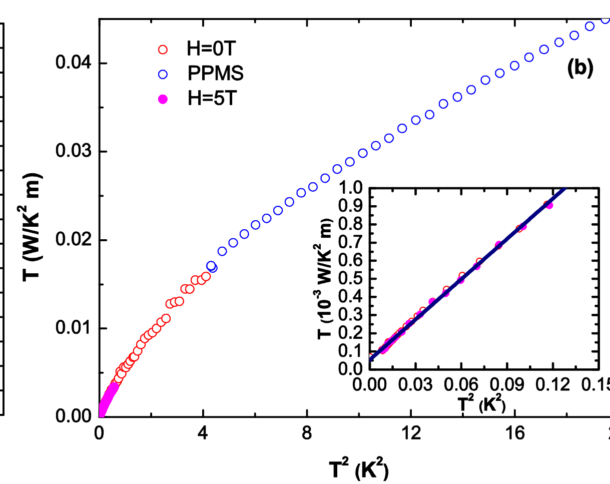




Thermal Conductivity

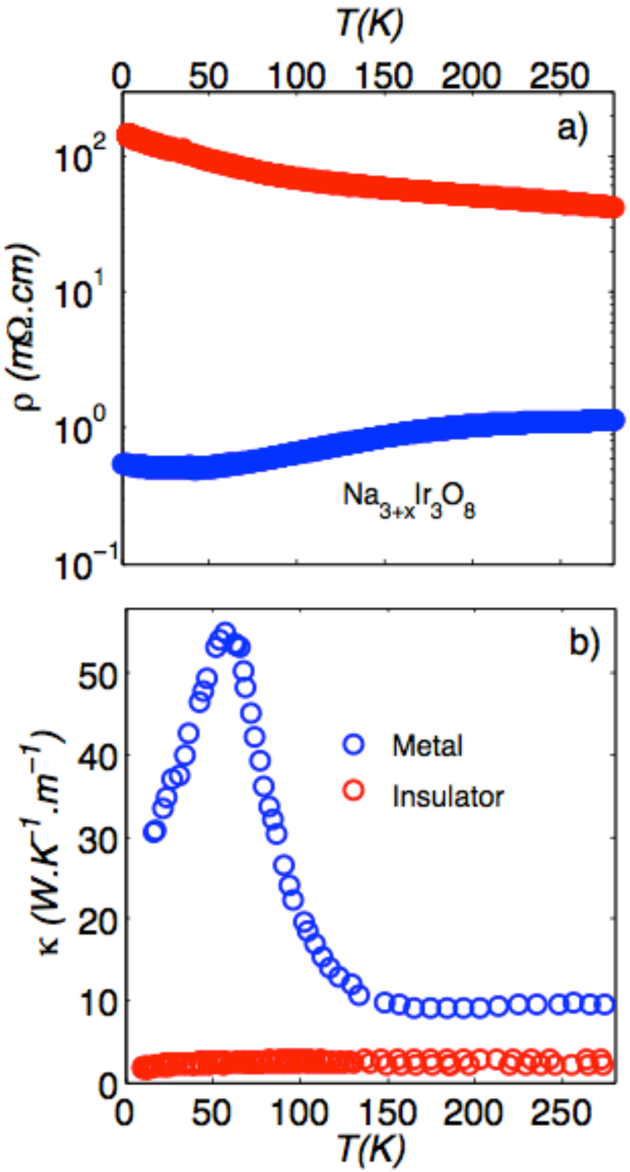
- No transition down to 75 mK
- $\kappa/T \rightarrow 0$ as $T \rightarrow 0$

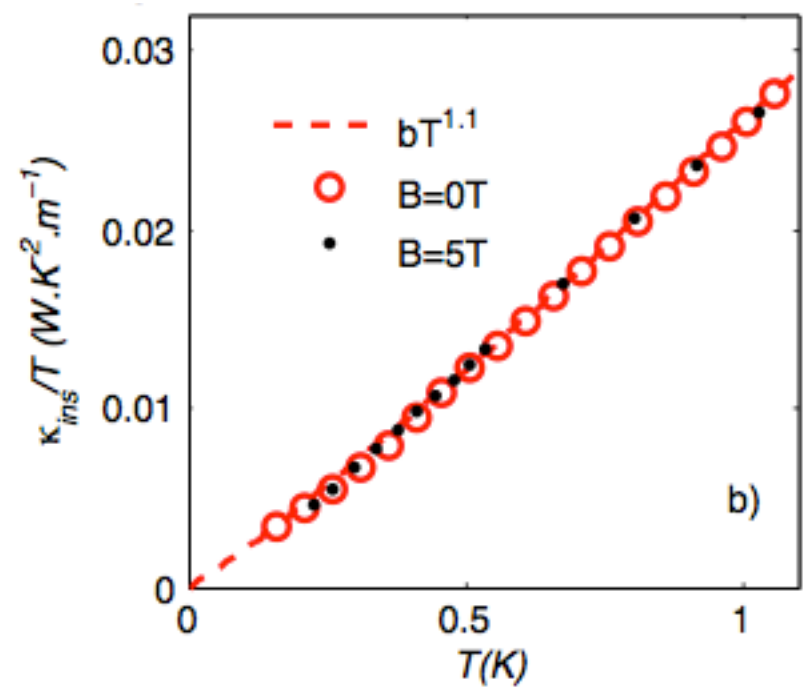




Yogesh Singh, et al.
Phys. Rev. B **88**, 220413(R) 2013

Thermal conductivity across the metal-insulator transition in single crystalline hyperkagome Na3+x Ir3 O8, B. Fauque, et al arxiv:1210:8792 (2014).

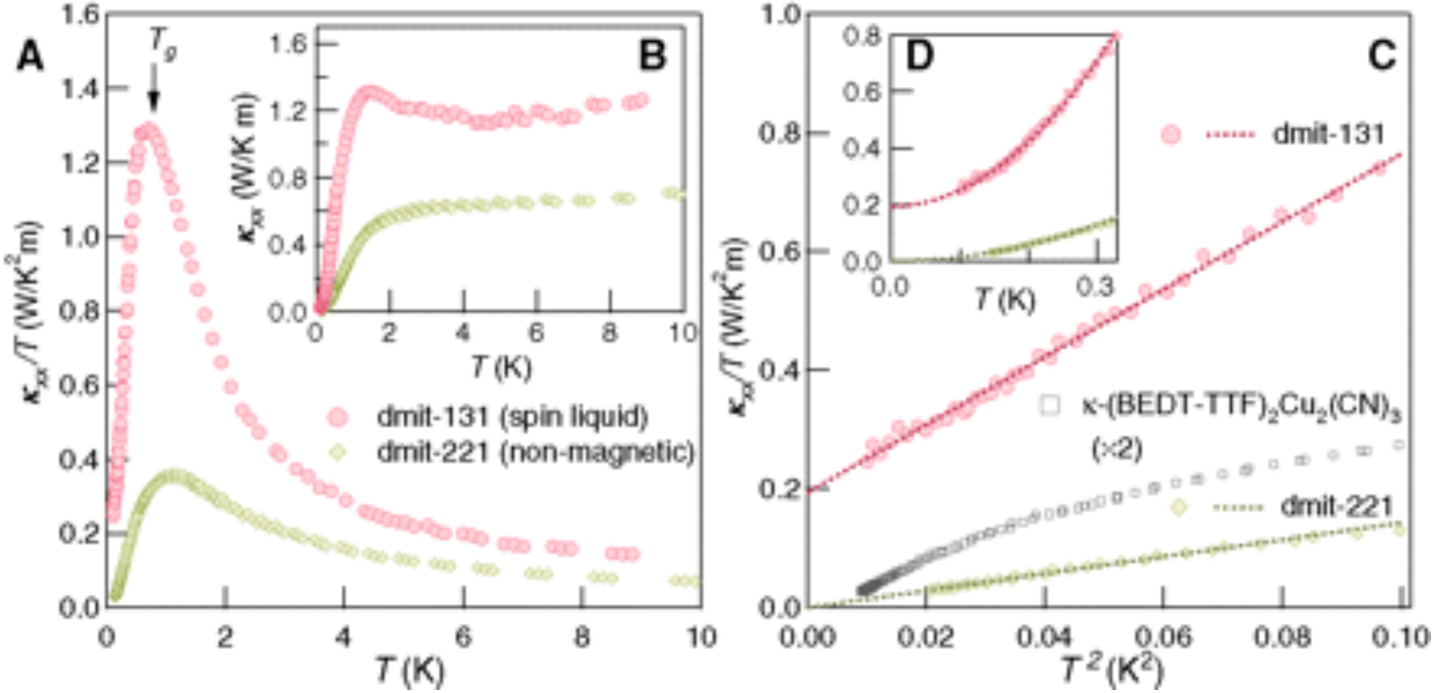




Comparison with other spin liquids

ET-dmit ($\kappa/T \approx 180$ mW/K^2 m, $\gamma \approx 20$ mJ/mol K^2)

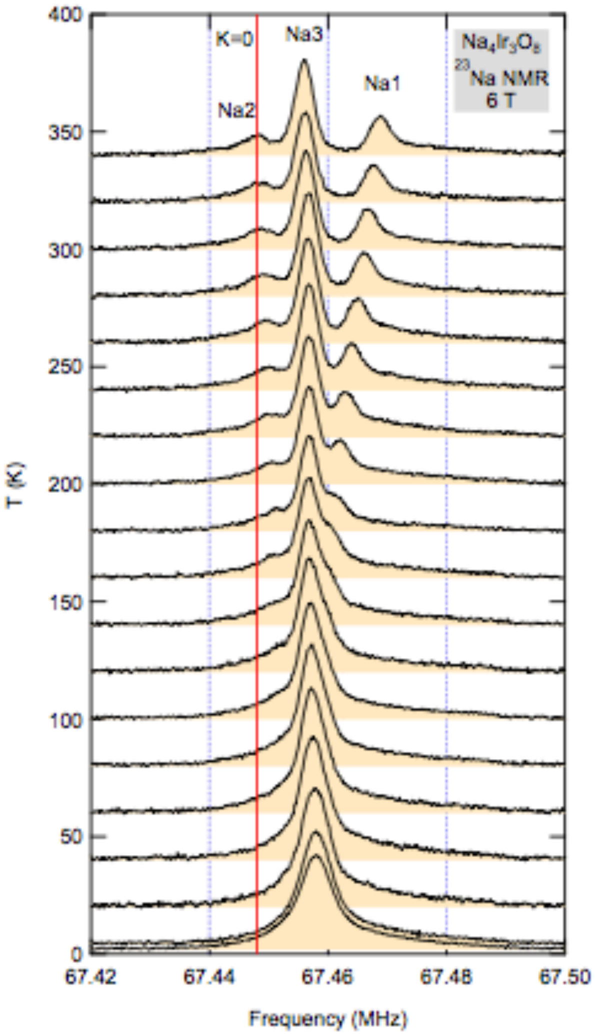
kappa- (BEDT-TTF)2Cu2(CN)3 ($\kappa/T \rightarrow 0$, $\gamma \approx 20$ mJ/mol K^2)

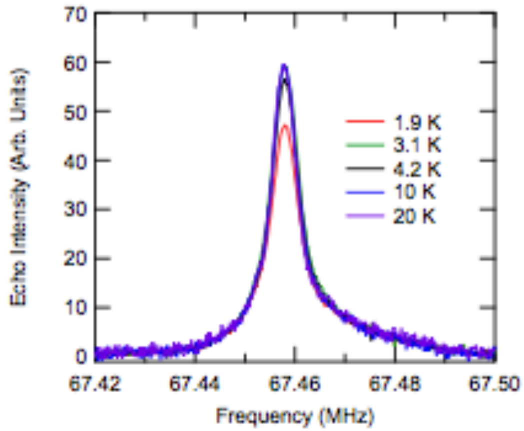


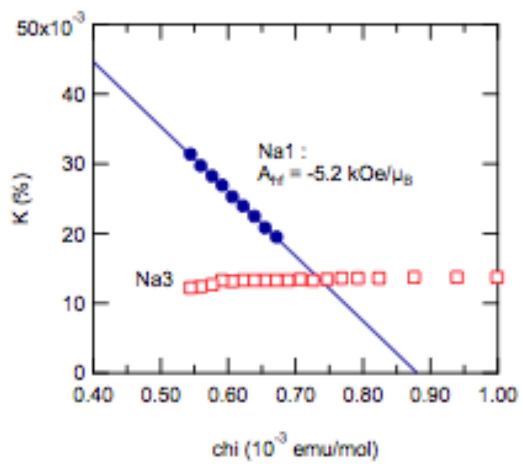
S. Nakajima *et al.*, J. Phys. Soc. Jpn. **81**, 063706 (2012).

^{23}Na NMR in $Na_4Ir_3O_8$

Seung-Ho Baek, IFW Dresden



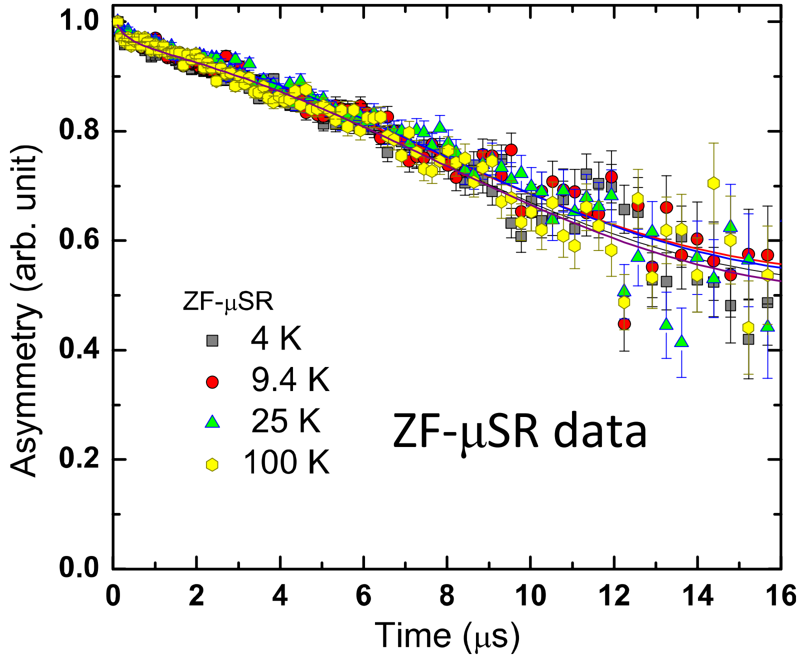


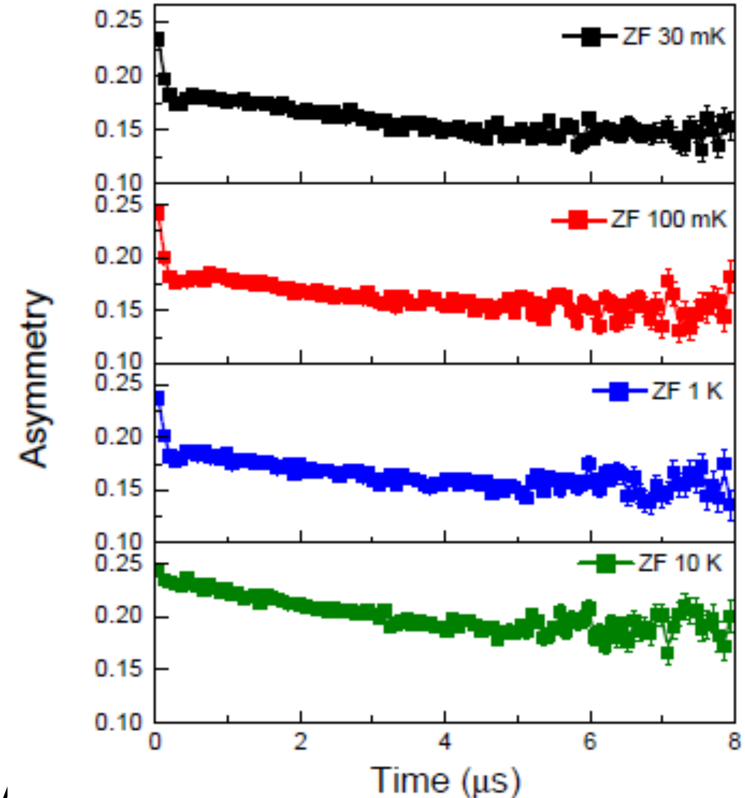


- At high temperatures, three NMR lines appear due to three different crystallographic Na sites.
- There is no signature of static magnetism down to 2 K.
- For Na1, the hf coupling constant is estimated to be -5.2 kOe per Bohr magneton.(The negative sign means that the dominant hf coupling is due to the core polarization term.)
- For Na3, there is essentially no hf coupling, which allows to estimate non-spin contribution from the spin-lattice relaxation rate.

μSR: Freezing below 2 K

Kwang-Yong Choi, Seoul





A fitting function $A_0P_{ZF}(t)=A_1G^{KT}(t,\Delta)\exp[-(\lambda t)^{\beta}]+A_{BG}$

→ $G^{KT}(t,\Delta)$ is a Kubo-Toyabe relaxation function due to nuclear moments.

→ The second moment of the field distribution Δ=0.0904 MHz is T-independent, supporting nuclear moments as its origin.

→ A_{BG} represents muons stopped outside the samples.

→ A (stretched) exponential function describes electronic spin fluctuations.

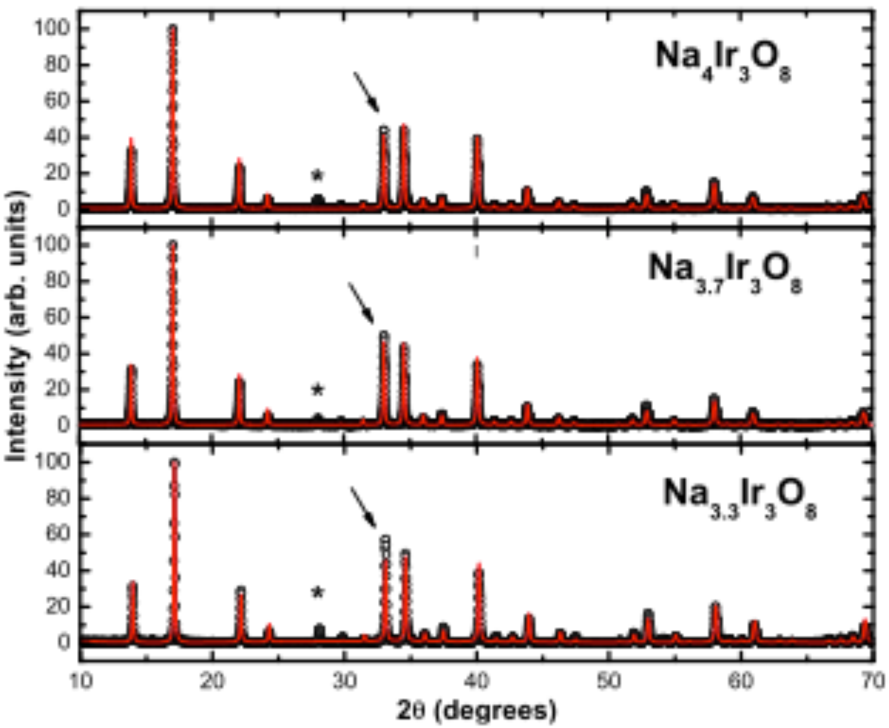
→ We observe no muon precessions down to T= 1.4 K. This means that no static electronic moments freeze or order and local moments are fluctuating at all measured temperatures.

→ The T-independent λ and β = 1.2 implies the persistence of a significant relaxation, indicative of electronic spin fluctuations with dynamics not set by a thermal scale.

- Perturb to Reveal
- Study $Na_{4-x}Ir_3O_8$
- Search for a nearby magnetic state
- Tune the system metallic

$Na_{4-x}Ir_3O_8$ (x = 0 – 0.7)

$P4_132$ (213)



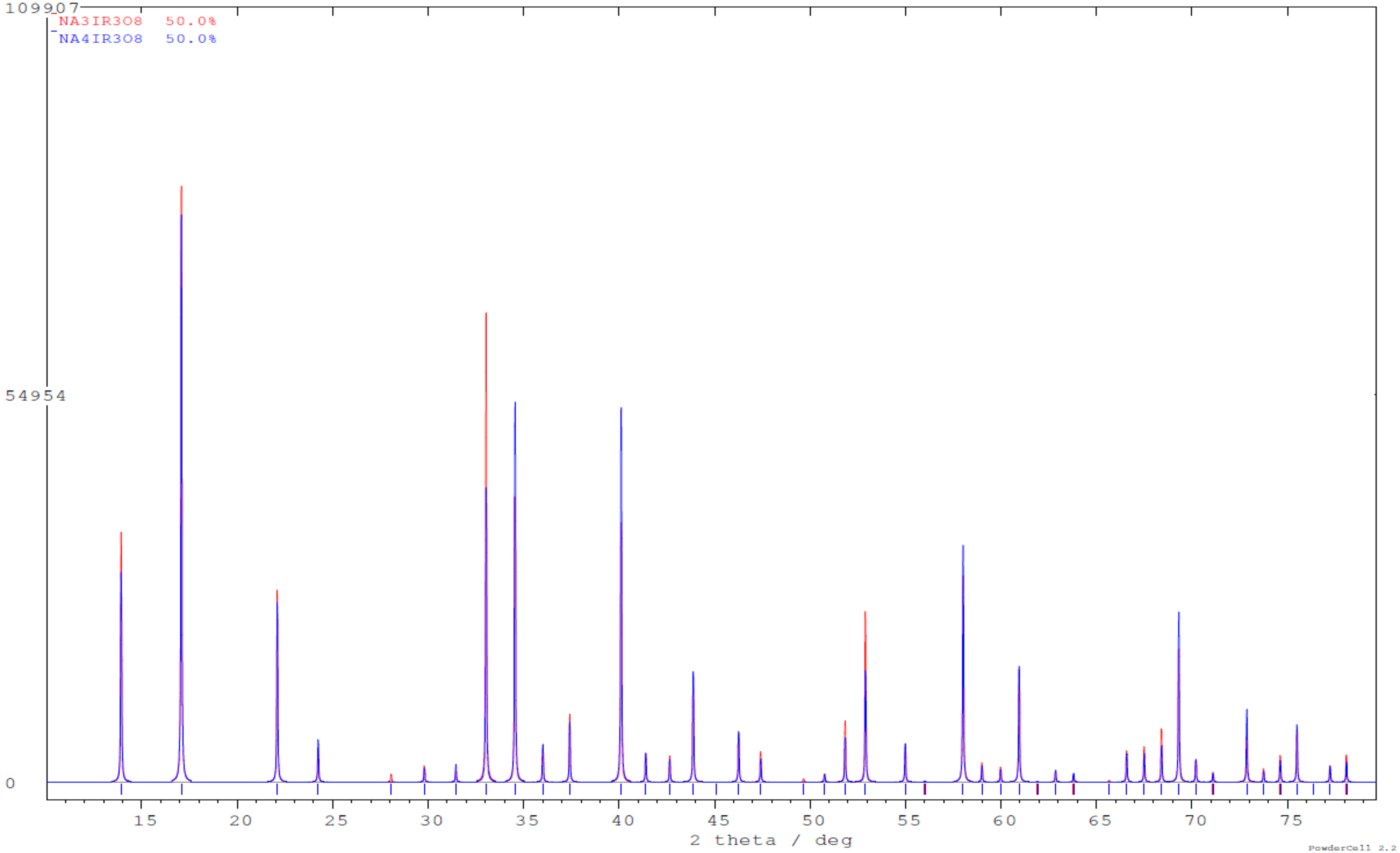
$Na_4Ir_3O_8$	$a = 8.981(2)$ Å					
atom	Wyck	*x*	*y*	*z*	*Occ.*	*B*(Å)
Ir	12d	1/8	0.141(3)	0.392(5)	1	0.4(1)
Na1	4a	3/8	3/8	3/8	1	1.8(6)
Na2	4b	7/8	7/8	7/8	0.71(1)	2.1(4)
Na3	12d	1/8	0.883(4)	0.131(2)	0.75	1.4(8)
O1	8c	0.142(6)	x	x	1	0.9(2)
O2	24e	0.124(6)	0.315(8)	0.352(4)	1	1.3(6)
$Na_{3.7}Ir_3O_8$	$a = 8.979(7)$ Å					
Ir	12d	1/8	0.137(3)	0.383(4)	1	0.8(3)
Na1	4a	3/8	3/8	3/8	1	2.2(1)
Na2	4b	7/8	7/8	7/8	0.64(1)	1.7(3)
Na3	12d	1/8	0.868(4)	0.129(4)	0.70(2)	2.4(8)
O1	8c	0.105(6)	0.105(6)	0.105(6)	1	1.0(7)
O2	24e	0.112(6)	0.335(8)	0.337(4)	1	2.1(3)
$Na_{3.3}Ir_3O_8$	$a = 8.980(3)$ Å					
Ir	12d	1/8	0.139(3)	0.386(5)	1	0.7(2)
Na1	4a	3/8	3/8	3/8	1	2.1(2)
Na2	4b	7/8	7/8	7/8	0.36(3)	2.6(4)
Na3	12d	1/8	0.876(4)	0.122(1)	0.64(2)	1.9(7)
O1	8c	0.105(6)	0.105(6)	0.105(6)	1	0.9(3)
O2	24e	0.112(6)	0.335(8)	0.337(4)	1	1.1(4)

A. Balodhi, A. Thamizhavel, Yogesh Singh, arxiv:1412:0455 (2014).

Spin-orbit coupling induced semi-metallic state in the 1/3 hole doped hyper-kagome $Na_3Ir_3O_8$

Tomohiro Takayama[1,*], Akiyo Matsumoto[2], Jürgen Nuss[1], Alexander Yaresko[1], Kenji Ishii[3], Masahiro Yoshida[3,4], Junichiro Mizuki[3,4] & Hidenori Takagi[1,2]

Comparison of $Na_4Ir_3O_8$ and $Na_3Ir_3O_8$ PXRD



Comparison of $Na_4Ir_3O_8$ and $Na_3Ir_3O_8$ structures

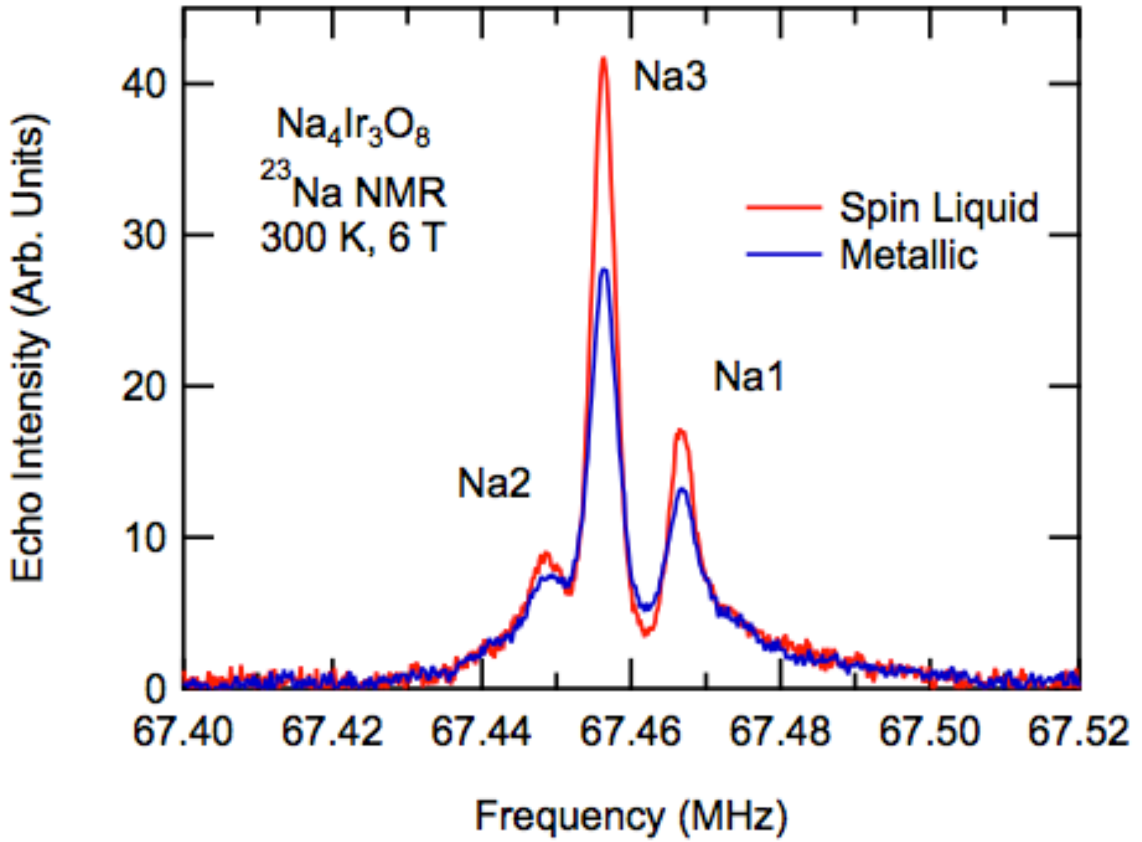
TABLE I: Atomic parameters obtained by refining x-ray powder diffraction for $Na_4Ir_3O_8$ at room temperature with a space group $P4_132$. The cubic lattice constant is $a = 8.985$ Å. g of Na2 and Na3 are fixed to 0.75 according to Ref. [10].

		x	y	z	g	B (Å)
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

Table 1 **Refined structural parameters of $Na_3Ir_3O_8$.** The space group is $P4_132$ (No. 213) and $Z = 4$, and the lattice constant is $a = 8.9857(4)$ Å. g and U_{iso} denote site occupancy and isotropic displacement parameter, respectively. The final R indices are $R = 0.0133$ and $wR = 0.0287$.

Atom	site	g	x	y	z	U_{iso} (Å^2)
Ir	12d	1	0.61264(1)	$x + 1/4$	5/8	0.00802(4)
Na(1)	4b	1	7/8	7/8	7/8	0.0122(5)
Na(2)	8c	1	0.2570(2)	x	x	0.0138(4)
O(1)	8c	1	0.1144(2)	x	x	0.0105(6)
O(2)	24e	1	0.1364(3)	0.9071(2)	0.9186(2)	0.0111(4)

NMR: Metallic $Na_4Ir_3O_8$



The slightly metallic sample x = 0.3 reveals a very similar spectrum with reduced intensities of the 3 Na lines

Transport and Magnetism of $Na_{4-x}Ir_3O_8$

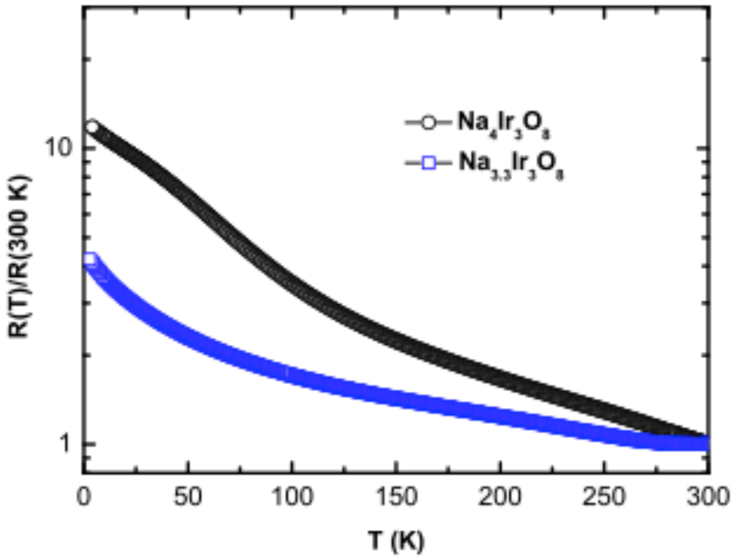


FIG. 2: (Color online) Resistance divided by the $T = 300$ K value $R(T)/R(300K)$ versus T of $Na_{4-x}Ir_3O_8$ ($x = 0, 0.7$).

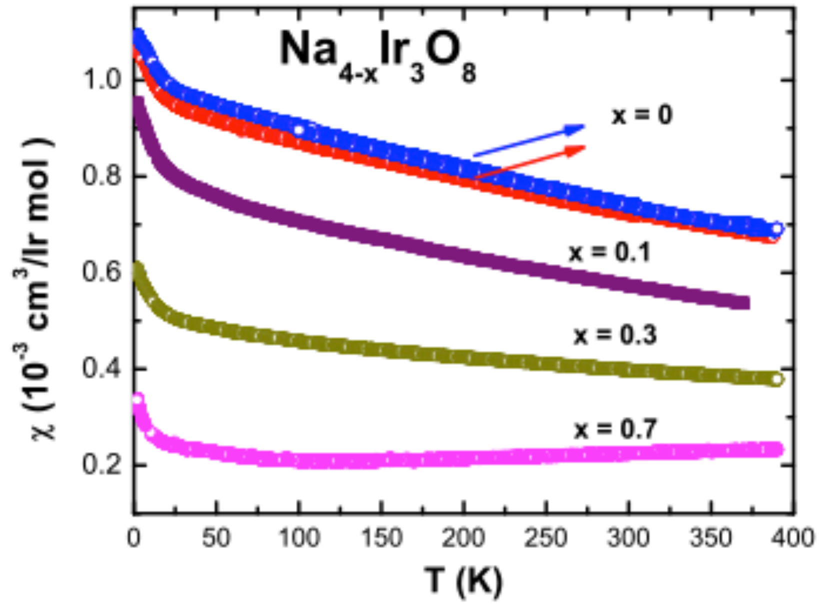


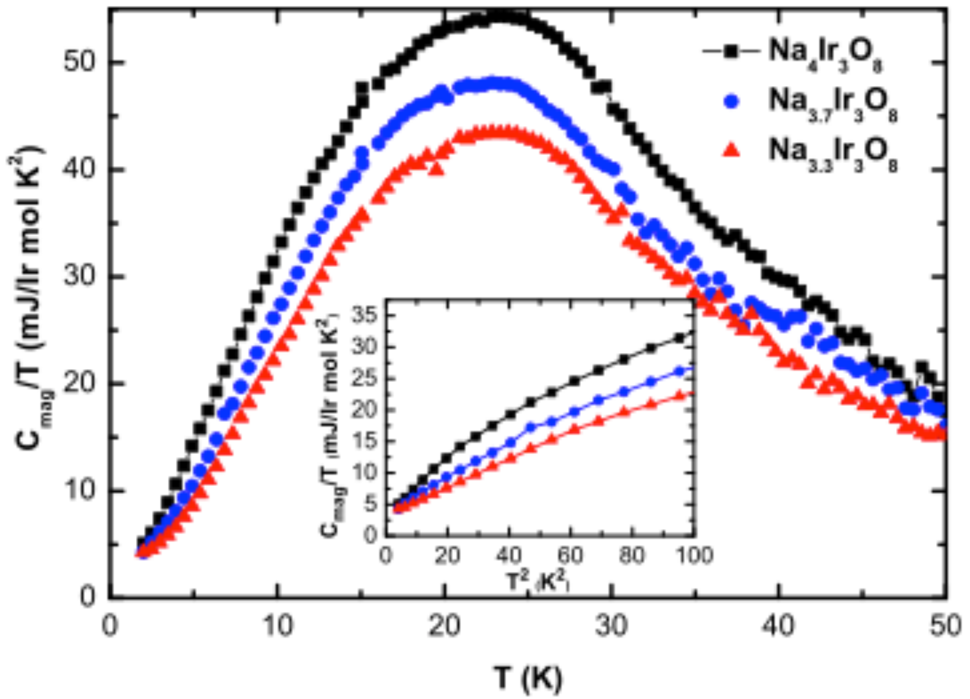
FIG. 3: (Color online) Magnetic susceptibility χ versus T of $Na_{4-x}Ir_3O_8$ ($x = 0, 0.1, 0.3, 0.7$) between $T = 2$ K and 400 K.

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

x	χ_0 (10^{-4} cm^3/Ir mol)	C (cm^3 K/Ir mol)	θ (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			

A. Balodhi, A. Thamizhavel, Yogesh Singh, arxiv:1412:0455 (2014).

Heat Capacity of $Na_{4-x}Ir_3O_8$



- The 25 K anomaly in C_{mag} is robust against hole doping
- **The anomaly could be an artifact of improper lattice subtraction**

A. Balodhi, A. Thamizhavel, Yogesh Singh, arxiv:1412:0455 (2014).

Summary for $Na_4Ir_3O_8$

- $Na_4Ir_3O_8$ is a highly frustrated magnet with $\theta_W \approx$ -600 K , no ordering T > 100 mK.

- Thermodynamic measurements as well as NMR and μSR strongly suggest SL (T > 1 K) with C and χ suggesting gapless excitations but k/T $\rightarrow$ 0 as T $\rightarrow$ 0.

- Freezing below 1K in μSR.

- Na-deficient samples show that SL is robust. No enhanced freezing observed in Na-deficient samples.

The Honeycomb lattice Iridates A_2IrO_3

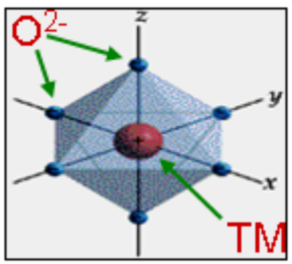
Honeycomb-lattice iridates Na_2IrO_3 and Li_2IrO_3

Kavita Mehlawat and Ashwini Balodhi	
Soham Manni and P. Gegenwart	Crystal synthesis and characterization
Sungkyun Choi and Radu Coldea	Structural refinement, μSR, INS
X. Liu, H. Gretarsson, Young-June Kim, J.P. Hill	Resonant x-ray scattering
R. Comin, A. Damascelli	ARPES
Jason N. Hancock, D. van der Marel	Optical conductivity
T. Berlijn, W. Ku, …	DFT calculations
R. Thomale, J. Reuther, S. Trebst	finite-temperature FRG calculations

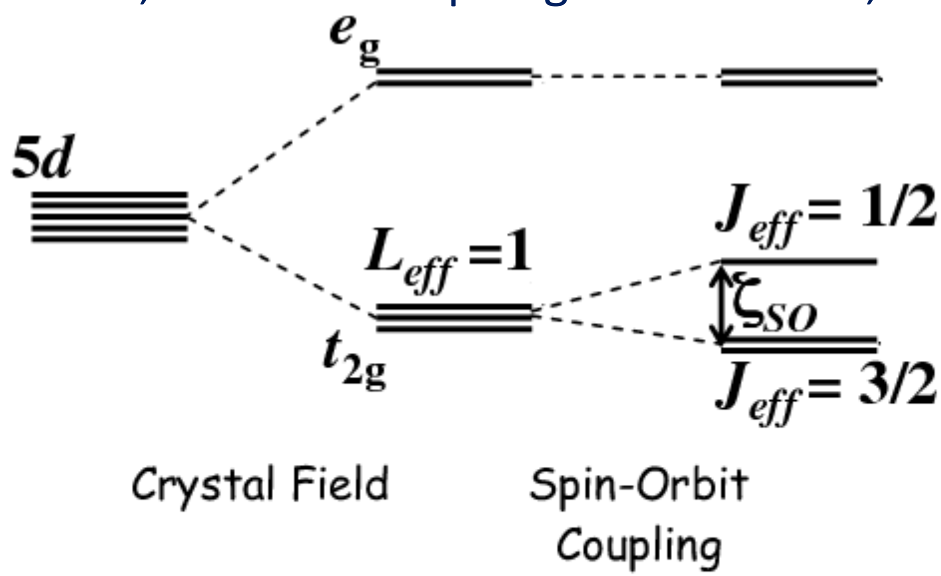
Introduction

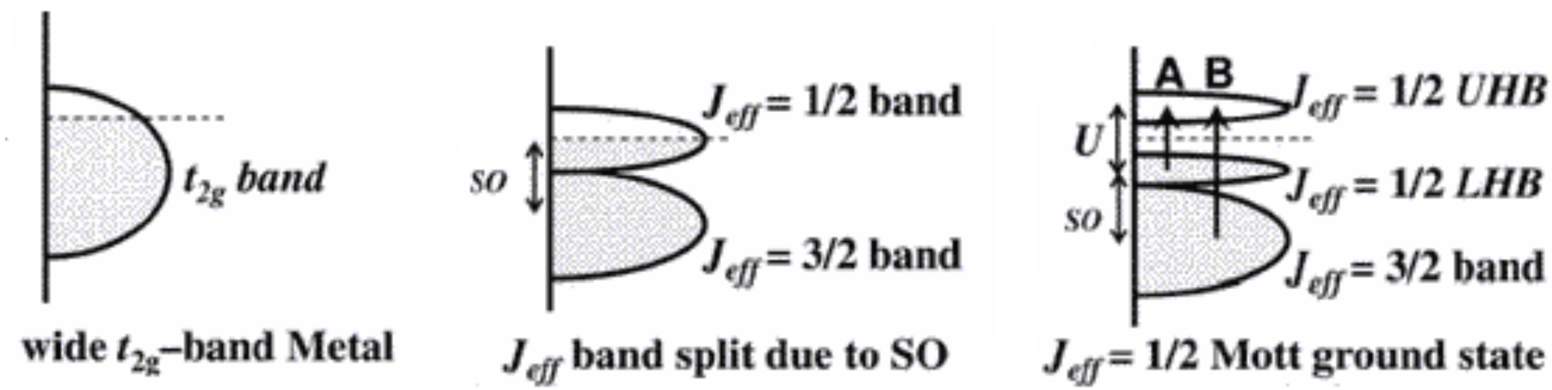
Large spin-orbit coupling in 5d transition-metal oxides → novel electronic states,

e.g. spin-orbit Mott insulators, correlated topological insulators, …



Ir^{4+}





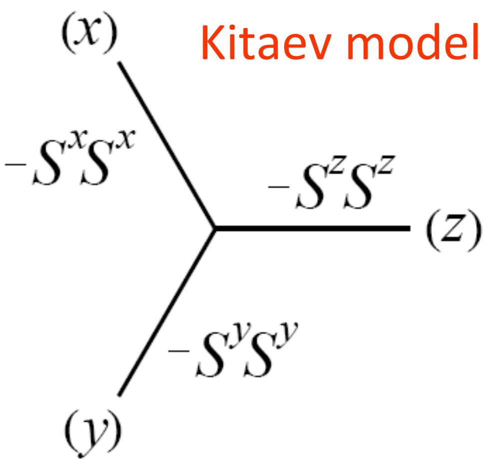
Spin-Orbit Mott Insulator

Sr_2IrO_4: B.J. Kim et al., PRL 2008, Science 2009

Heisenberg-Kitaev model

J. Chaloupka, G. Jackeli, G. Khaliullin PRL 2010

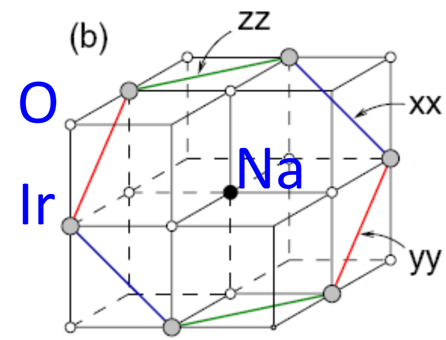
Kitaev model:



exact solution:

spin-liquid with fractional excitations

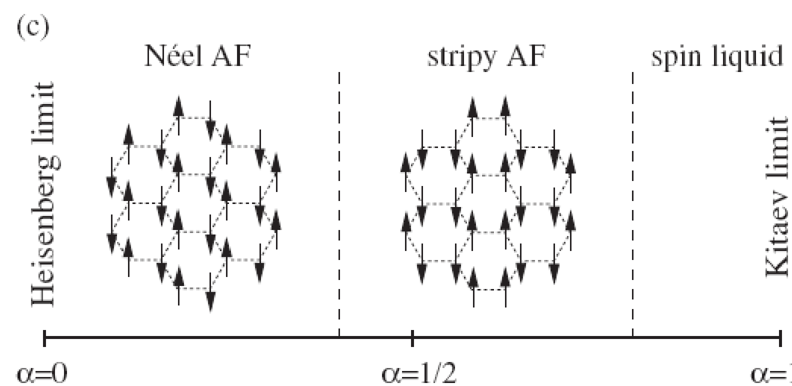
Direct hopping between NN Ir t_{2g} orbitals → Heisenberg interaction



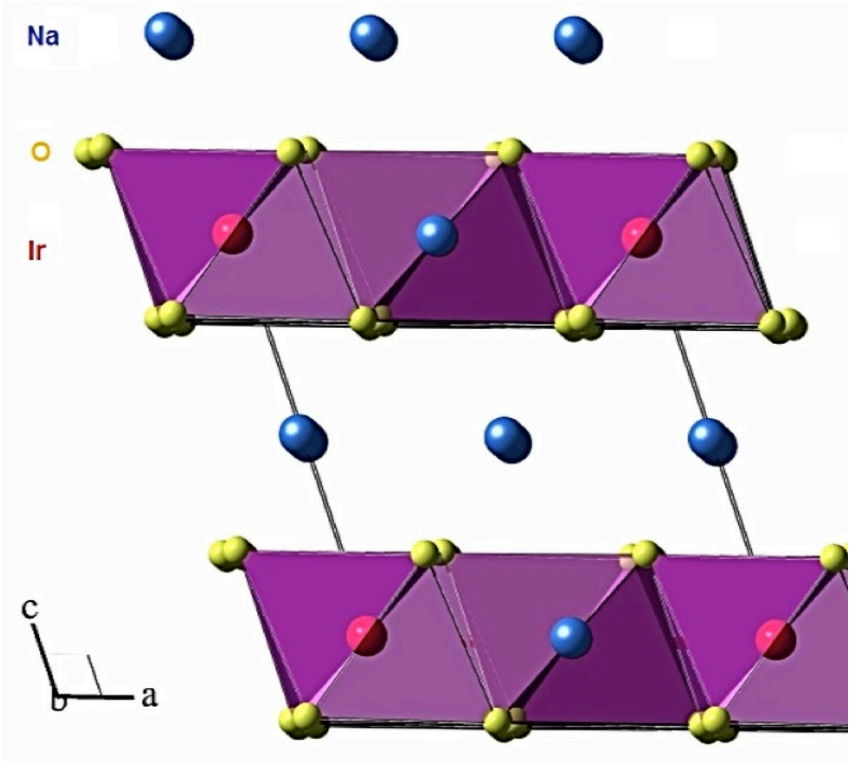
Na_2IrO_3

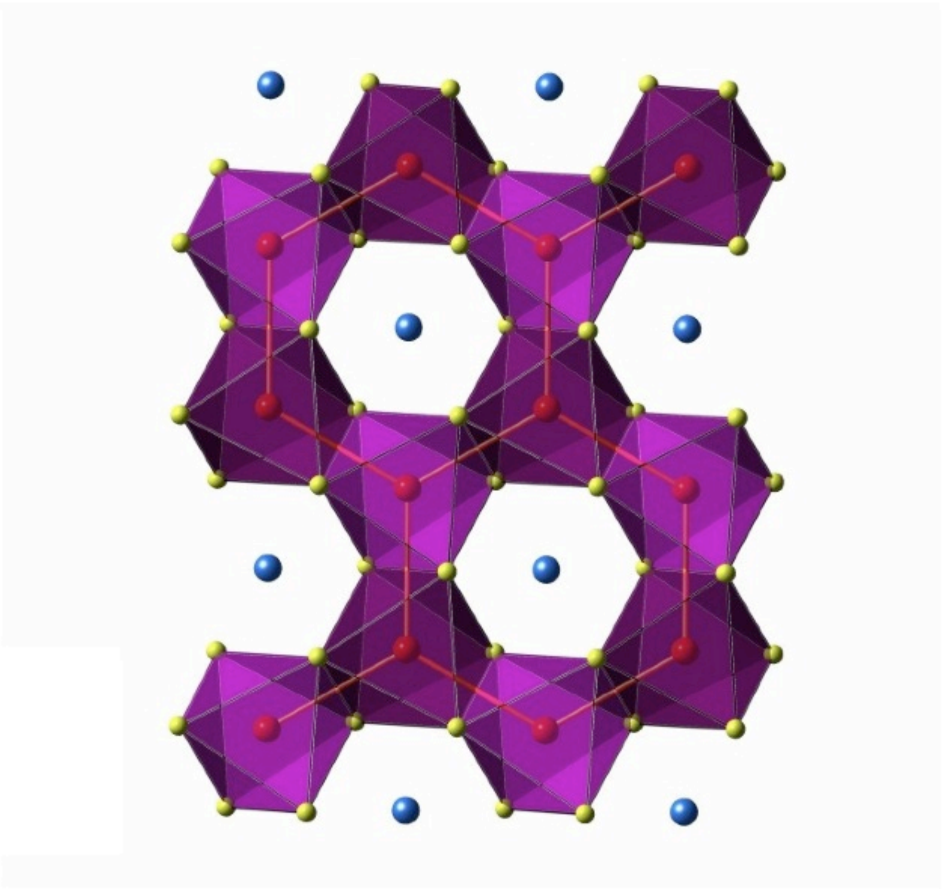
$$\mathcal{H}/J = (1-\alpha)\sum_{\mathrm{NN}} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - 2\alpha \sum_{\mathrm{NN}} S_i^{\gamma} S_j^{\gamma}$$

Heisenberg (AF) unfrustrated — Kitaev (FM)



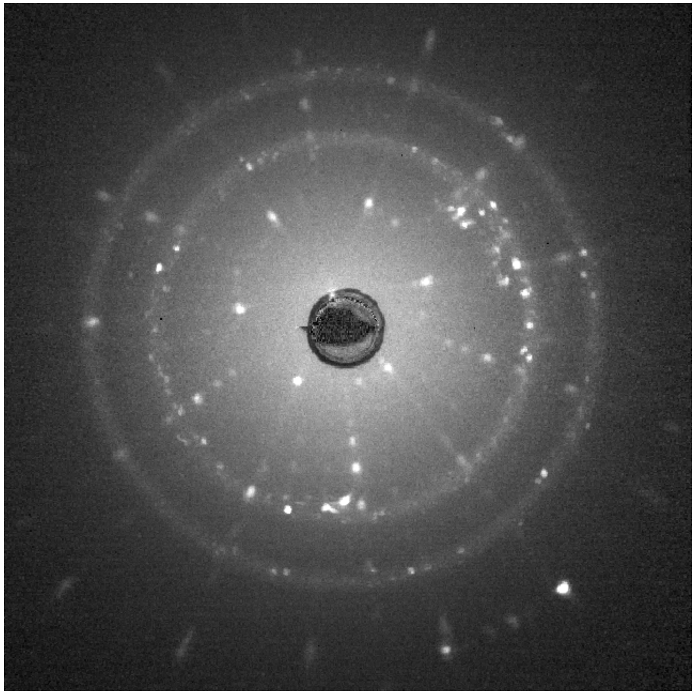
Structural properties

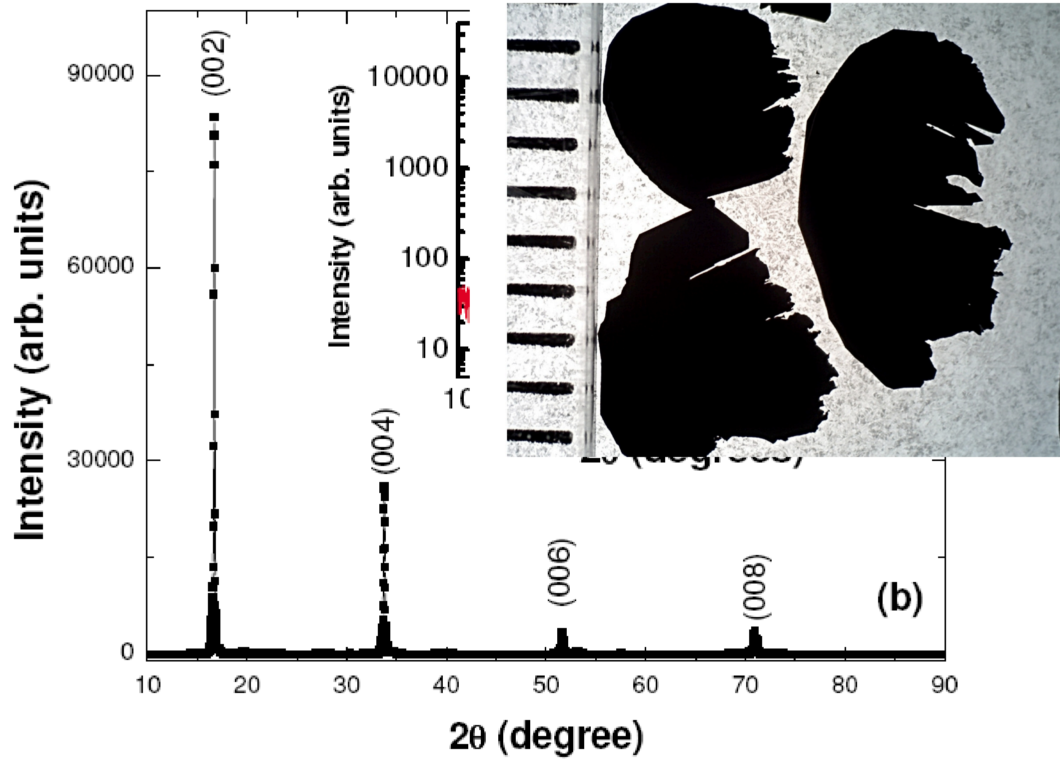




Yogesh Singh and P. Gegenwart, PRB **82** (2010) 064412

Synthesis of Na_2IrO_3

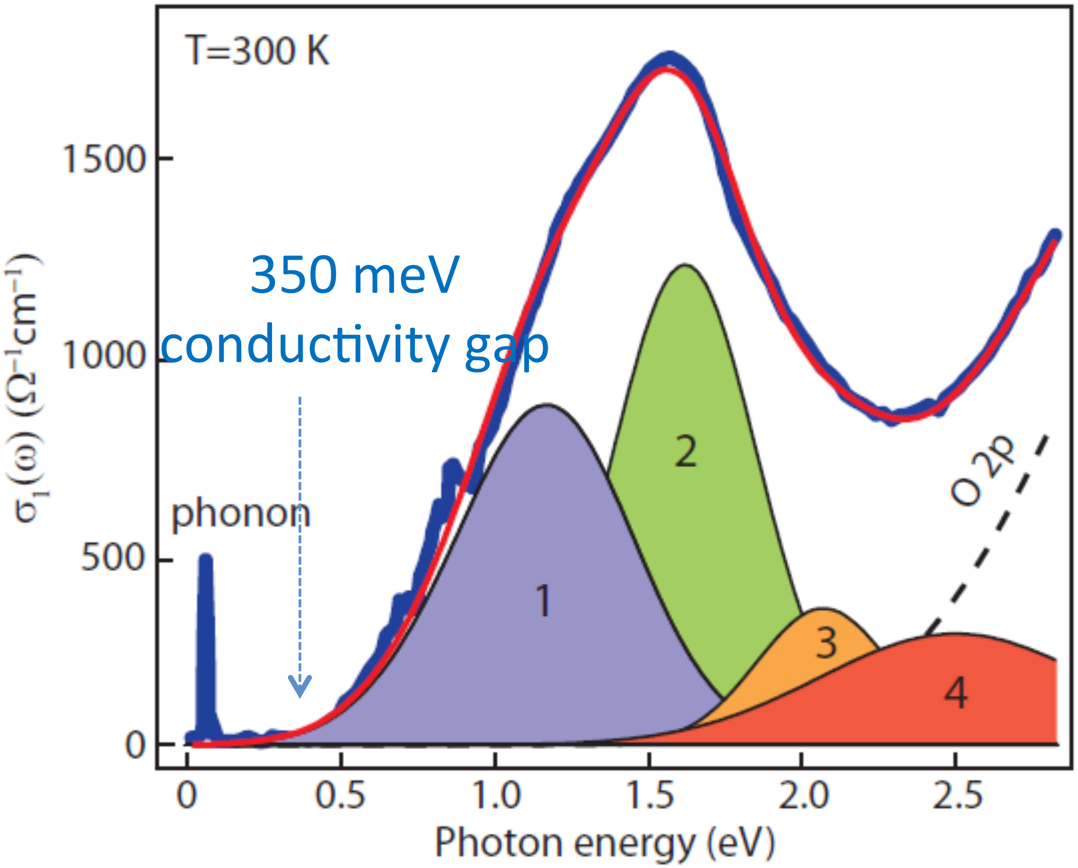


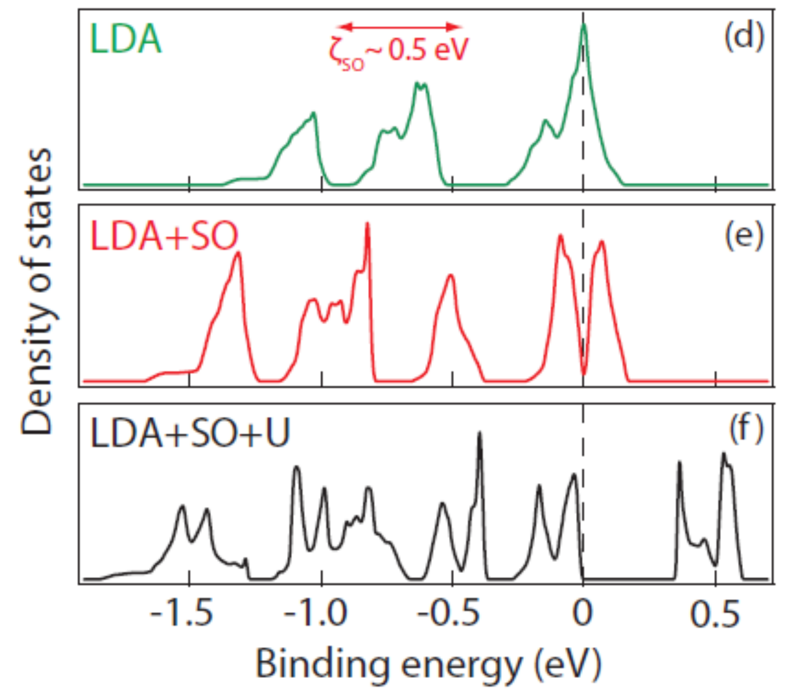


- Polycrystal: solid-state synthesis (900°C) from Na_2CO_3 and IrO_2
- Single crystal (5×3×0.1 mm^3): Growth T=1050 °C – 1150 ^{o}C

Yogesh Singh and P. Gegenwart, PRB **82** (2010) 064412

Optical spectroscopy

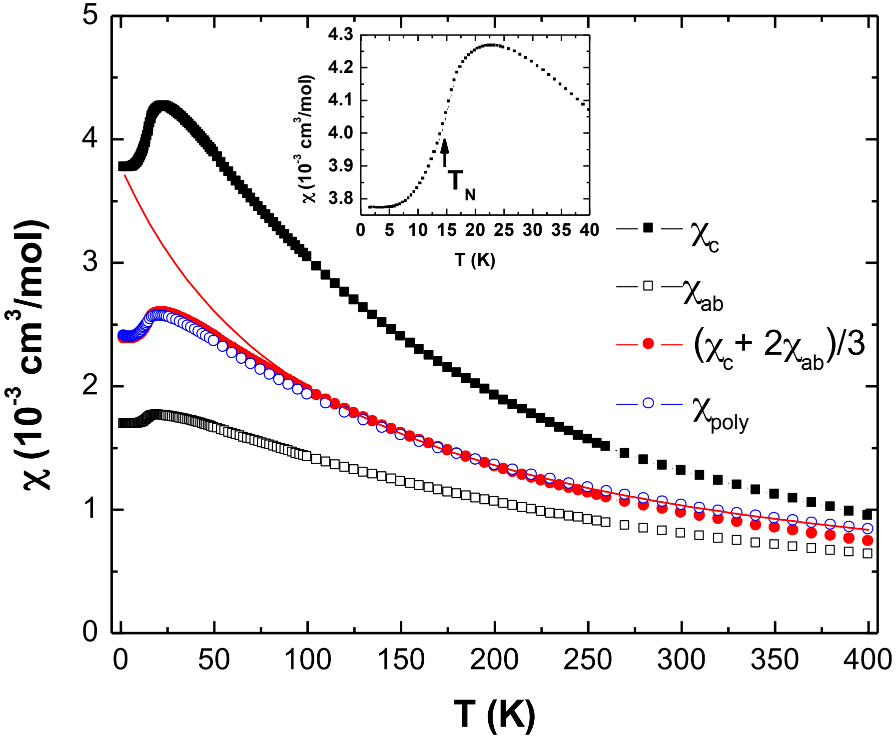


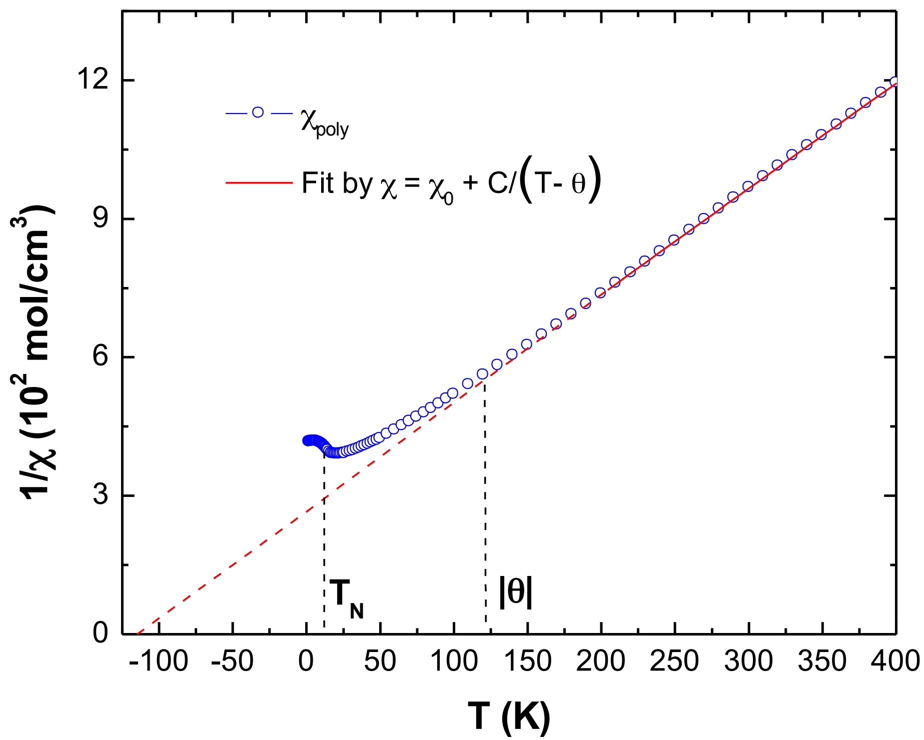


- 4-peak DOS from trigonal CEF and SO coupling
- Already SO opens gap, perfect fitting by including U = 3 eV (J_H = 0.6 eV)

R. Comin, G. Levy, B. Ludbrook, Z.-H. Zhu, C.N. Veenstra, J.A. Rosen, Yogesh Singh, P. Gegenwart, D. Stricker, N.J. Hancock, D. van der Marel, I.S. Elfimov, A. Damascelli, PRL **109**, 266406 (2012)

Magnetic susceptibility



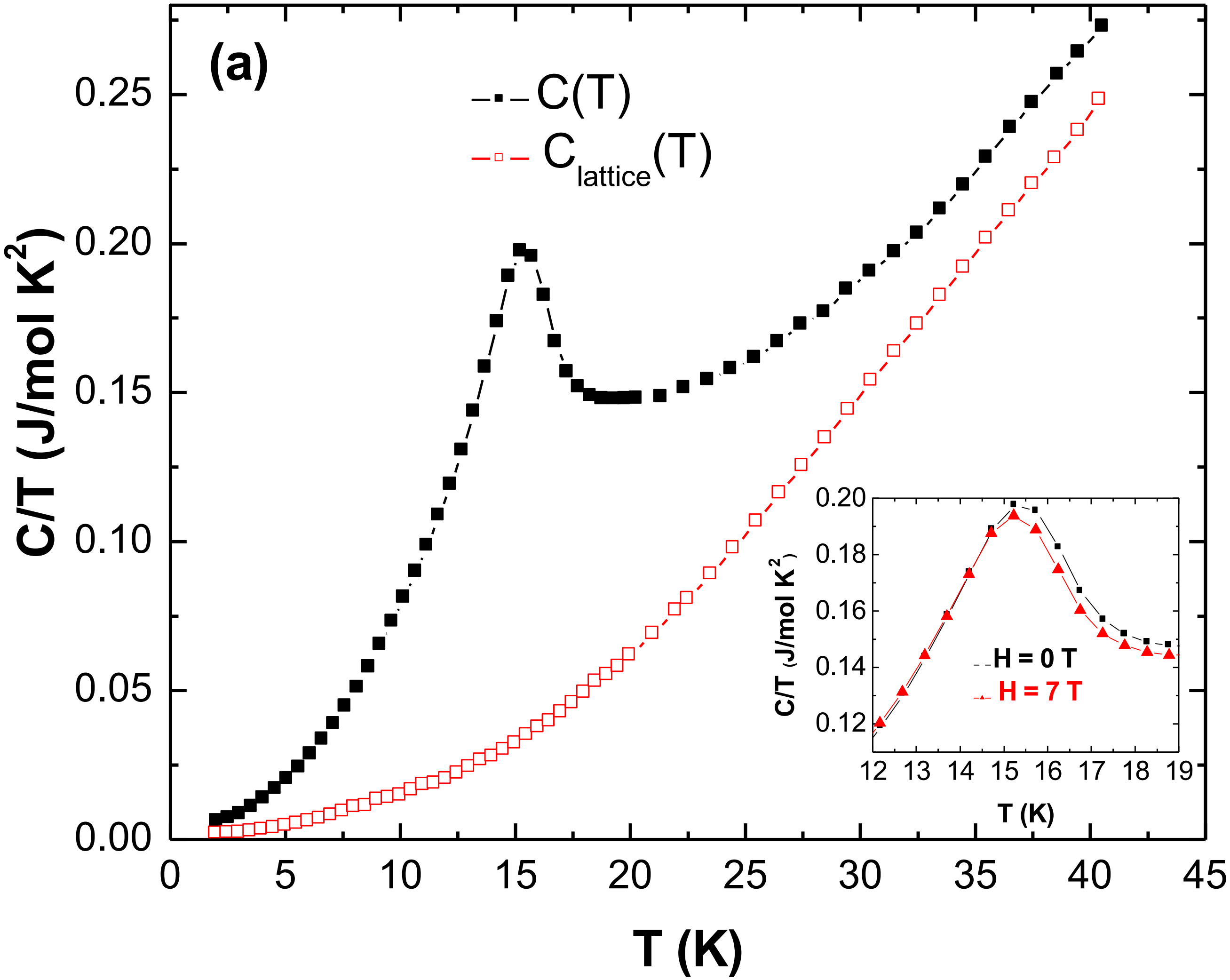


- CW fit reveals μ_{eff} = 1.81μ_B (assuming g=2) → S_{eff} = ½ state
- χ anisotropy may result from trigonal crystal field (→ g-factor anisotropy)
- Weiss temperature Θ = -120 K but T_N = 15 K

→ large frustration (*f* = 8)!

Yogesh Singh and P. Gegenwart, PRB **82** (2010) 064412

Heat capacity

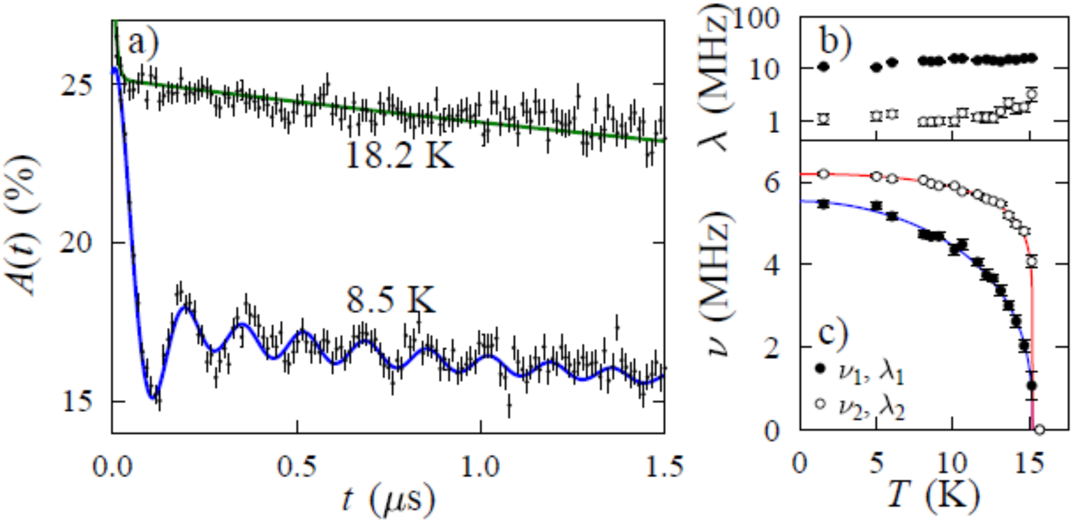


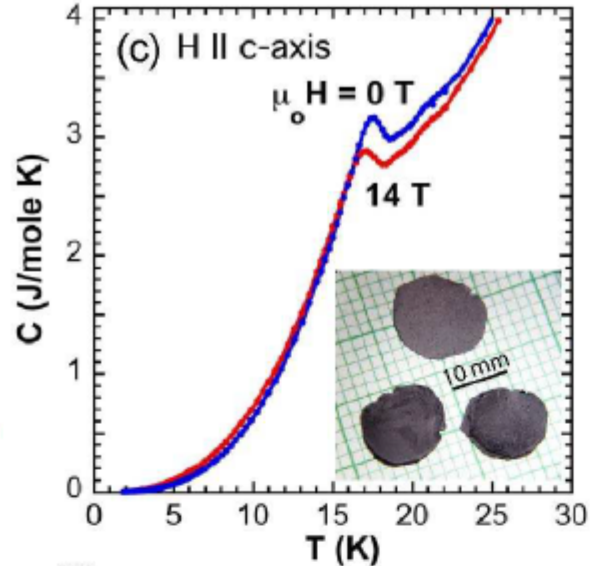
- C shows sharp lamda-like anomaly at T_N = 15 K
- Entropy $S(T_N) \approx 20\%$ Rln2 only

Nature of Magnetic ordering

μSR

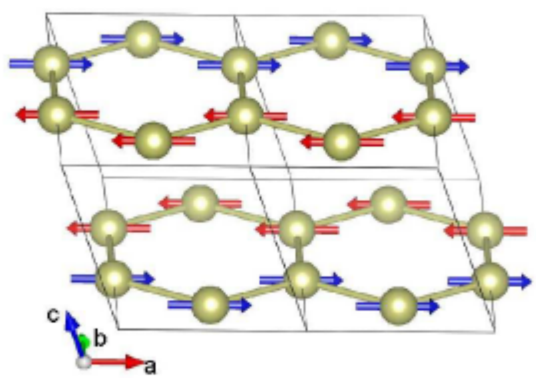
S.K. Choi et al., PRL **108** (2012) 127204.

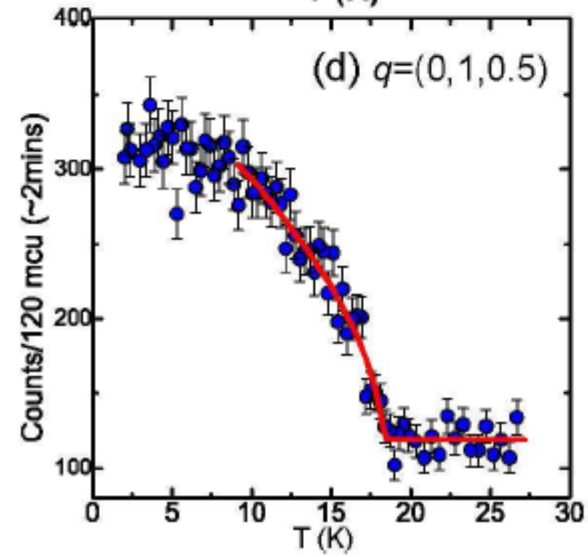




Neutron scattering:

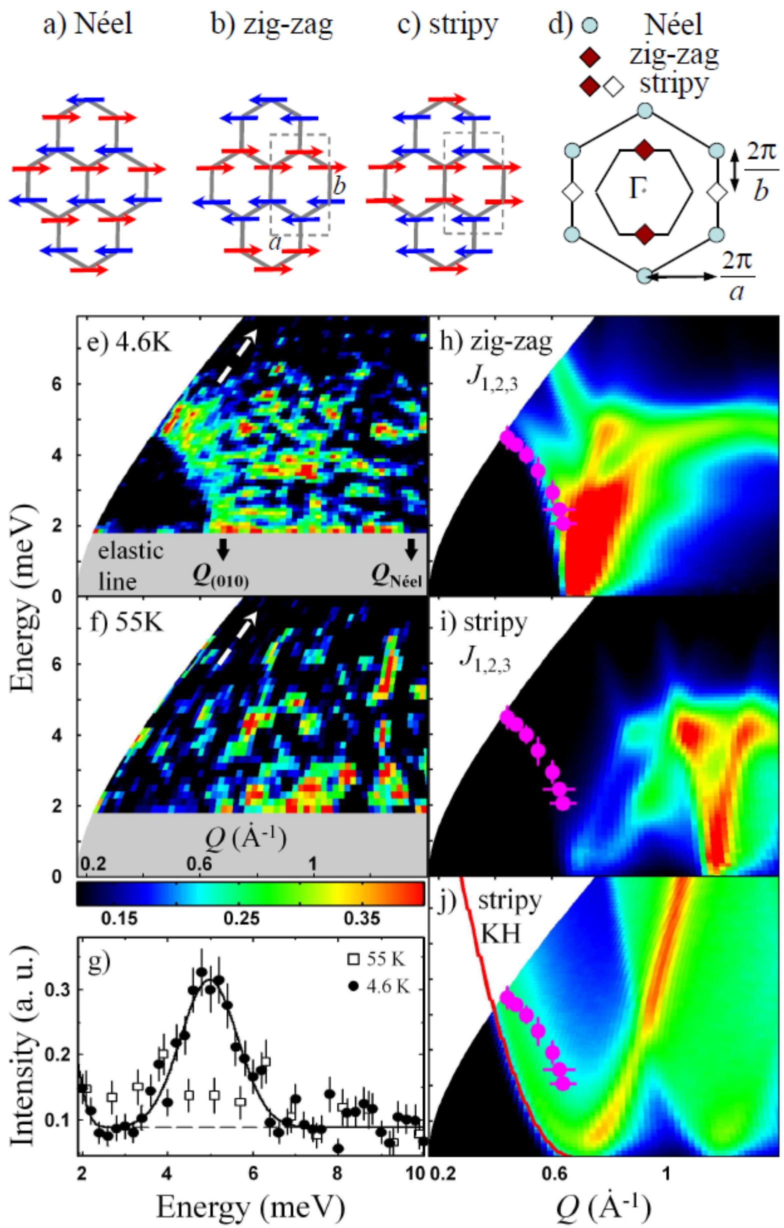
- **Zigzag-order** AF stacked along c
- Ordered moment : 0.22 μ_B





Feng Ye at al. PRB **85** (2012) 180403(R).

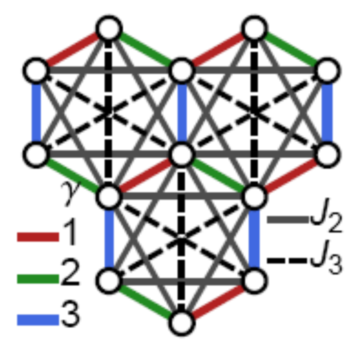
Powder INS: magnetic excitations



S.K. Choi et al. PRL **108**, 127204 (2012)

- Dispersion boundary for inelastic excitations at low Q, incompatible with Néel AF
- Data compatible with calculation for spin-wave dispersion for zig-zag ordering in $J_1J_2J_3$ model using J_1 = 4.35 meV, J_2/J_1 = 0.75, J_3/J_1 = 0.9
- Additional Kitaev term $\alpha \leq 0.2$

(I. Kimchi and Y.-Z. You, PRB 2011: **Kitaev-Heisenberg-J2-J3-Model**)



Magnetic excitations: RIXS

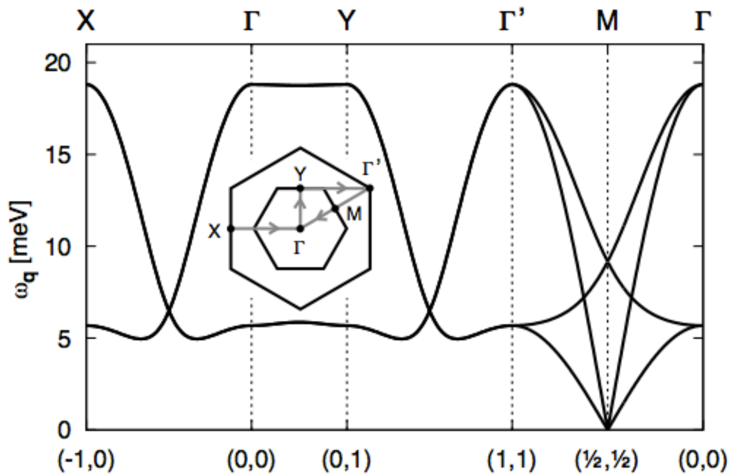
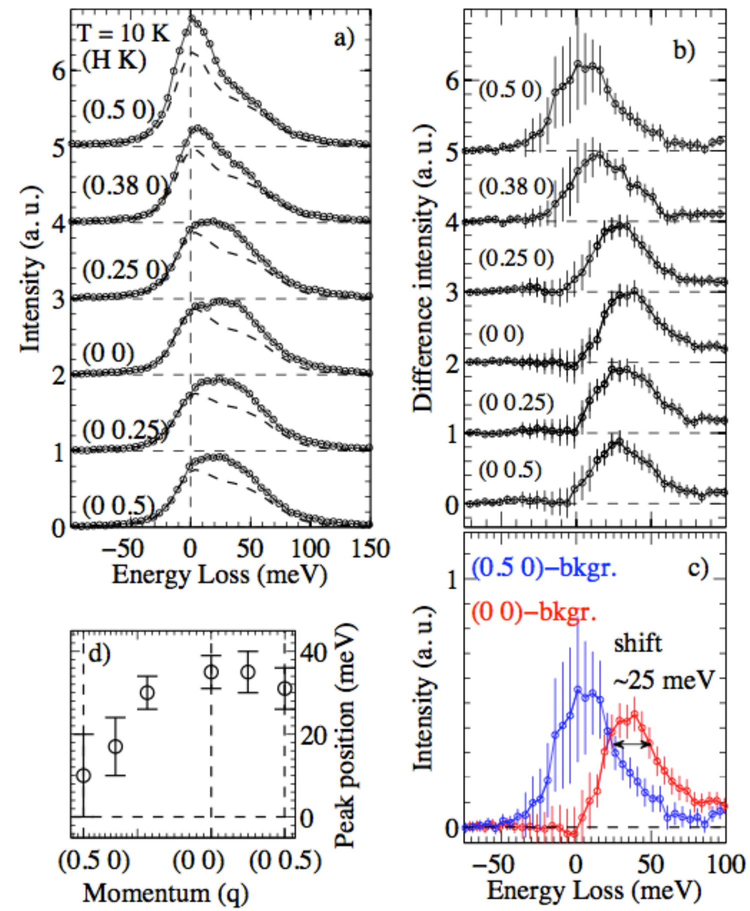


FIG. 3: Magnon spectra in the zigzag phase calculated using Eq. (4) with $(J, K) = (-4.01, 10.45)$ meV. The inset shows the path along the symmetry directions in the reciprocal space; notations of Ref. [4] are used.

Jiří Chaloupka, George Jackeli, Giniyat Khaliullin

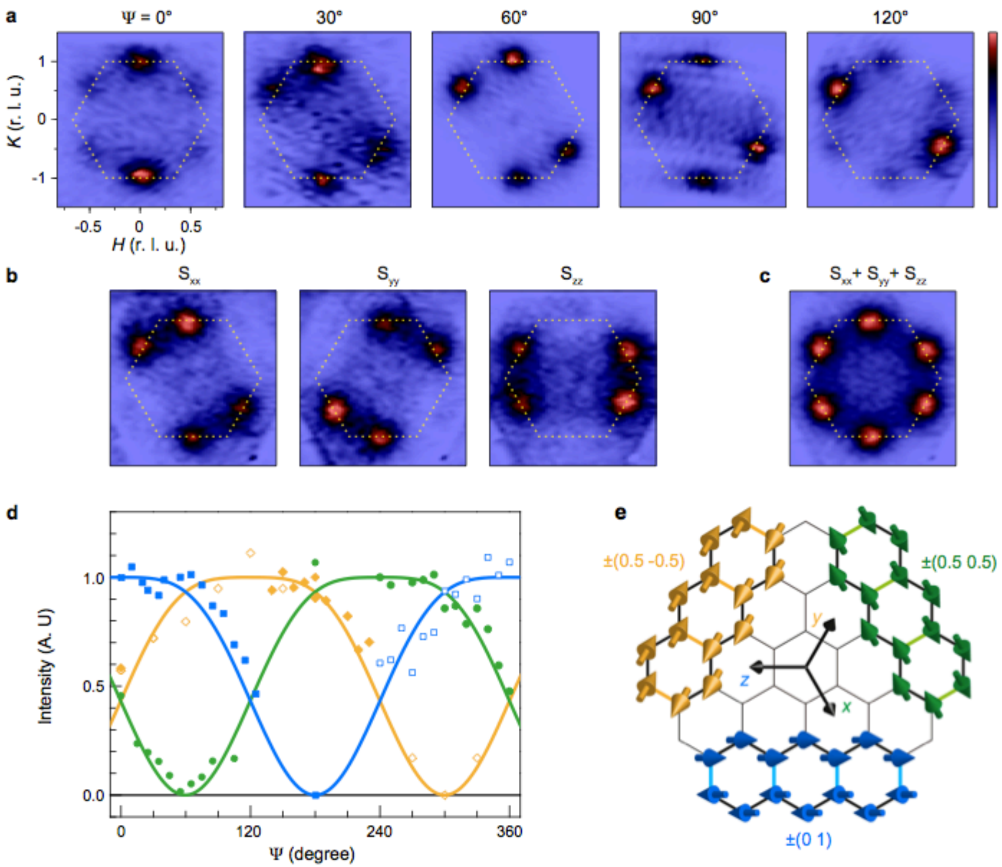
Phys. Rev. Lett. 110, 097204 (2013)

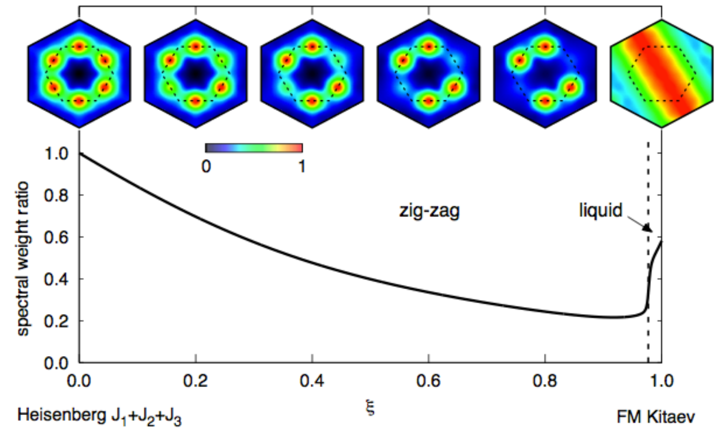


H. Gretarsson, J. P. Clancy, Yogesh Singh, P. Gegenwart, J. P. Hill, Jungho Kim, M. H. Upton, A. H. Said, D. Casa, T. Gog, Young-June Kim

Phys. Rev. B, 87, 220407 (R) (2013)

Direct Evidence of bond-directional exchange in Na_2IrO_3



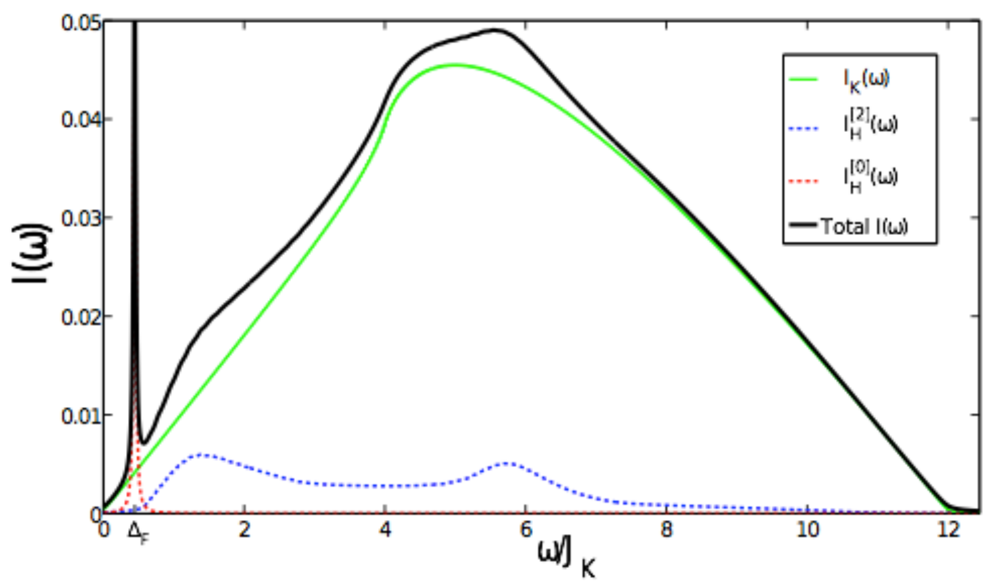


S. H. Chun, BJK, et al. (2015)

Prediction of Raman Response of Kitaev Spin-Liquid in A_2IrO_3

J. Knolle, Gia-Wei Chern, D. L. Kovrizhin, R. Moessner, and N. B. Perkins, PRL (2014)

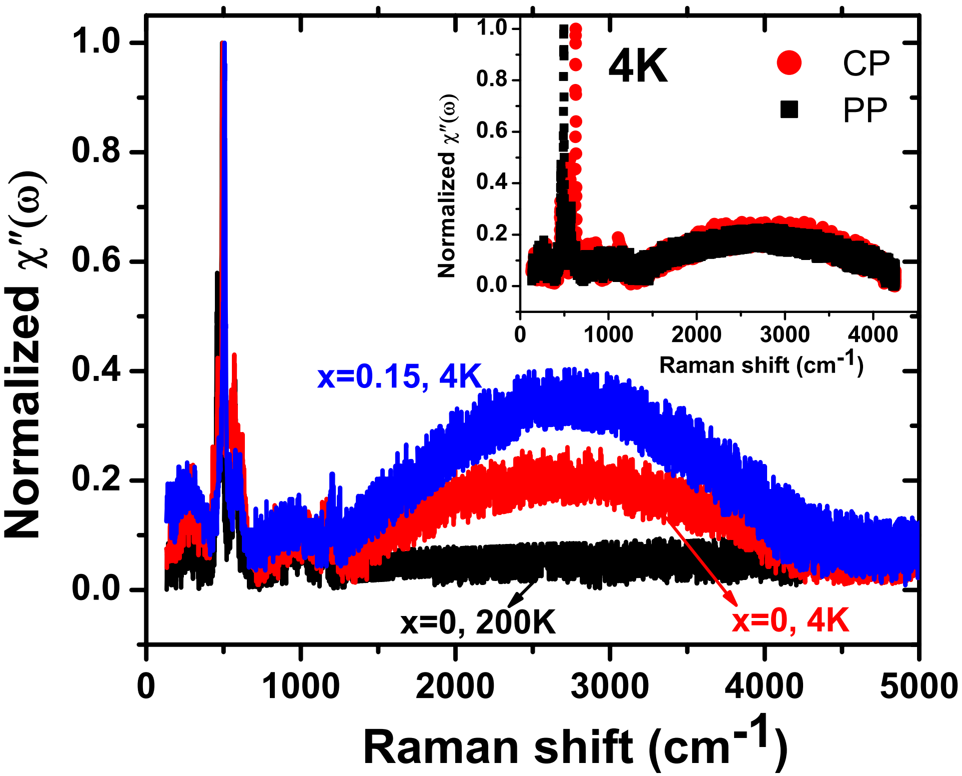
- Assumption: strong Kitaev limit, Heisenberg included as perturbation (JH/JK = 0.1)
- Kitaev contribution is a Broad Polarization independent band centered at 6JK and band-edge at 12JK
- Heisenberg term leads to a sharp spike at 0.45JK
- Results expected to be robust to inclusion of other Heisenberg-like terms provided they are small.



Experimental Raman response of Na_2IrO_3

S.N. Gupta, D. K. Mishra, Kavita Mehlawat, A. Balodhi, D. V. S. Muthu, Yogesh Singh, and A. K. Sood, **arXiv:1408.2239 (2014)**

- Observe a broad continuous Raman band centered at high energies
- The band is polarization independent
- J_K = 60 meV
- Band seen even below T_N



Summary for Na_2IrO_3

- Large frustration, T_N = 15 K, magnetic scale ~ 100 meV
- Inelastic Magnetic Scattering has shown dispersion consistent with dominant non-Heisenberg interactions
- Raman scattering shows a quasi-continuous, polarization independent band which is a spin liquid like response
- We estimate J_K ~ 60 meV.