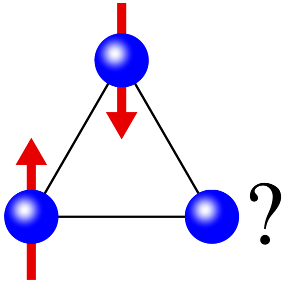
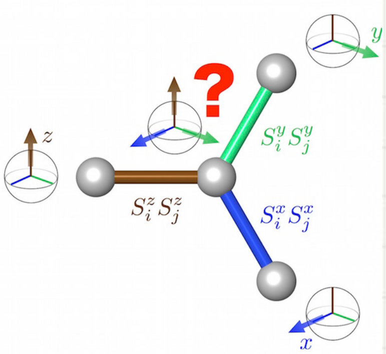
Cu_2IrO_3 and K_2IrO_3: new platforms for Kitaev physics

Yogesh Singh

Indian Institute of Science Education and Research Mohali





Collaborators

K_2IrO_3

Kavita Mehlawat	IISER Mohali
Radu Coldea	Oxford

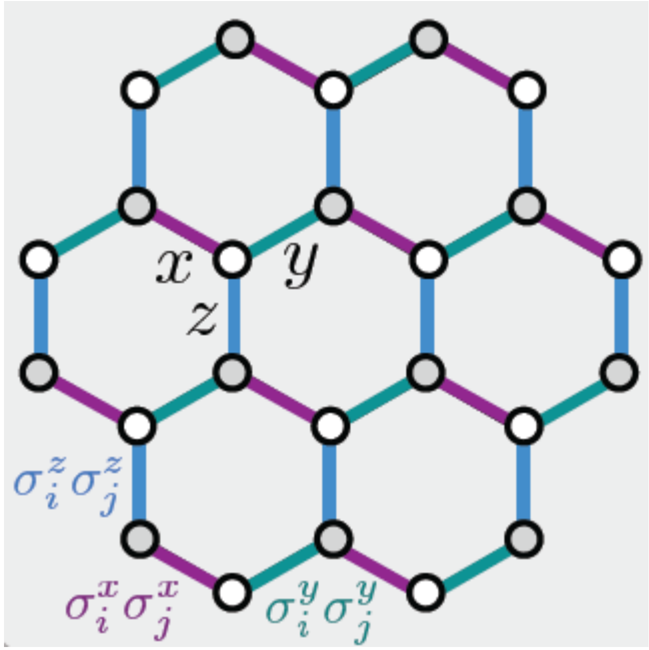
Cu_2IrO_3

Anzar Ali	IISER Mohali
Kwan-Yong Choi	Chung-Ang University, Seoul
	PSI

Outline

- Kitaev Honeycomb model
- A_2IrO_3 : old Kitaev materials
- $H_3LiIr_2O_6$
- K_2IrO_3 and Cu_2IrO_3: new Kitaev materials
- Conclusions

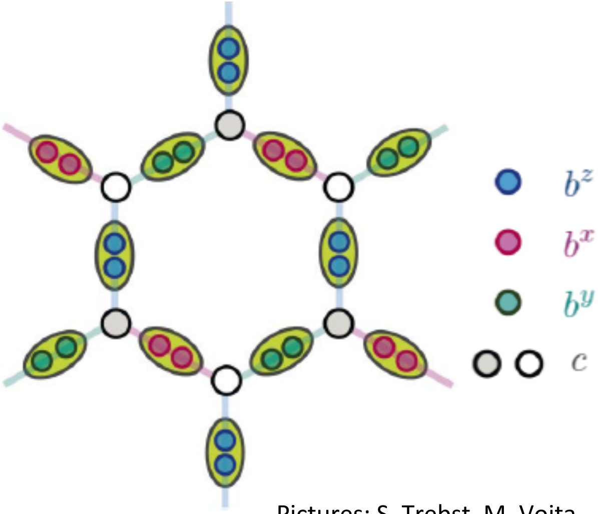
The Kitaev model



$$H_{\text{Kitaev}} = \sum_{\gamma-\text{links}} J_\gamma \sigma_i^\gamma \sigma_j^\gamma$$

Ann. Phys. **321**, 2–111 (2006).

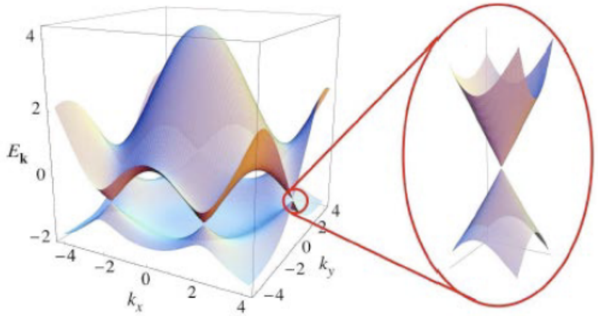
- Exactly Solvable
- GS = Z2 Spin Liquid
- Gapped or Gapless
- Majorana Excitations
- In H, gapped phase, anyonic excitations



Pictures: S. Trebst, M. Vojta

- Bond frustration
- Exact solution by mapping to Majorana fermions

→ quantum spin liquid with spin fractionalization,
itinerant Majoranas: Dirac cones,
localized ones: “flux order” W_p=+1



PRL 102, 017205 (2009) PHYSICAL REVIEW LETTERS week ending 9 JANUARY 2009

Mott Insulators in the Strong Spin-Orbit Coupling Limit: From Heisenberg to a Quantum Compass and Kitaev Models

G. Jackeli[1,*] and G. Khaliullin[1]

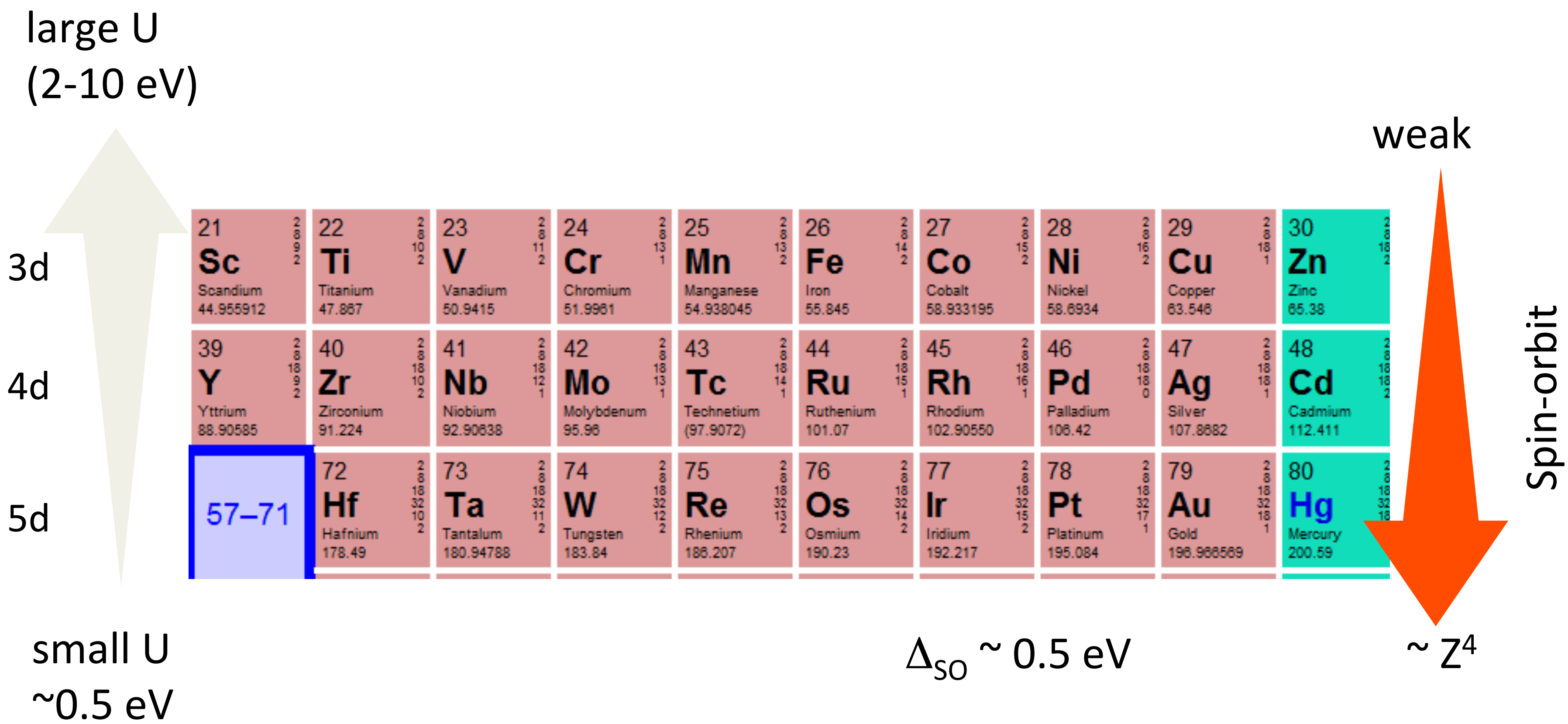
[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

(Received 21 August 2008; published 6 January 2009)

We study the magnetic interactions in Mott-Hubbard systems with partially filled t_{2g} levels and with strong spin-orbit coupling. The latter entangles the spin and orbital spaces, and leads to a rich variety of the low energy Hamiltonians that extrapolate from the Heisenberg to a quantum compass model depending on the lattice geometry. This gives way to "engineer" in such Mott insulators an exactly solvable spin model by Kitaev relevant for quantum computation. We, finally, explain "weak" ferromagnetism, with an anomalously large ferromagnetic moment, in Sr_2IrO_4.

Idea: engineer Kitaev exchange by the help of strong spin-orbit interaction

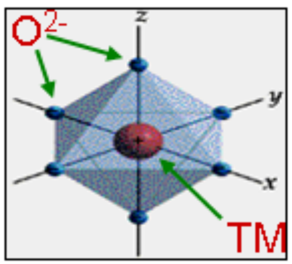
3d vs 5d transition metal oxides

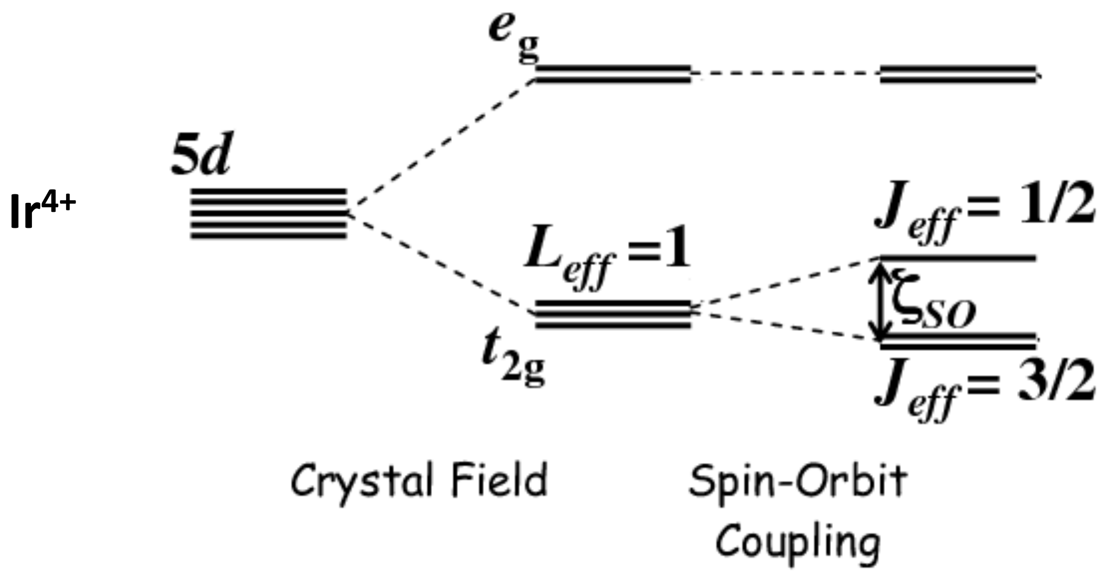


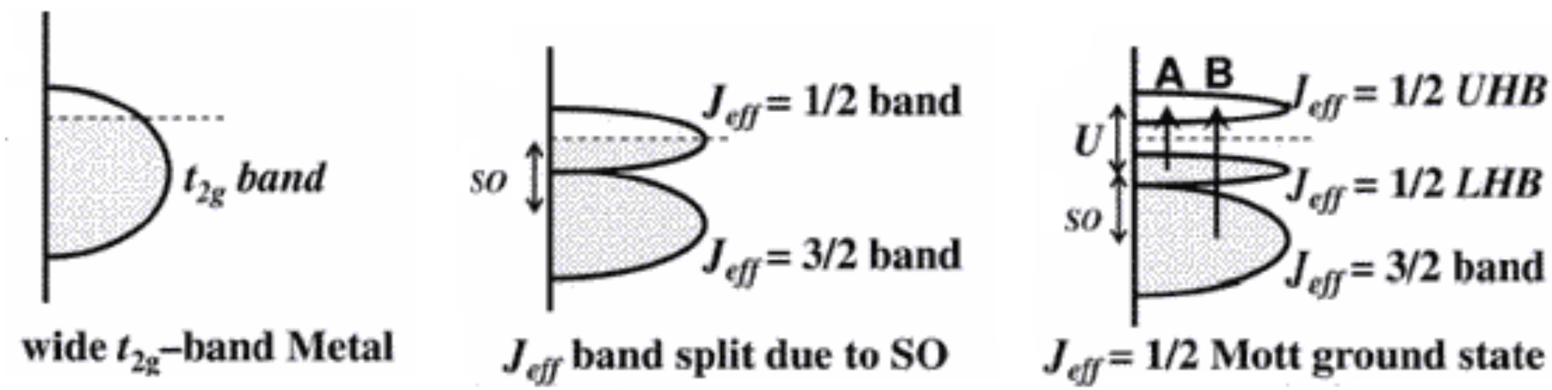
5d: interplay of U and SO coupling

Designing Kitaev Interactions: Jackeli-Khaliullin Mechanism

Large spin-orbit coupling in 5d transition-metal oxides → novel electronic states, e.g. spin-orbit Mott insulators, correlated topological insulators, …



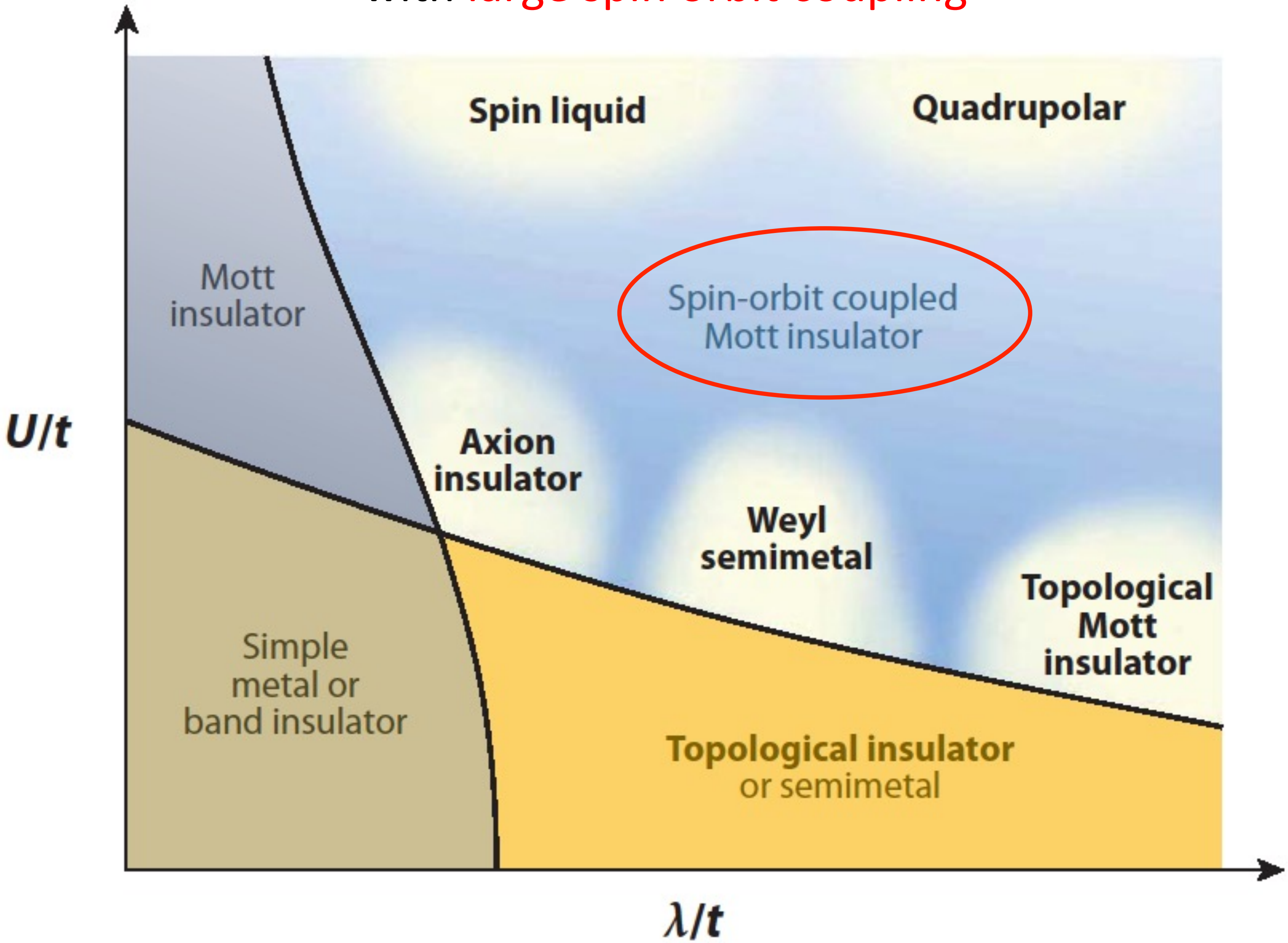




Spin-Orbit Mott Insulator

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

Topological quantum phases in correlated electron systems with large spin orbit coupling

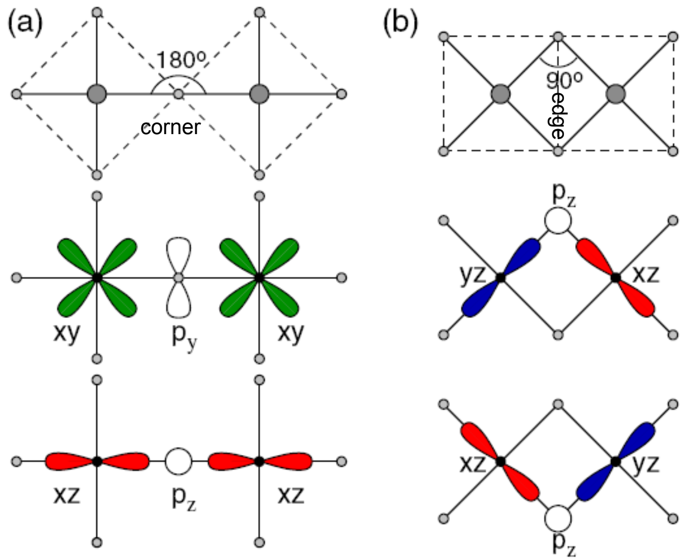


W.Witczak-Krempa, G. Chen, Y.B. Kim, L. Balents, Annu. Rev. Condens. Matter Phys. **5**, 57 (2014).

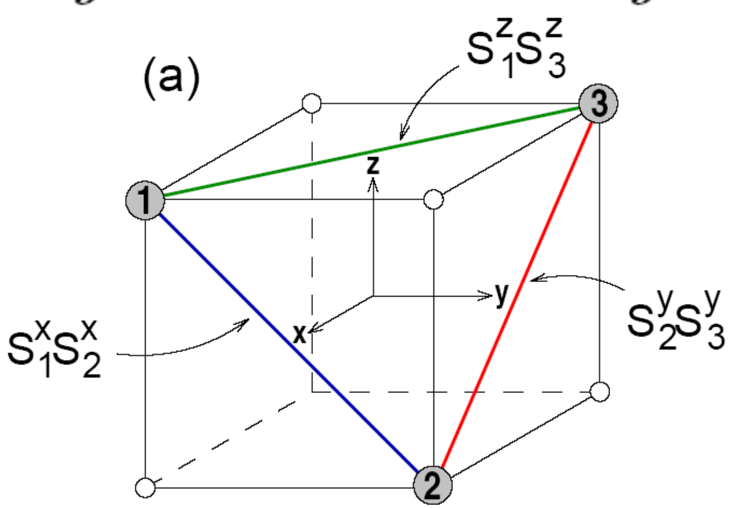
Designing Kitaev Interactions: Jackeli-Khaliullin Mechanism

$$\left| J_{eff} = 1/2, m_{eff} = \pm 1/2 \right\rangle = \frac{1}{\sqrt{3}} \left(\left| xy, \mp\sigma \right\rangle \mp \left| yz, \pm\sigma \right\rangle + i \left| zx, \pm\sigma \right\rangle \right)$$

→ wave function of doublet = coherent superposition of different orbital and spin states
→ bond geometry important for magnetic interaction:



$$\mathcal{H}_{ij}^{(\gamma)} = -J S_i^{\gamma} S_j^{\gamma}$$



Perovskite:
→ *Heisenberg*

Pyrochlore, honeycomb, kagome:
destructive interference of Heisenberg interaction

G. Jackeli and G. Khaliullin PRL 2009

Deviations from Kitaev Model

- Local Distortions : lift t_{2g} degeneracy, J_{eff} character changes
- More General Hopping (direct d-d): Heisenberg
- Longer range interactions: J_2, J_3, K_2, DM
- Higher Order Interactions (from t_{2g}-e_g mixing): modify J, K

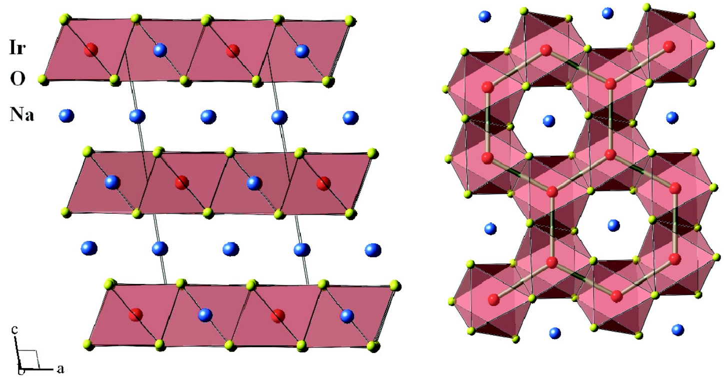
Generalized Hamiltonian

$$\mathcal{H}_{ij} = J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j + K_{ij}\;S_i^{\gamma} S_j^{\gamma} + \Gamma_{ij}\left(S_i^{\alpha} S_j^{\beta} + S_i^{\beta} S_j^{\alpha}\right)$$

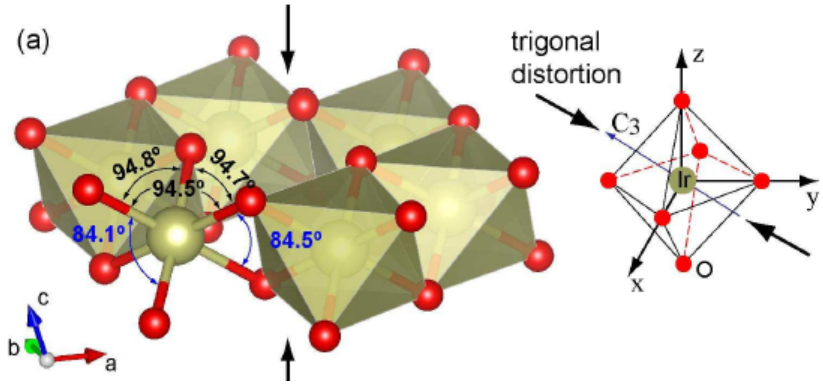
S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, R. Valenti, J. of Phys. Cond. Matt. (2017).

Candidate materials

Na_2IrO_3



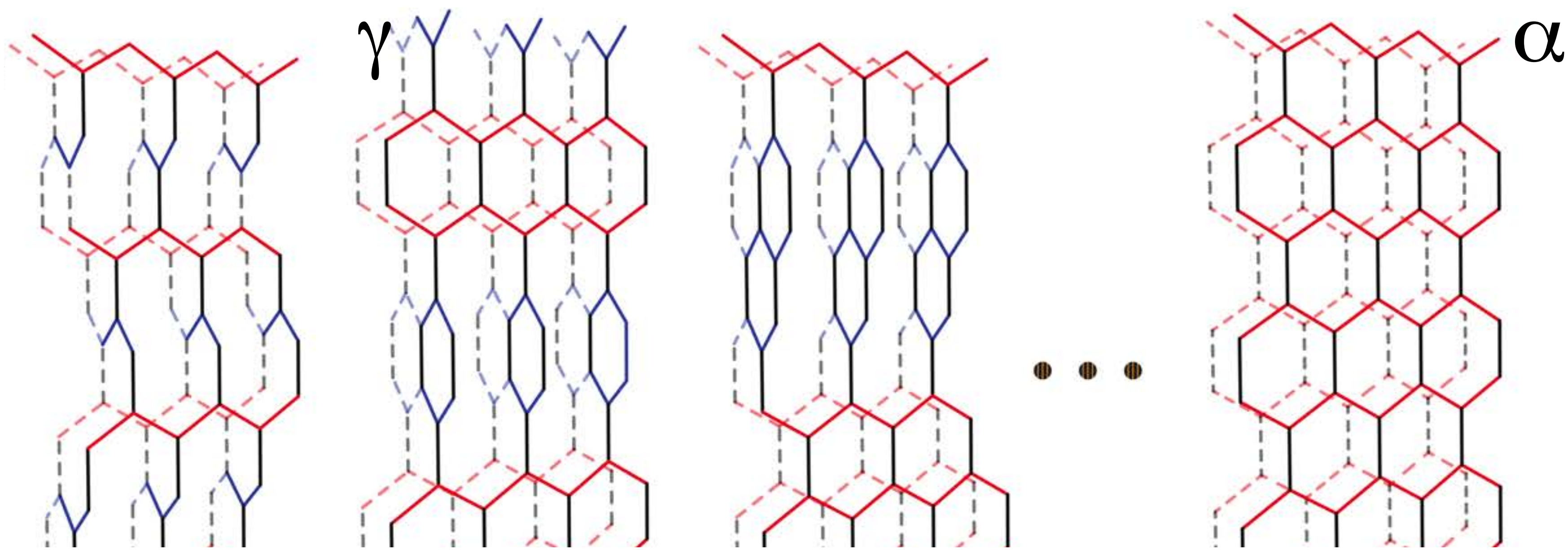
(a) (b)



Li_2IrO_3

Hyper-Honeycomb Stripy-Honeycomb Honeycomb

β γ α



Yogesh Singh and PG, PRB 2010, Modic et al., Nat. Comm. 2014, Takayama et al., PRL 2015

Electronic Parameters

TABLE I. Summary of electronic parameters for honeycomb materials Na_2IrO_3, α-Li_2IrO_3, Li_2RhO_3, and α-$RuCl_3$. The latter material is discussed in section III B. The source(s) of each estimate is indicated; RIXS = "Resonant Inelastic X-ray Scattering", PE = "Photoemmission", Δ_{ch} refers to the charge gap, while Δ refers to the trigonal crystal field splitting, as defined in section II C 1.

Property	Na_2IrO_3	α-Li_2IrO_3	Li_2RhO_3	α-$RuCl_3$
Δ_{ch} [a]	~ 0.35 eV (PE[83], $\sigma(\omega)$[83,84], $\rho(T)$[74])	~ 0.15 eV ($\rho(T)$[69])	~ 0.08 eV ($\rho(T)$[82])	$1.1 - 1.9$ eV[b] (PE[85–87], $\sigma(\omega)$[88,89])
λ	$0.4 - 0.5$ eV (RIXS[90,91], $\sigma(\omega)$[91])		$0.1 - 0.15$ eV (*ab-initio*[40])	$0.1 - 0.15$ eV ($\sigma(\omega)$[61])
Δ	$20 - 50$ meV (RIXS[90,91], *ab-initio*[44,45])		~ 60 meV (*ab-initio*[40])	~ 20 meV (*ab-initio*[41,45])
$10Dq$	~ 3.3 eV (RIXS[91,92])		–	$\sim 2.0 - 2.2$ eV (PE[87], XAS[93], $\sigma(\omega)$[89,93], *ab-initio*[61,93])
J_H	$0.25 - 0.30$ eV ($\sigma(\omega)$[91], *ab-initio*[44])		–	~ 0.4 eV ($\sigma(\omega)$[89])
U	$1.3 - 1.7$ eV ($\sigma(\omega)$[91], *ab-initio*[44])		–	~ 2.4 eV ($\sigma(\omega)$[89])

[a] Estimates of Δ_{ch} based only on $\rho(T)$ may be unreliable.
[b] Analysis of $\rho(T)$ for α-$RuCl_3$ yields $\Delta_{ch} \sim 0.15$ eV, which is likely far underestimated; see discussion in the text.

S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, R. Valenti, J. of Phys. Cond. Matt. (2017).

A_2IrO_3 are J_{eff} = ½ SO Mott Insulators

Magnetic Parameters for Kitaev Materials

TABLE II. Summary of magnetic parameters for honeycomb Na_2IrO_3, α-Li_2IrO_3, Li_2RhO_3, and α-$RuCl_3$. The latter material is discussed in section III B. See text for relevant references.

Property	Na_2IrO_3	α-Li_2IrO_3	Li_2RhO_3	α-$RuCl_3$
μ_{eff} (μ_B)	1.79	1.83	2.03	2.0 to 2.7
Θ_{iso} (K)	~ -120	-33 to -100	~ -50	$\sim +40$
Θ_{ab} (K)	-176	$\Theta_{ab} > \Theta_c$	–	+38 to +68
Θ_c (K)	-40	–	–	-100 to -150
T_N (K)	$13-18$	~ 15	(6)	7 to 14
Order	Zigzag	Spiral	Glassy	Zigzag
k-vector	$(0, 1, \frac{1}{2})$	$(0.32, 0, 0)$	–	$(0, 1, \frac{1}{2})$

S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, R. Valenti, J. of Phys. Cond. Matt. (2017).

A_2IrO_3 are J_{eff} = ½ SO Mott Insulators but not Kitaev QSL's

Exchange Interactions in A_2IrO_3

TABLE III. Bond-averaged values of the largest magnetic interactions (in units of meV) within the plane for Na_2IrO_3 computed using various methods. "Pert. Theo." refers to second order perturbation theory, "QC" = quantum chemistry methods, "ED" = exact diagonalization.

Method	J_1	K_1	Γ_1	Γ'_1	K_2	J_3
Pert. Theo.[44]	+3.2	−29.4	+1.1	−3.5	−0.4	+1.7
QC (2-site)[43]	+2.7	−16.9	+1.0	–	–	–
ED (6-site)[45]	+0.5	−16.8	+1.4	−2.1	−1.4	+6.7

TABLE IV. Values of the largest magnetic interactions (in units of meV) within the plane for α-Li_2IrO_3 obtained from various methods. "QC" = quantum chemistry methods, "ED" = exact diagonalization.

Method	J_1^Z	J_1^X	K_1^Z	K_1^X	Γ_1^Z	Γ_1^X	K_2	Γ_2	$\|\mathbf{D}_2\|$	J_3
QC (2-site)[43]	−19.2	+0.8	−6.0	−11.6	+1.1	−4.2	–	–	–	–
ED (6-site)[45]	−3.1	−2.5	−6.3	−9.8	+9.4	+8.7	−3.7	+3.4	+2.7	+6.0

S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, R. Valenti, J. of Phys. Cond. Matt. (2017).

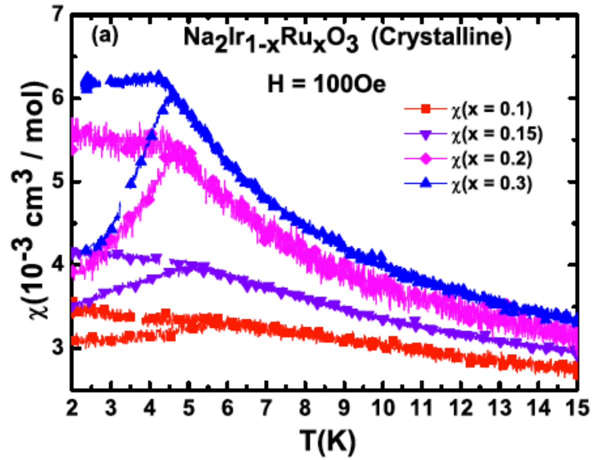
A_2IrO_3 are J_{eff} = ½ SO Mott Insulators proximate to Kitaev's QSL

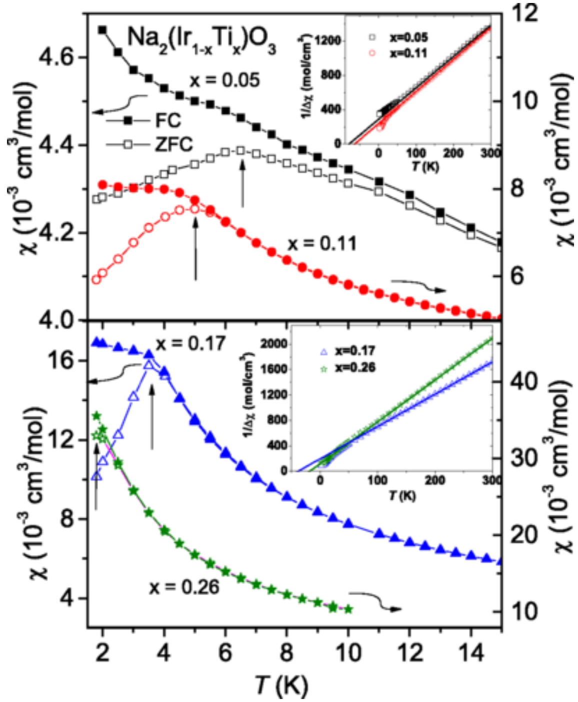
How can A_2IrO_3 be tuned towards Kitaev limit ?

- Chemical substitutions/doping
- Pressure
- Magnetic field
- ……….

Chemical substitution and Pressure Effects

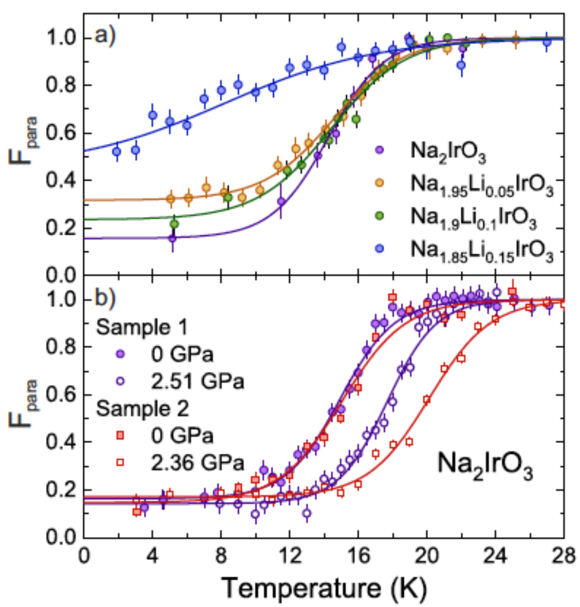
Mehlawat, Singh, PRB (2015)

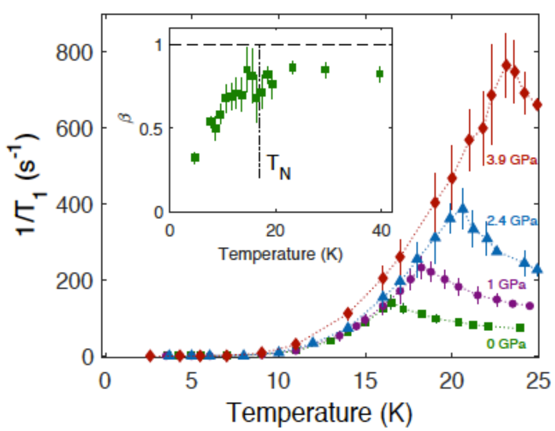


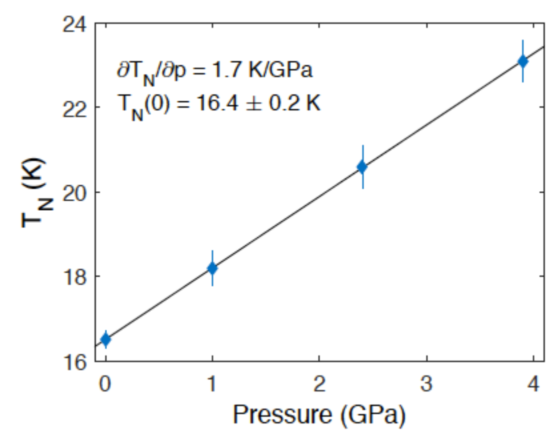


Manni, Gegenwart, PRB (2014)

- Disorder on Ir sub-lattice leads to Glassy state
- Disorder at Na sub-lattice leads to inhomogeneous magnetic order
- Hydrostatic pressure leads to enhancement of T_N



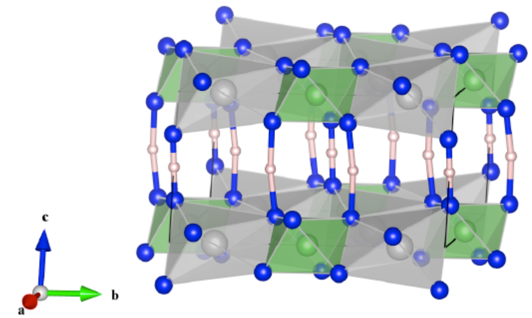




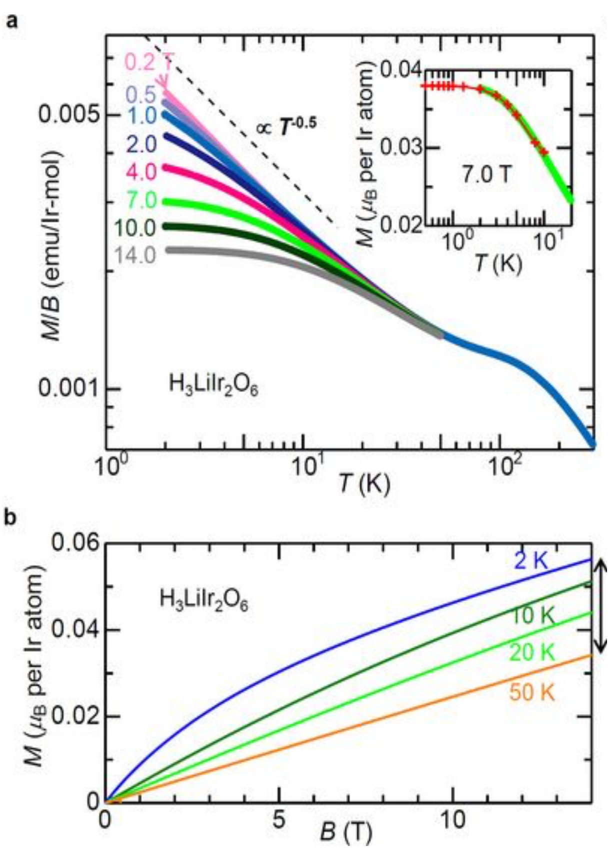
Simutis,…Mehlawat,..Singh… PRB 98 (10), 104421 (2018).

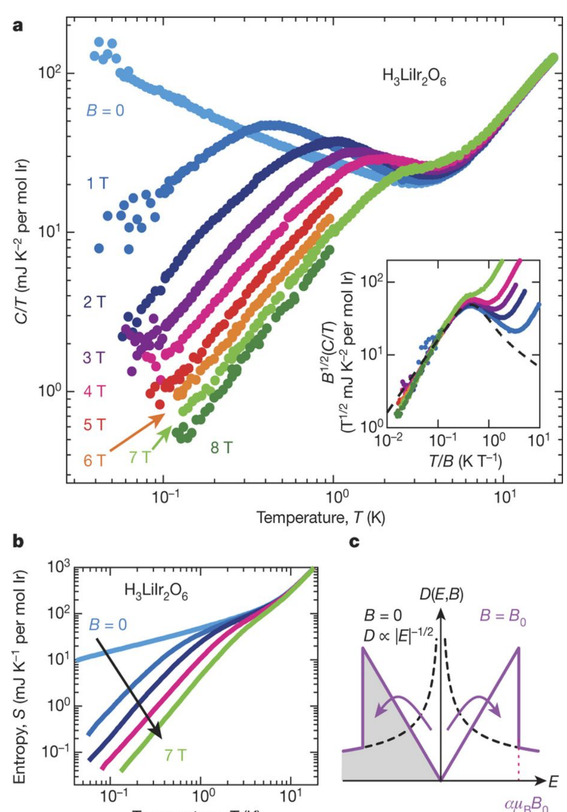
New Kitaev QSL candidate $H_3LiIr_2O_6$

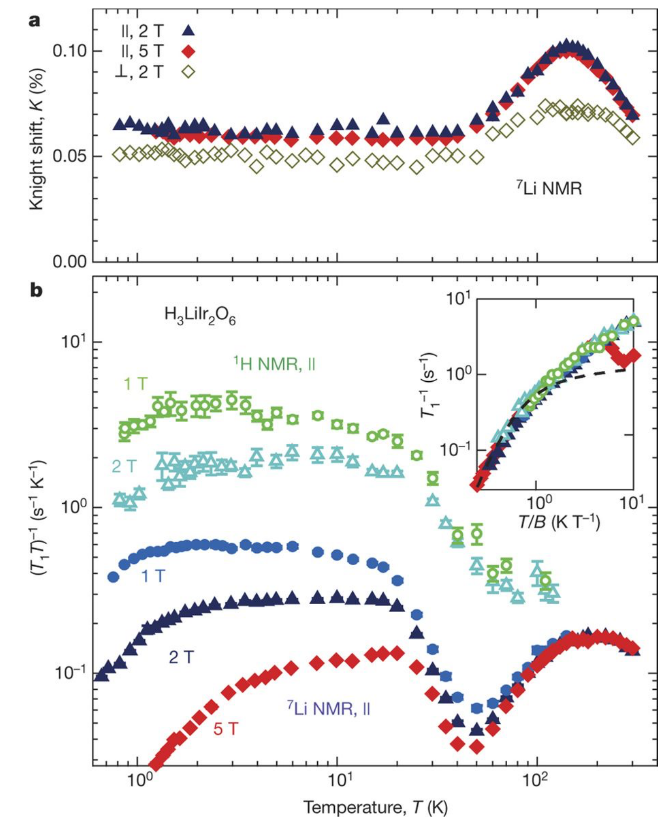
α-Li_2IrO_3 + H_2SO_4 —(180 °C, 4 days)→ $H_3LiIr_2O_6$ + NaCl



K. Kitagawa,…Takagi, et al. *Nature* **554**, 341 (2018)

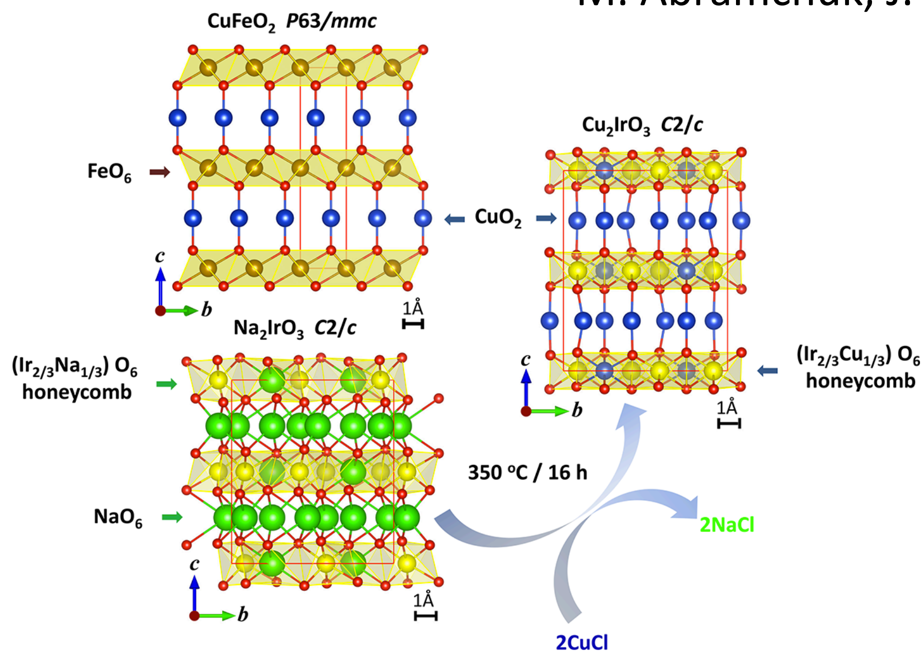


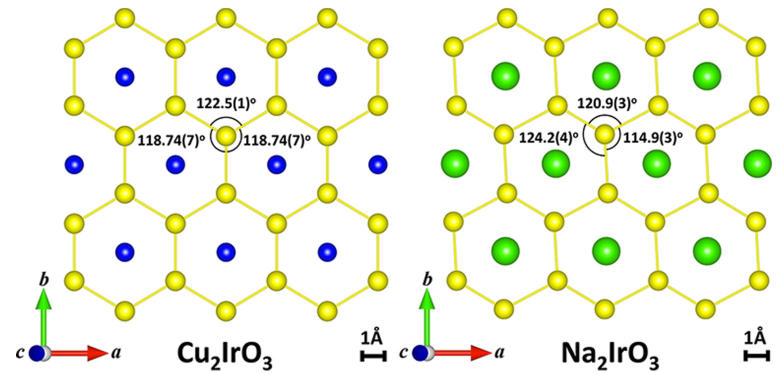


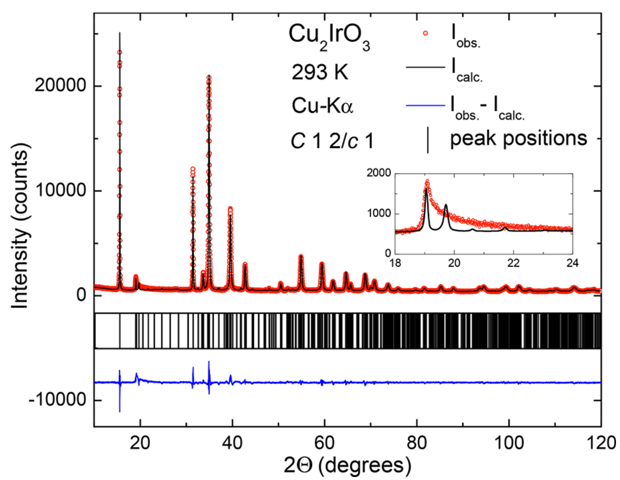


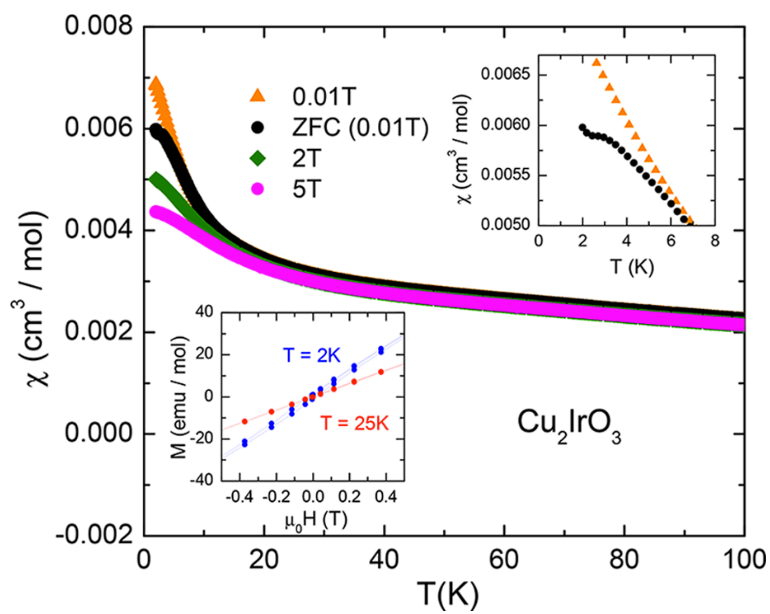
New Kitaev material Cu_2IrO_3

M. Abramchuk, J. Am. Chem. Soc. **139**, 15371 (2017).



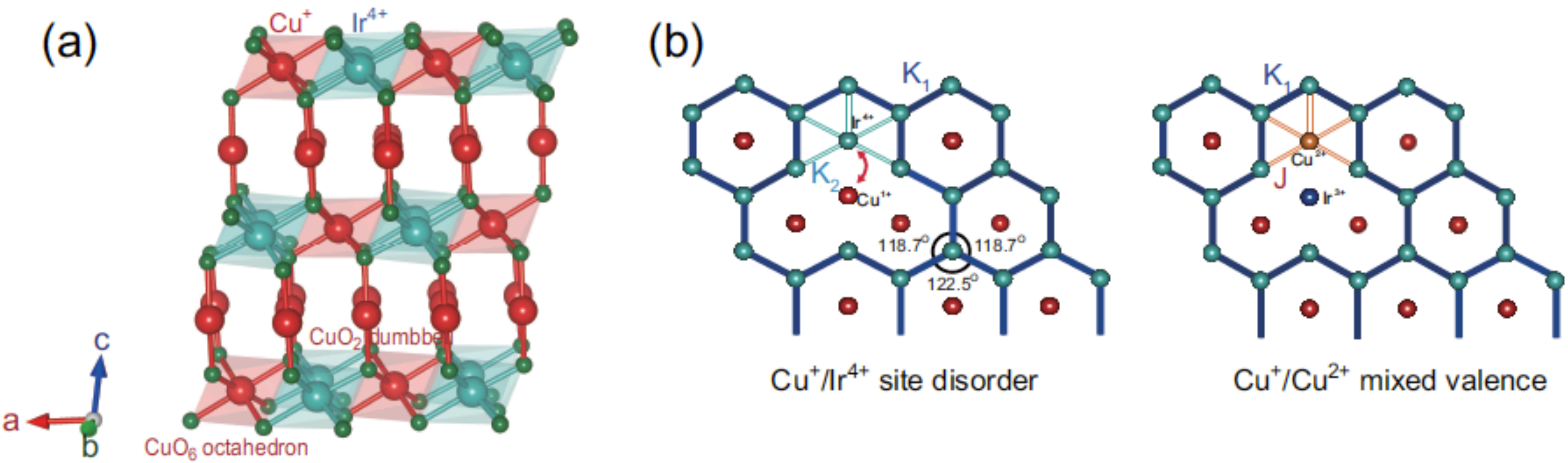






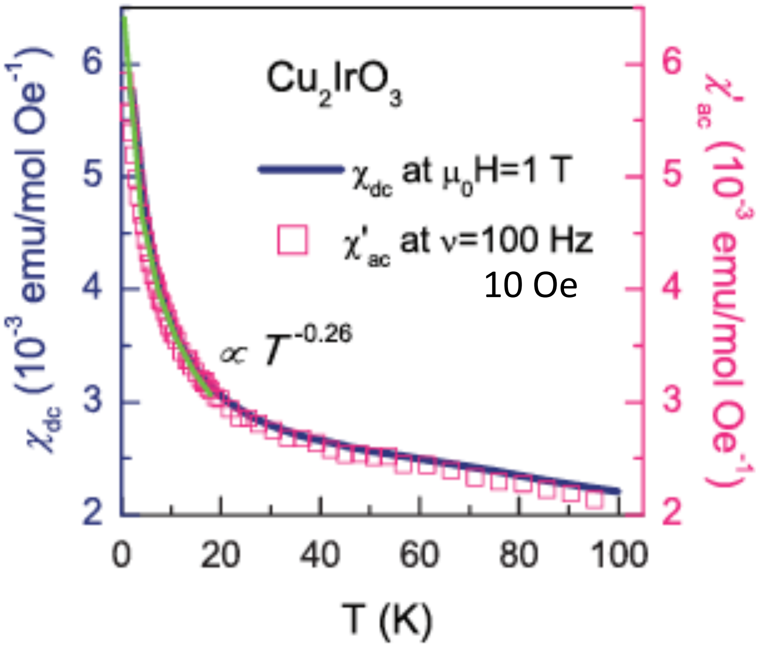
Synthesis and Structure

$$Na_2IrO_3 + 2CuCl \xrightarrow[\text{inert}]{375\ ^{o}C} Cu_2IrO_3 + NaCl$$

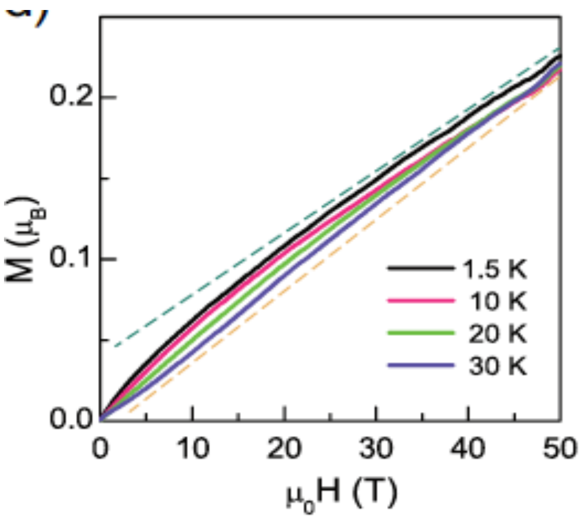


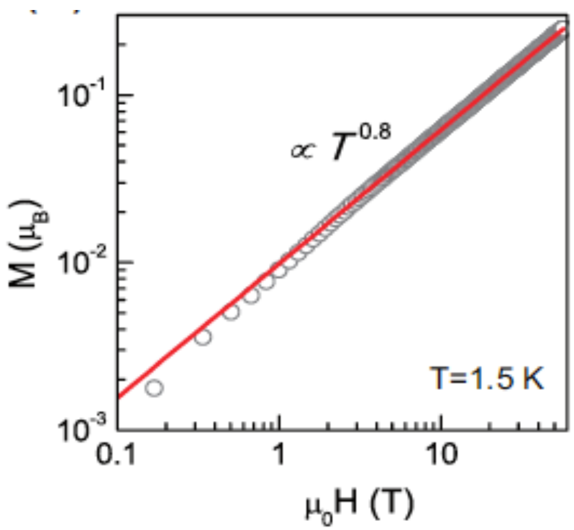
Quenched disorders due to Cu^{+}/Ir^{4+} and/or Cu^{2+}/Ir^{3+} site mixing

Cu_2IrO_3 : Magnetic Properties



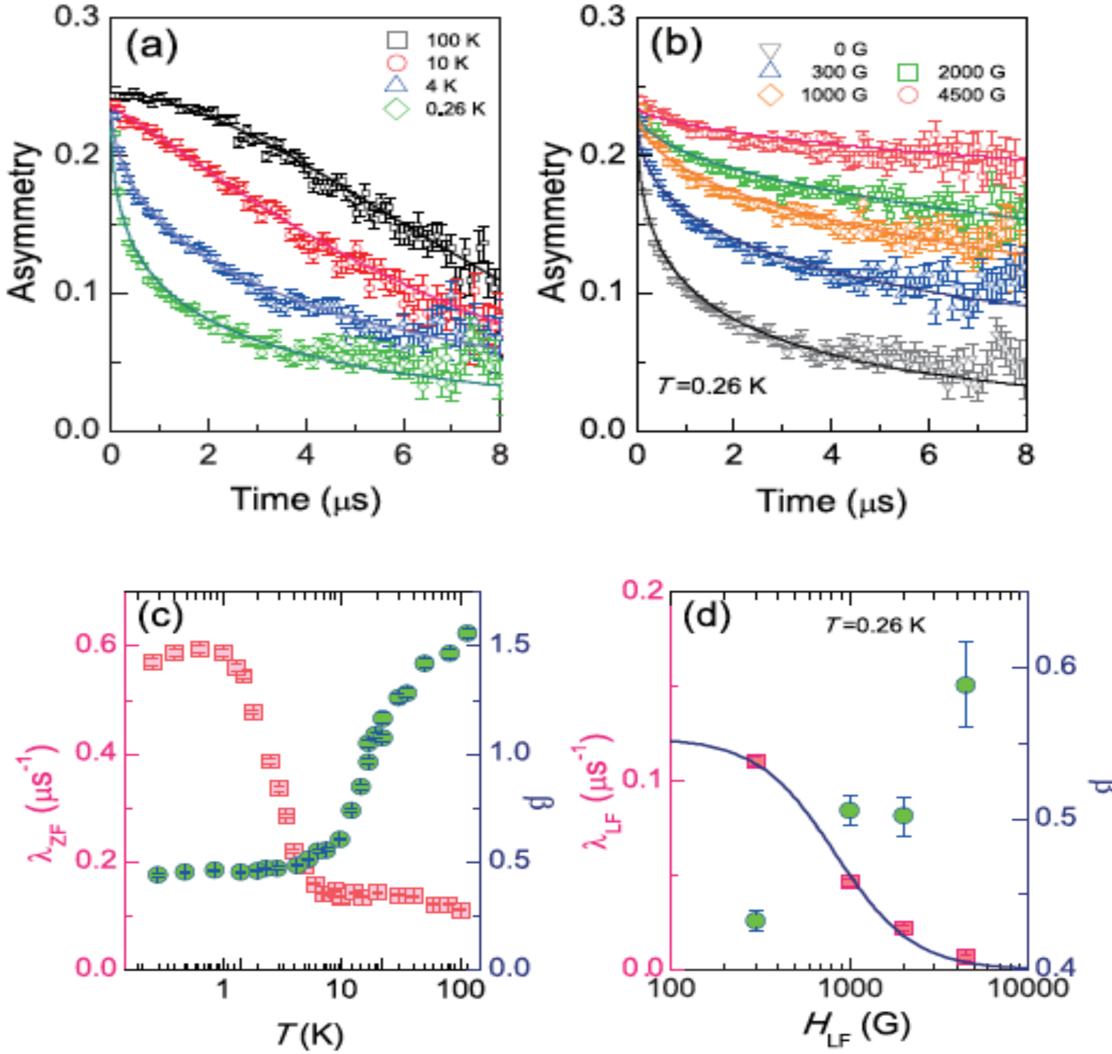
- Curie Weiss behavior at high T
- C = 0.386(5) cm^3 K/mol ~ S_{eff} = ½
- θ = -110 K
- No freezing in ac χ down to 1.8 K
- Sub Curie law $\chi \sim T^{-\alpha}$ with α = 0.24 below 20 K
- At low T, $M(H) \sim H^{1-\alpha^*}$ with α^* = 0.2





S.-k. Ma.. Phys. Rev. Lett. 43, 1434 (1979).
J. E. Hirsch.. Phys. Rev. B 22, 5339 (1990).
Bhatt and Lee, PRL **48**, 344 (1982).
Paalanen, Graebner, Bhatt, Sachdev, PRL 61, 597 (1988)
I. Kimchi..Nat. Commun. 9, 4367 (2018).

muSR : absence of static magnetism + persistent dynamics



- Down to 0.26 K, no oscillating component : dynamic fluctuations
- $B_{loc} \approx 4.4$ G from ZF μSR
- Even for H = 4500 G, there is a substantial relaxation
- λ and β are T independent below 3 K
- However, β = 0.5 is small (canonical spin glass β ~ 0.25-0.3)

Suggests disorder in the presence of liquid like state

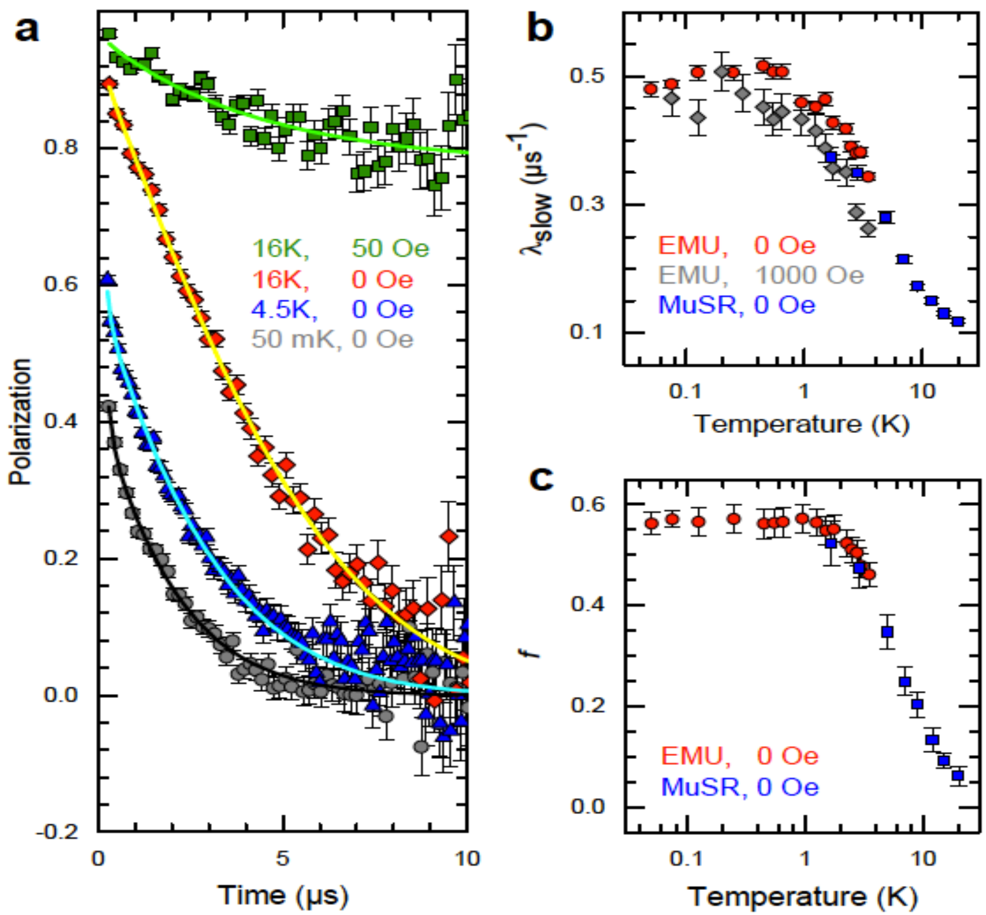
Competition between static and dynamic magnetism in the Kitaev spin liquid material Cu_2IrO_3

Eric M. Kenney[1], Carlo U. Segre[2], William Lafargue-Dit-Hauret[3], Oleg I. Lebedev[4], Mykola Abramchuk[1],

Adam Berli ... Iordvinova[4],

Jessica. L. I ... iel J. Graf[1],

& Fazel Ta



nature COMMUNICATIONS

ARTICLE

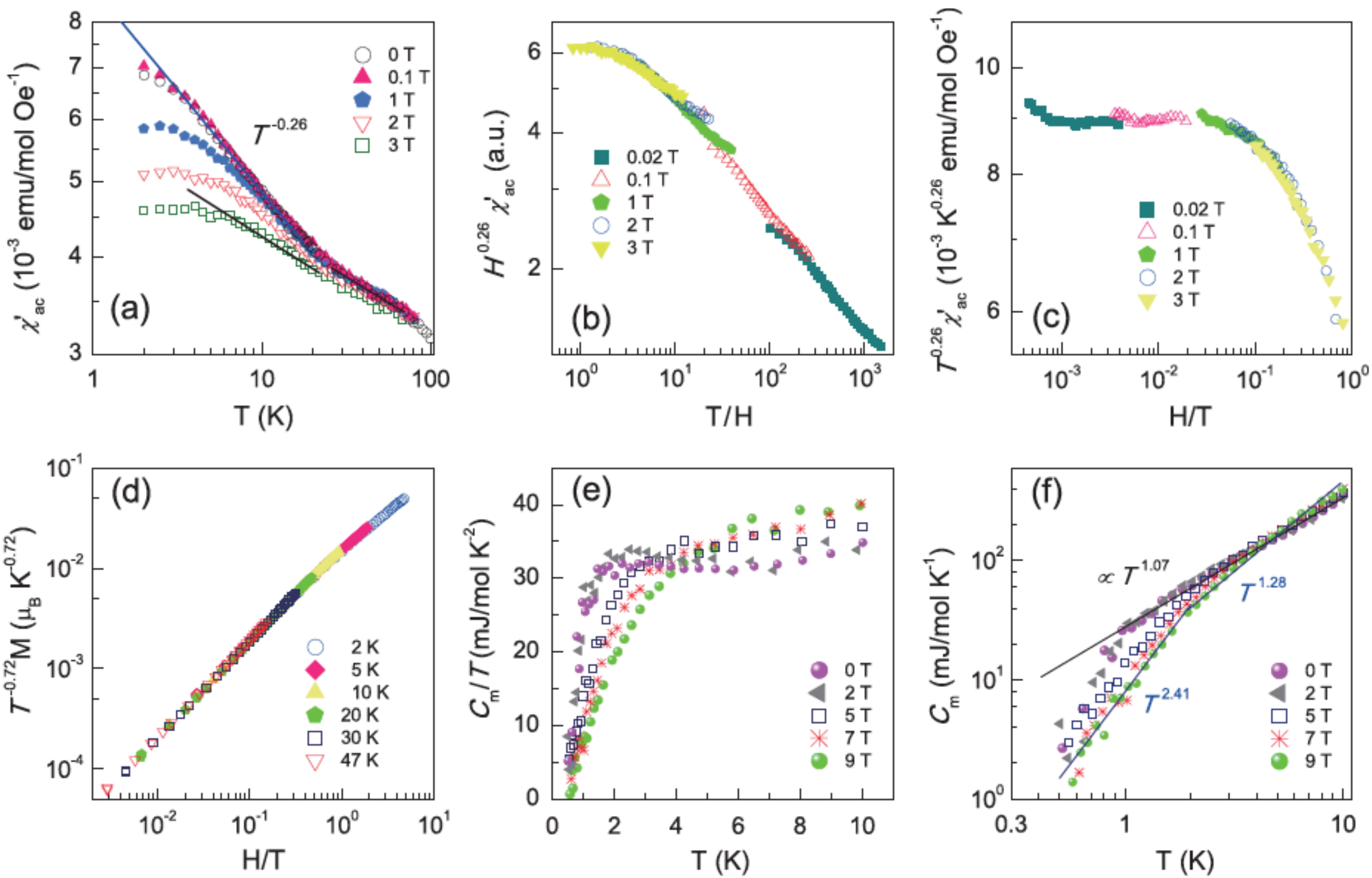
DOI: 10.1038/s41467-018-06800-2 OPEN

Scaling and data collapse from local moments in frustrated disordered quantum spin systems

Itamar Kimchi[1], John P. Sheckelton[2], Tyrel M. McQueen[2,3] & Patrick A. Lee[1]

Recently measurements on various spin-1/2 quantum magnets such as $H_3LiIr_2O_6$, $LiZn_2Mo_3O_8$, $ZnCu_3(OH)_6Cl_2$ and 1T-TaS_2—all described by magnetic frustration and quenched disorder but with no other common relation—nevertheless showed apparently universal scaling features at low temperature. In particular the heat capacity $C[H, T]$ in temperature T and magnetic field H exhibits T/H data collapse reminiscent of scaling near a critical point. Here we propose a theory for this scaling collapse based on an emergent random-singlet regime extended to include spin-orbit coupling and antisymmetric Dzyaloshinskii-Moriya (DM) interactions. We derive the scaling $C[H, T]/T \sim H^{-\gamma} F_q[T/H]$ with $F_q[x] = x^q$ at small x, with $q \in \{0, 1, 2\}$ an integer exponent whose value depends on spatial symmetries. The agreement with experiments indicates that a fraction of spins form random valence bonds and that these are surrounded by a quantum paramagnetic phase. We also discuss distinct scaling for magnetization with a q-dependent subdominant term enforced by Maxwell's relations.

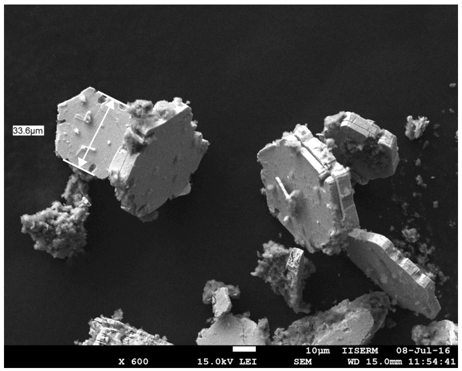
Scaling of χ_{ac} and M but not C

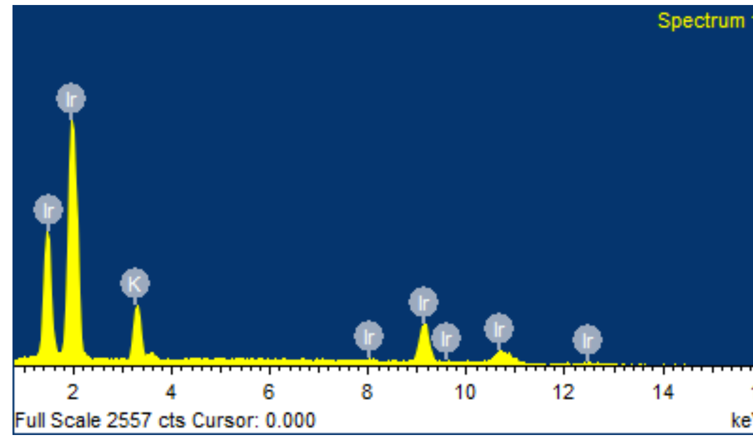


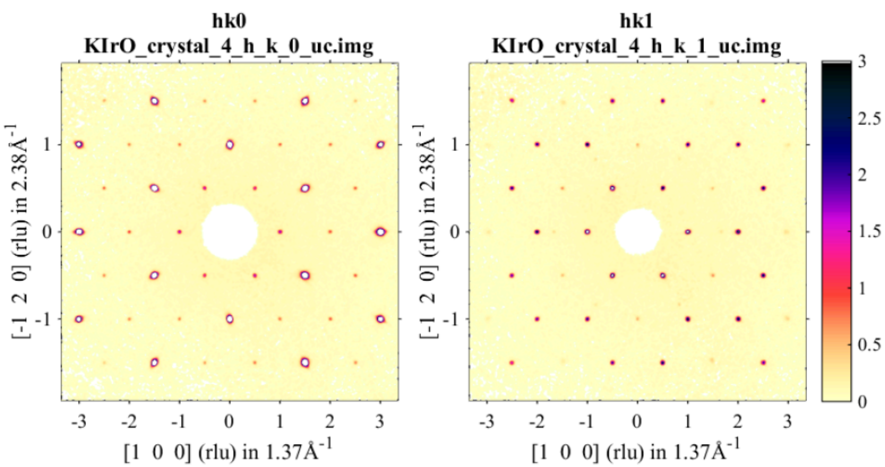
Cu_2IrO_3 shows behaviour consistent with a QSL with quenched disorder

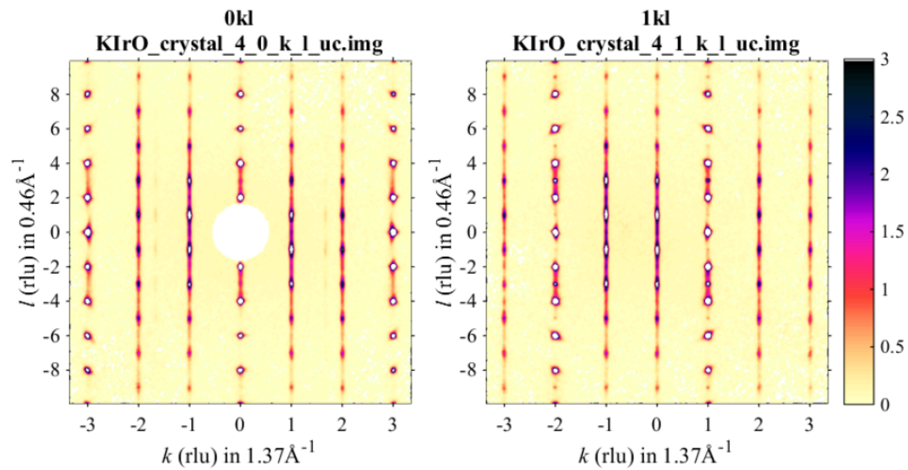
K_2IrO_3 : a new Kitaev Material

K_2IrO_3 Crystals



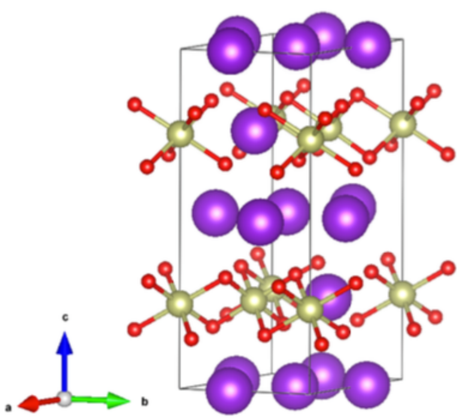




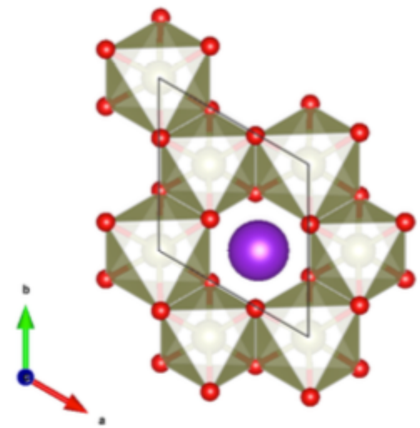


K_2IrO_3, 2-layer Structure*

- Space grp P 6_322 (182), a = b = 5.282 A, c = 13.544 A
- Two KIr_2O_6 layers per unit cell
- Almost perfect honeycomb with Ir-Ir = 3.047 A and 3.051 A
- Separation between Ir honeycomb layers = 6.6 A
- Separation of Ir honeycombs in Na_2IrO_3 = 5 A
- Different stacking compared to A_2IrO_3



K_2IrO_3 structure made up of KIr_2O_6 layers separated by K layers

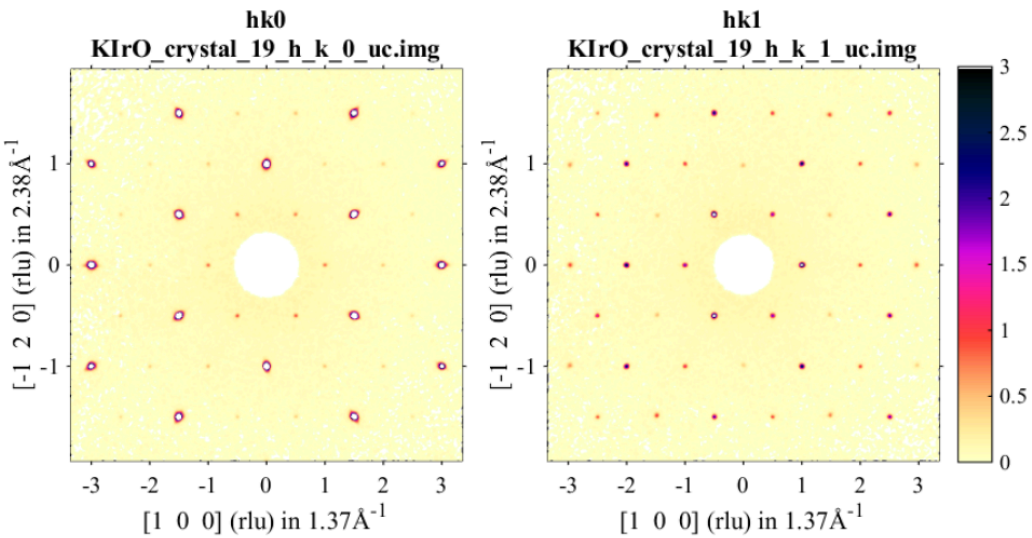


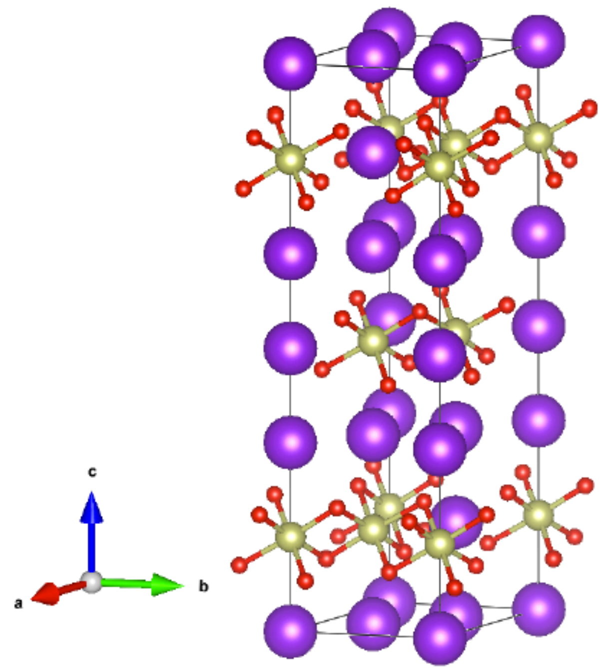
KIr_2O_6 layers made up of edge sharing IrO_6 octahedra *viewed down the c-axis*

** A majority of the obtained crystals had the above structure. However, crystals with a different but qualitatively similar structure and crystals with two different morphologies (hexagonal and square sheets) were obtained. The structure and properties of these square planar crystals are being investigated.*

K_2IrO_3, 3-layer Structure

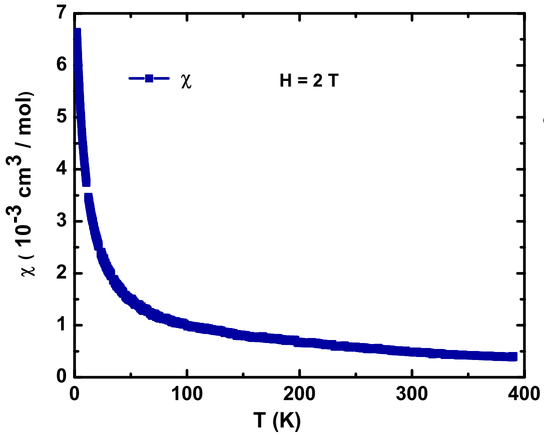
- *Rhombohedral*
- *Space grp R3 (148), a = b = 5.282 A, c = 20.27 A*
- *Almost perfect honeycomb with Ir-Ir = 3.047 A and 3.051 A*
- *Separation between Ir honeycomb layers = 6.8 A*
- *Separation of Ir honeycombs in Na_2IrO_3 = 5 A*

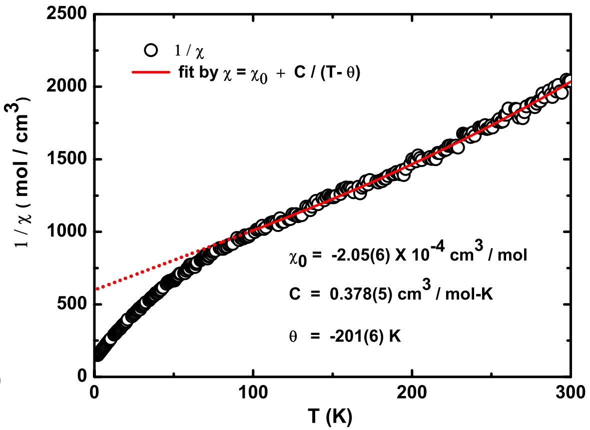


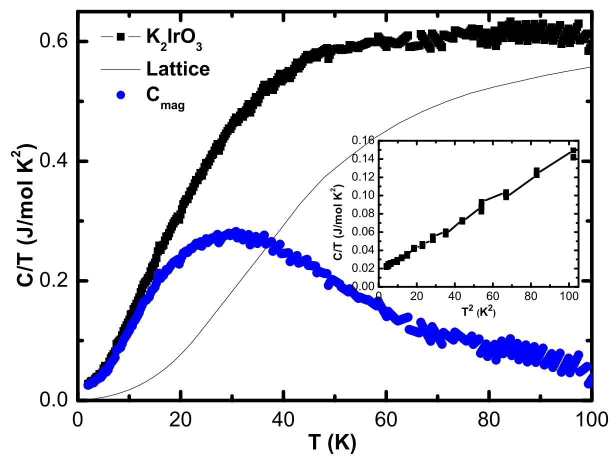


Magnetic and thermal properties of K_2IrO_3

Magnetic Susceptibility and Heat Capacity of K_2IrO_3 crystals







- Strong localized magnetism : Mott insulator
- $S_{eff} = ½, \theta = -200$ K
- No ordering or freezing to 2 K
- Large frustration, $|\theta|/T_N > 100$

- C_{mag} shows broad bump around 30 K
- Finite C/T at T = 0
- $\gamma = 13$ mJ/mol K^2
- $S_{mag} \sim 50\%R\ln 2$

Possible QSL with gapless excitations, but different from Kitaev QSL

Conclusions and Future Work

- Cu_2IrO_3 and K_2IrO_3 are new Kitaev QSL candidates
- Cu_2IrO_3 shows properties consistent with random singlets in a QSL background
- Need to understand different scaling of χ, M and C
- K_2IrO_3 : a new platform for Kitaev physics
  a. Controllable synthesis of the two structures
  b. Microscopic probes of magnetism: NMR, μSR
  c. Dynamics : INS, NMR, Raman
  d. Thermal transport