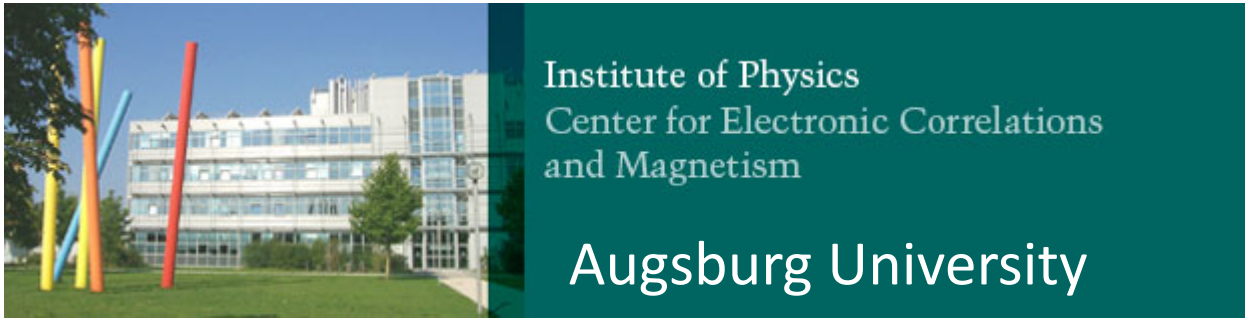
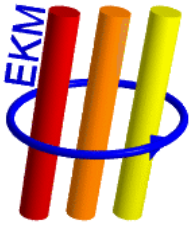
Magnetic properties of honeycomb iridates and rhodates

Philipp Gegenwart





Outline

- Intro: Kitaev exchange in spin-orbit Mott insulators
- Synthesis, structure, electronic and magnetic properties of Na_2IrO_3, α- and β-Li_2IrO_3 and Li_2RhO_3

Acknowledgments




Yogesh Singh*, Soham Manni+, Friedrich Freund, Anton Jesche

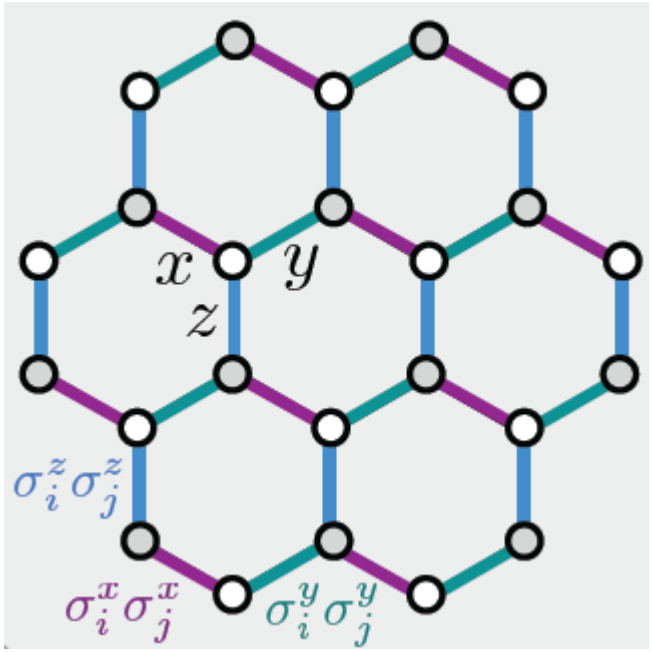
*since 02/2011: IISER Mohali
+ since 01/2015: Ames Lab

Sungkyun Choi, Steph Williams, Radu Coldea — Neutron scattering, μSR, XRD

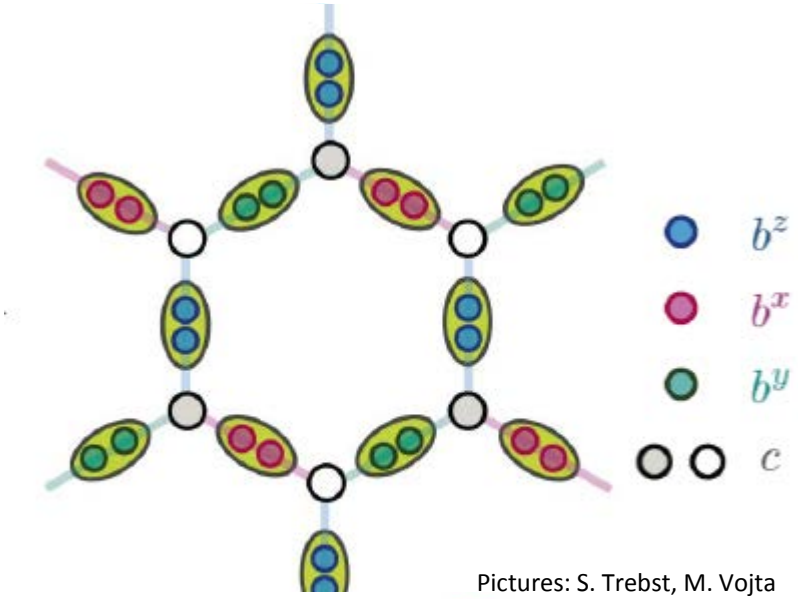
F. Lüpke, M. Wenderoth — Scanning tunneling microscopy

S.J. Blundell, F.R. Foronda, T. Lancaster, P. Khuntia, M. Baenitz — μSR and NMR on Li_2RhO_3

The Kitaev model

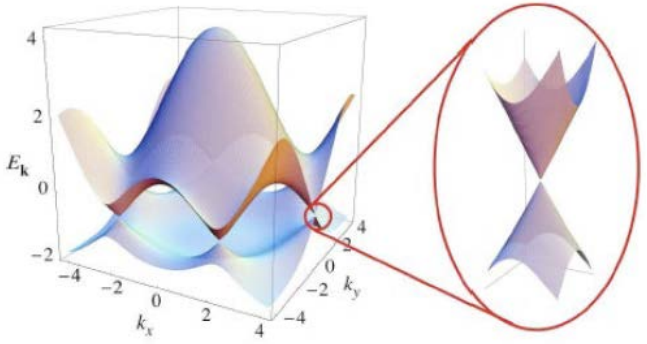


$$H_{\text{Kitaev}} = \sum_{\gamma-\text{links}} J_\gamma \sigma_i^\gamma \sigma_j^\gamma$$



Pictures: S. Trebst, M. Vojta

- Bond frustration
- Exact solution by mapping to Majorana fermions
- Equal bonds: gapless topological quantum spin liquid, energy spectrum with Dirac cones



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]

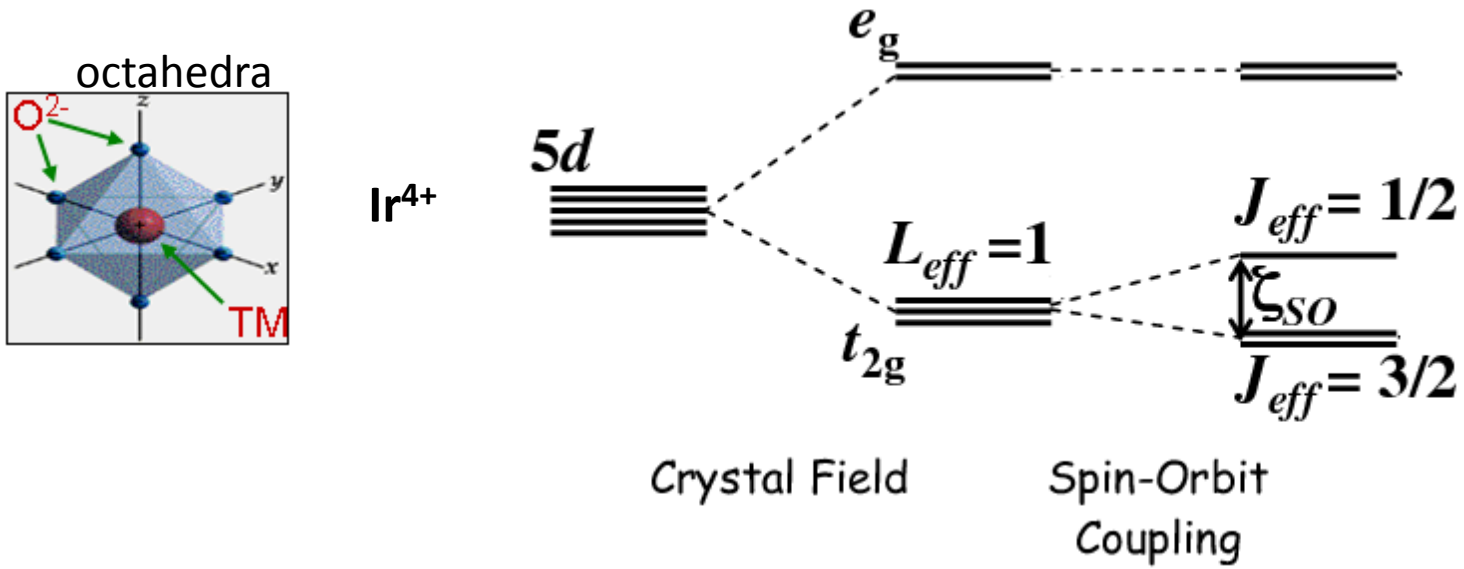
[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

(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

IrO_6 based Spin-orbit Mott insulators



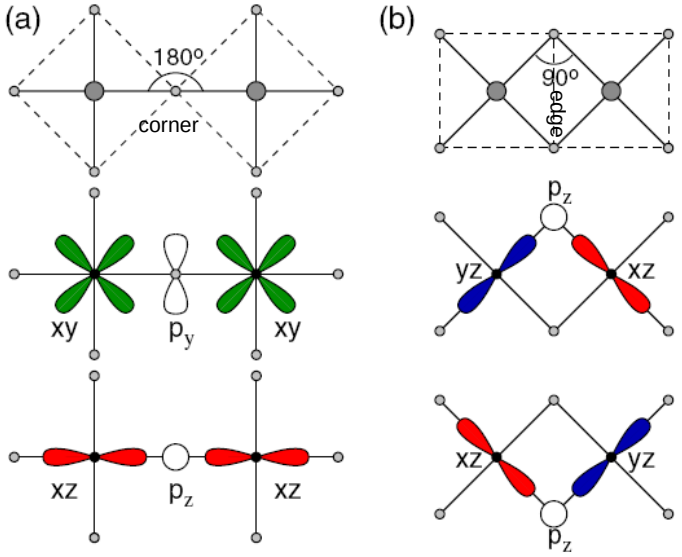
Spin-Orbit Mott Insulator

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

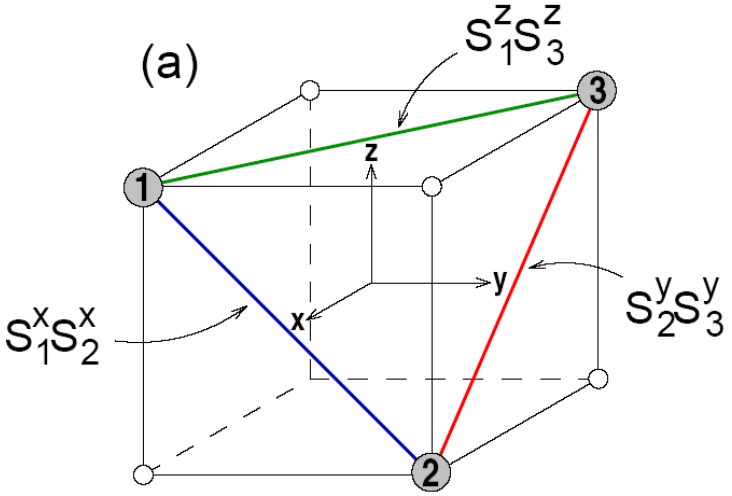
$$\left| J_{eff} = 1/2, m_{eff} = \pm 1/2 \right\rangle = \frac{1}{\sqrt{3}} \left(\left| xy, \mp\sigma \right\rangle \mp \left| yz, \pm\sigma \right\rangle + i \left| zx, \pm\sigma \right\rangle \right)$$

→ wave function of doublet = coherent superposition of different orbital and spin states

→ bond geometry important for magnetic interaction:



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



Perovskite:

→ *Heisenberg*

Pyrochlore, honeycomb, kagome:

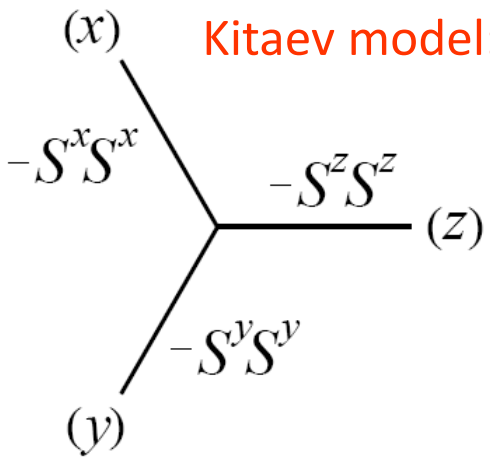
destructive interference of Heisenberg interaction!

Ising but with varying quantization direction!

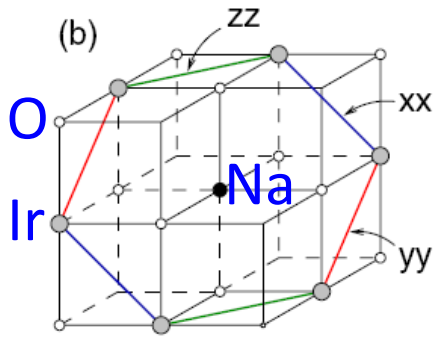
G. Jackeli and G. Khaliullin PRL 2009

Heisenberg-Kitaev model

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



Kitaev model:



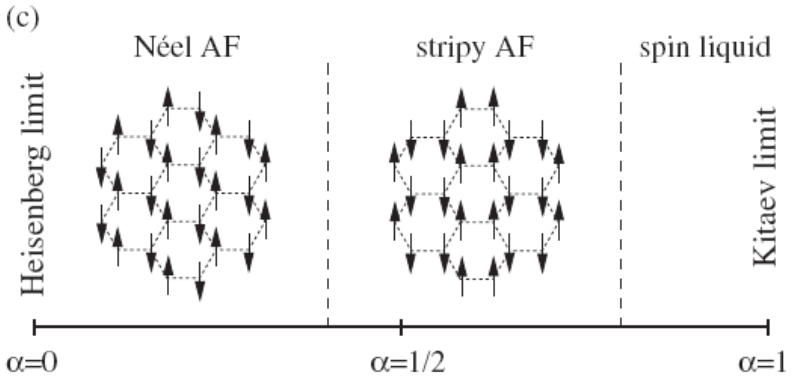
Na_2IrO_3

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

Heisenberg (AF)
unfrustrated

Kitaev (FM)
highly frustrated

Competition of bond-dependent interactions → quantum spin-liquid with emergent topological excitations



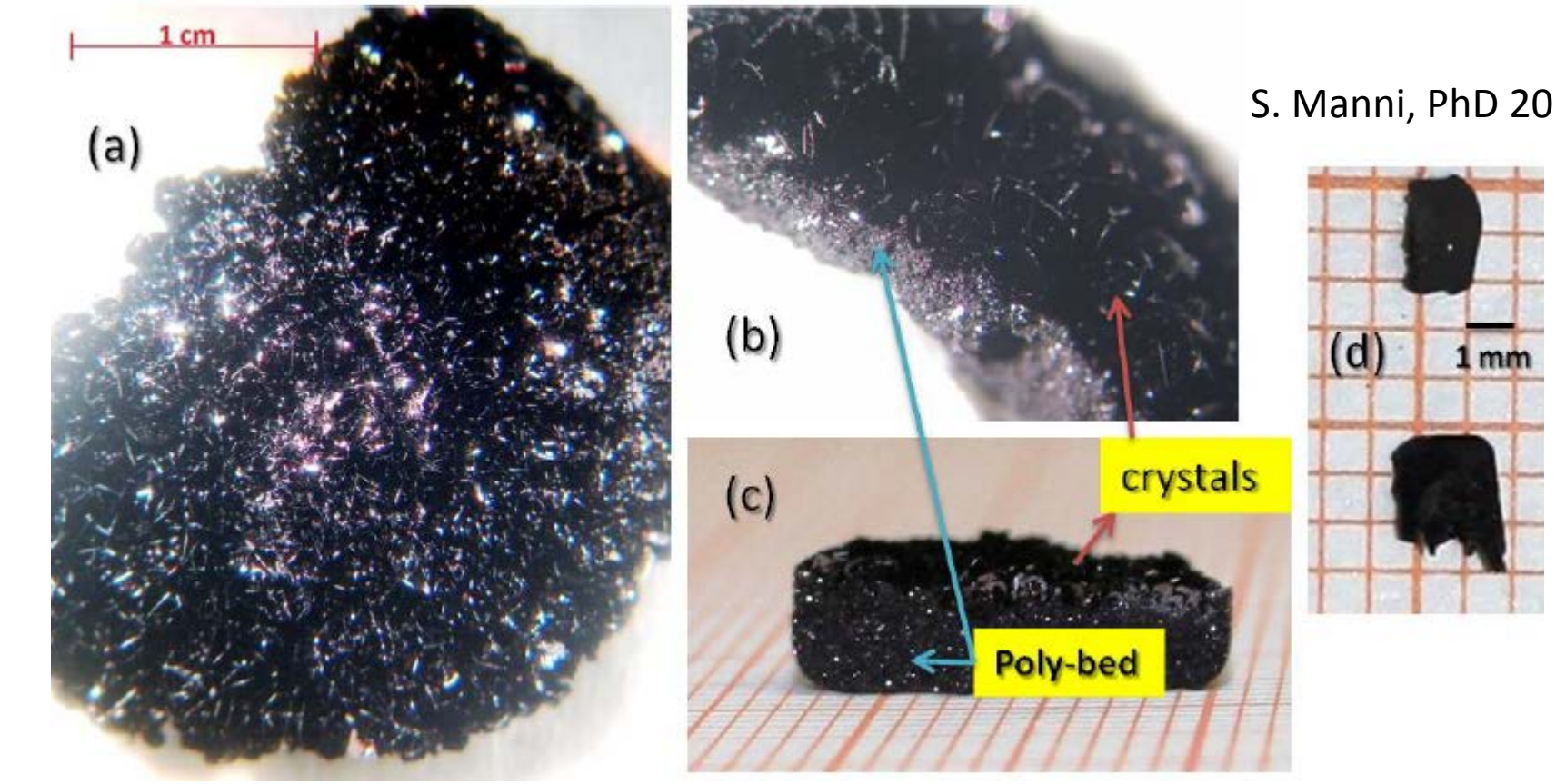
Direct hopping between NN Ir t_{2g} orbitals
→ Heisenberg interaction
Distortions
→ Additional anisotropic exchange

Synthesis and structure

Na_2IrO_3 synthesis

Na_2IrO_3 polycrystal by solid state reaction:

$Na_2CO_3 + Ir \xrightarrow{O2} Na_2IrO_3 + CO_2$, heat treatments after grinding up to 950 °C



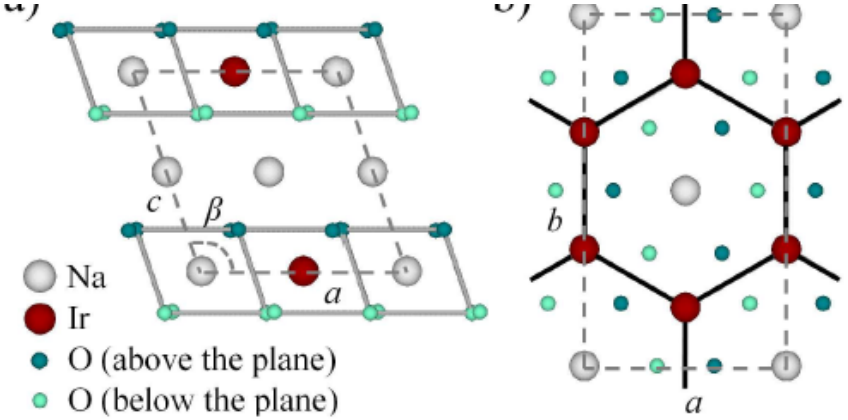
S. Manni, PhD 2014

+ 10% extra IrO_2 heated in Al crucible to 1050°C, cooling to 900°C, air quenching:

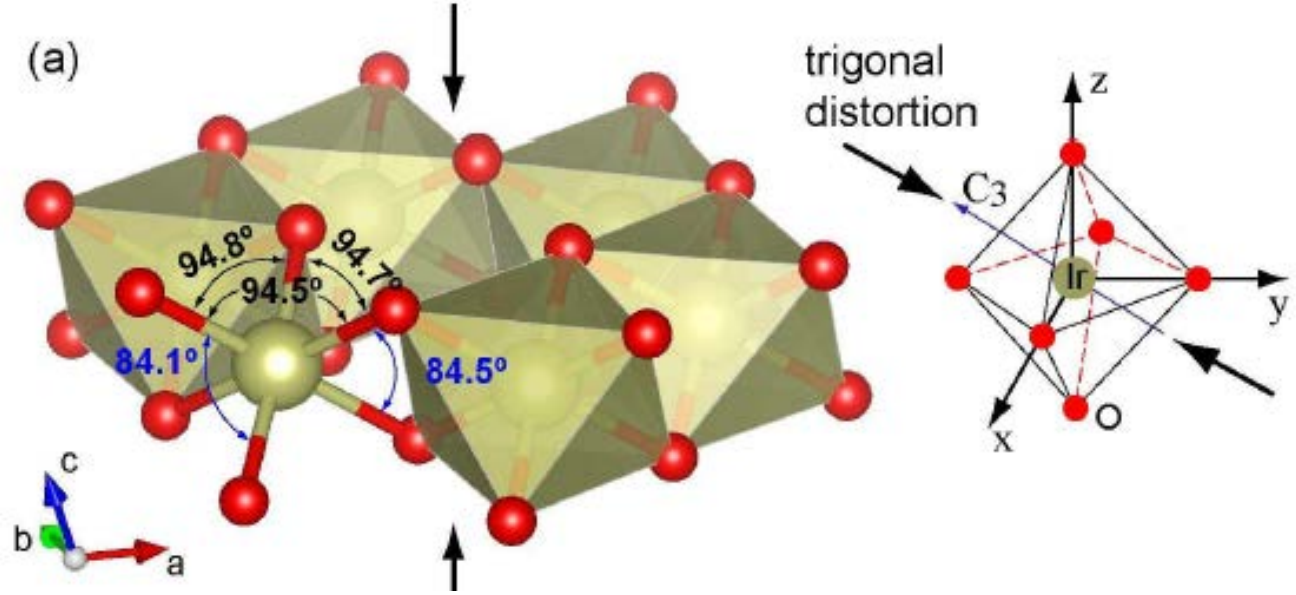
→ Plate-like crystals vertically standing on poly-bed

→ Surface of crystals degrades in air!

Structural properties of Na_2IrO_3

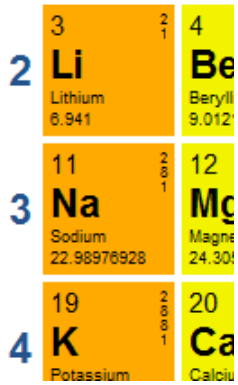


- C2/m structure with regular honeycomb planes (10% stacking faults)
- Bonding angles differ from 90°



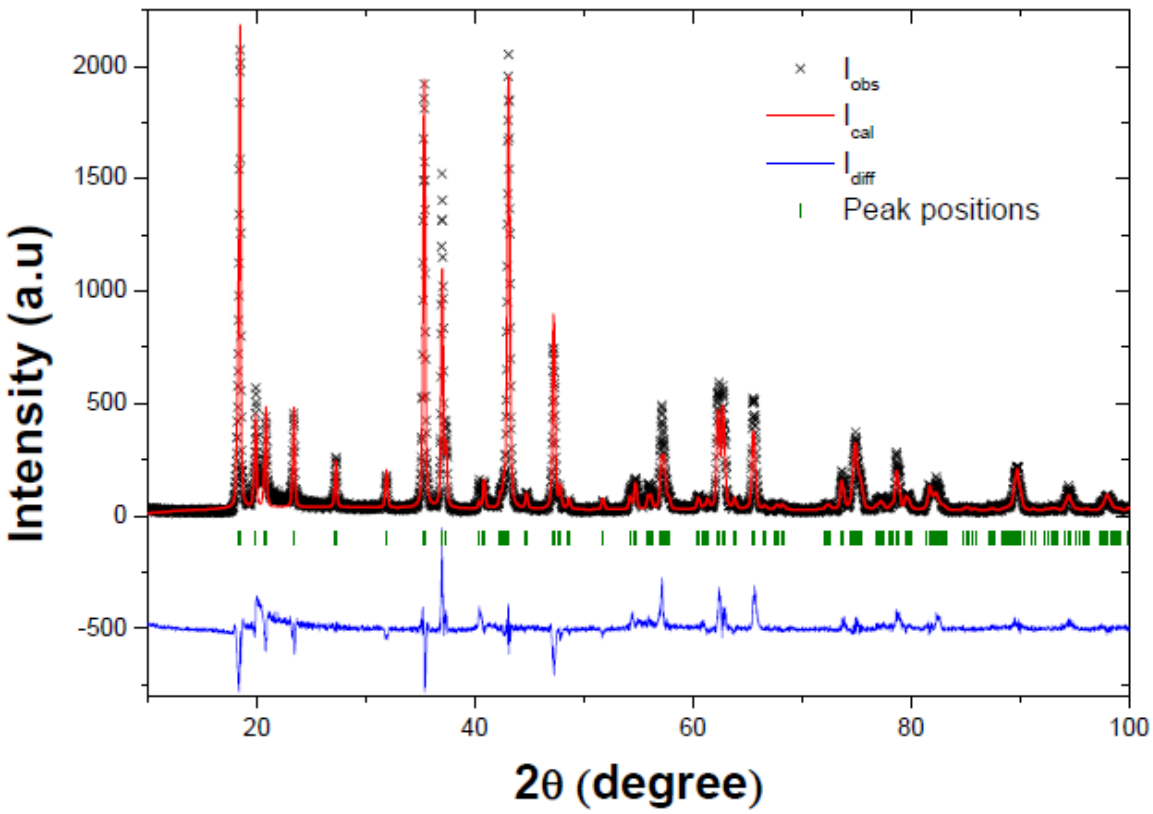
Yogesh Singh, P. Gegenwart, PRB **82** (2010) 064412. Feng Ye et al. Phys. Rev. B **85**, 180403(R) (2012). S.K. Choi et al., PRL **108**, 127204 (2012).

α-Li_2IrO_3



α-Li_2IrO_3

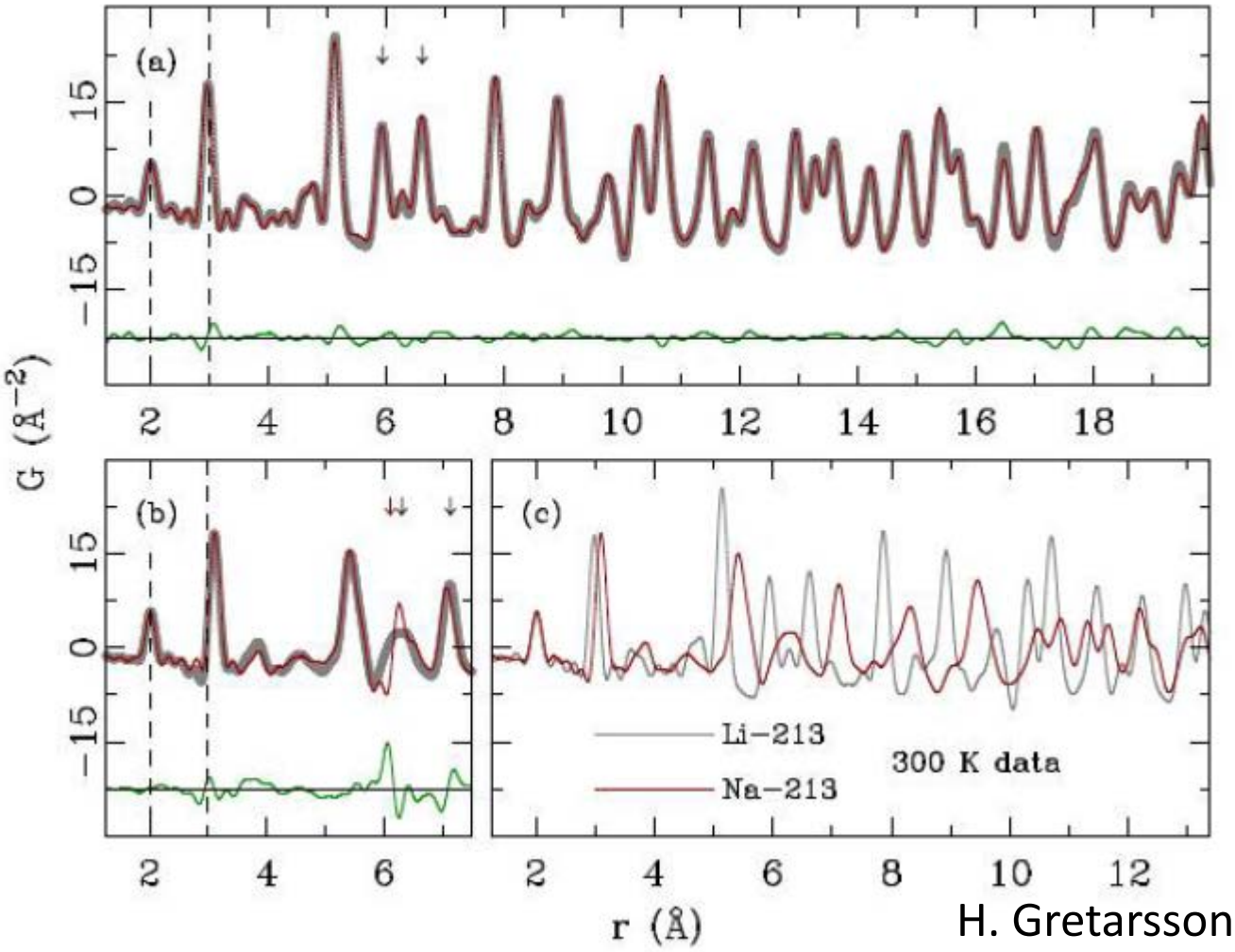
- Isostructural
- 20% volume reduction
- 5% reduction of c/a ratio



Polycrystal: adding LiCl flux after calcination, T_{max} = 850°C, higher T: β-Li_2IrO_3
Single crystals only very recently (later…)

Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst, P. Gegenwart, PRL **108** (2012) 127203
S. Manni, PhD, 2014

Pair distribution analysis of synchrotron x-ray data:

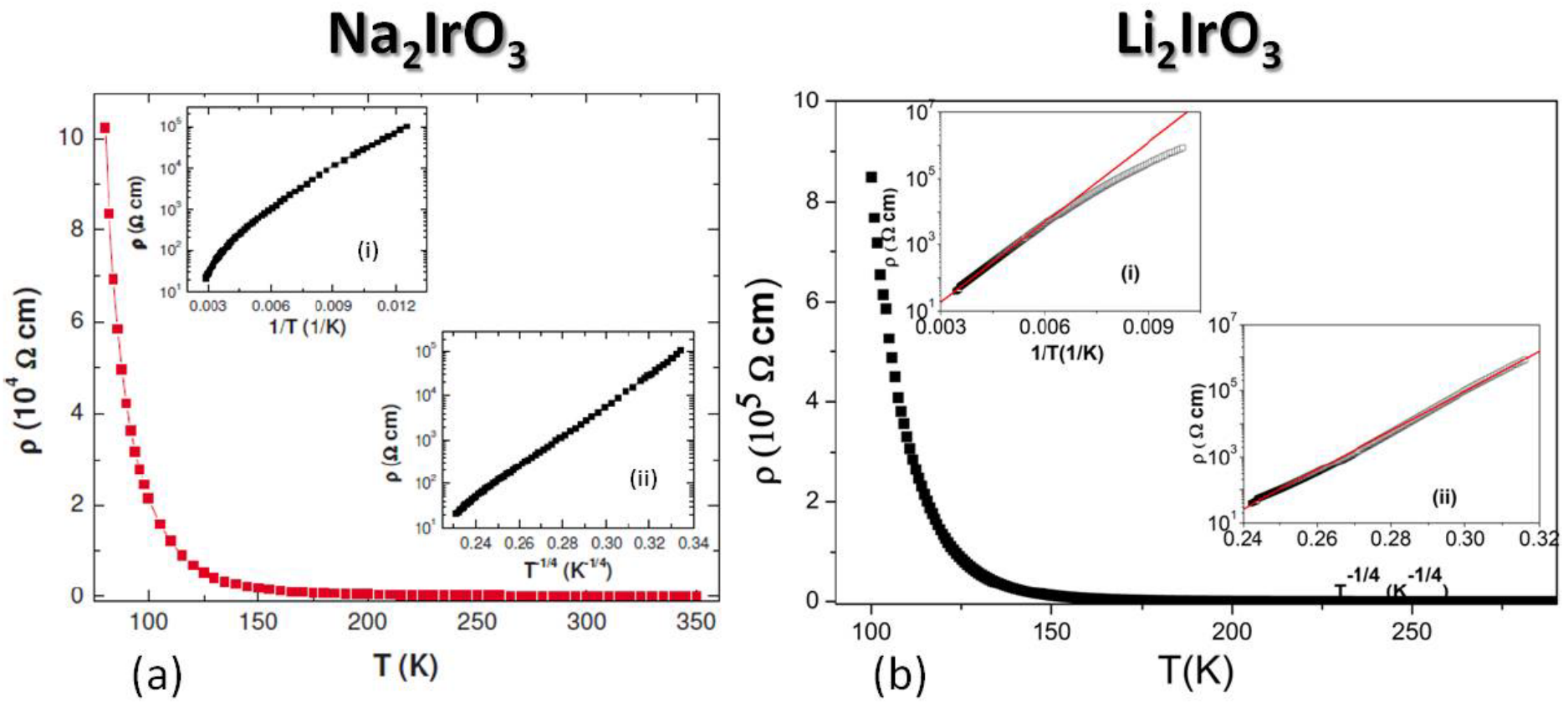


H. Gretarsson et al. PRL 2013

- Ir-Ir distance reduced for Li compared to Na system
- Ir-O-Ir bond angles: 93.6-94.8° (Li), 91-98° (Na)

Electronic properties

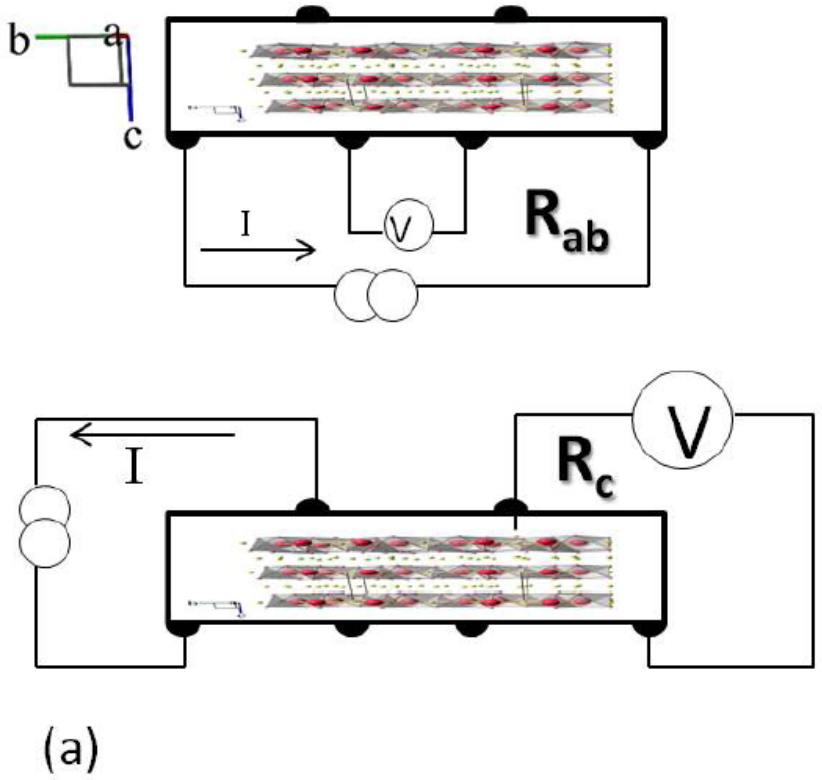
Bulk electrical resistivity



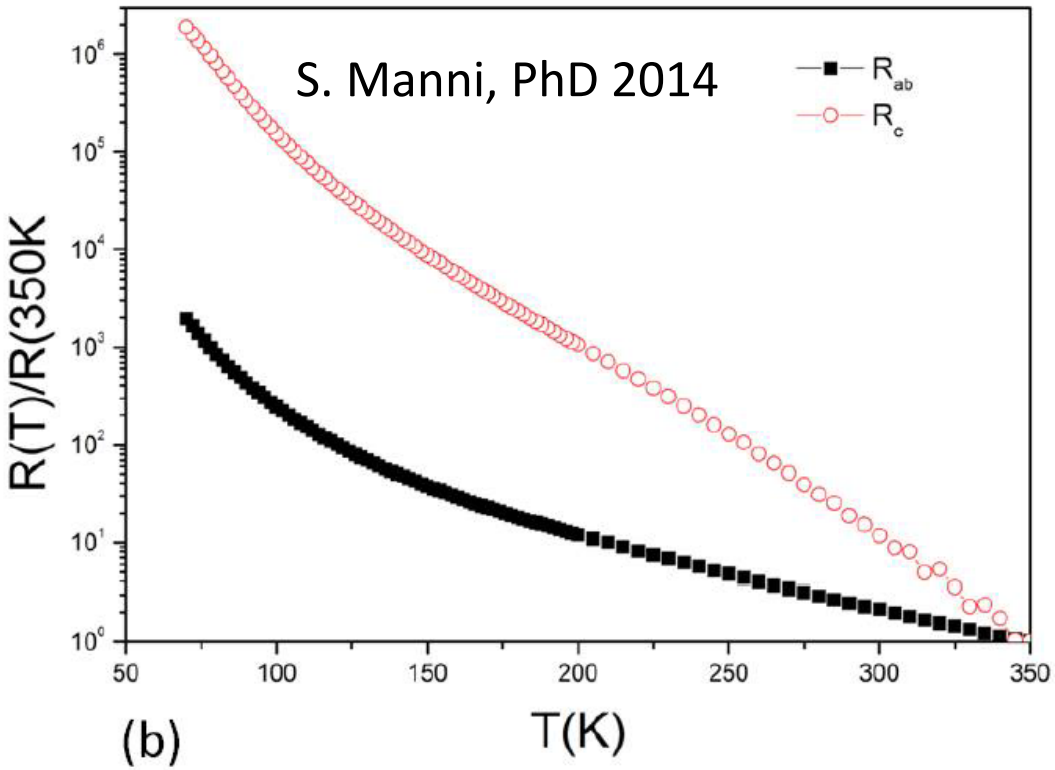
S. Manni, PhD 2014

- Arrhenius (activated) behavior only at high T, variable-range hopping at lower T
- Gap size of order 350 meV (Na-system) and 160 meV (Li-system)
- Na-system: size of gap confirmed by optics and ARPES

Na_2IrO_3



(a)

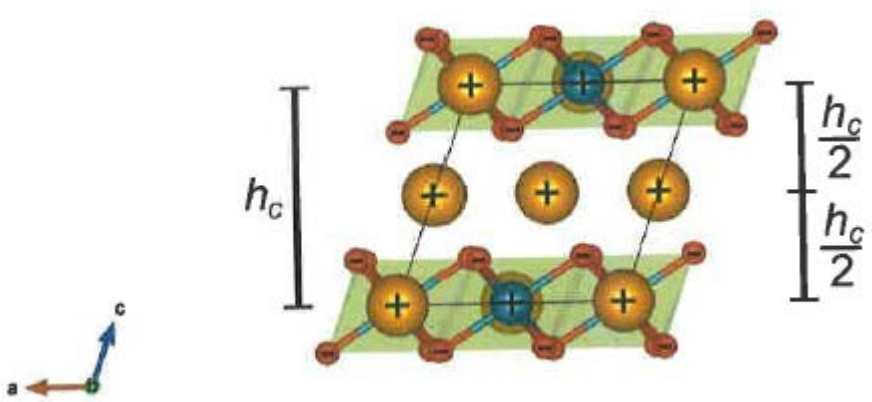


(b)

- Anisotropy: better conductivity in honeycomb planes than across the planes
- No indication of conducting state at surface

Scanning tunneling microscopy

F. Lüpke, Master Thesis 2013, F. Lüpke, S. Manni, S.C. Erwin, I.I. Mazin, P. Gegenwart, M. Wenderoth, Phys. Rev. B 91 (2015) 041405(R).

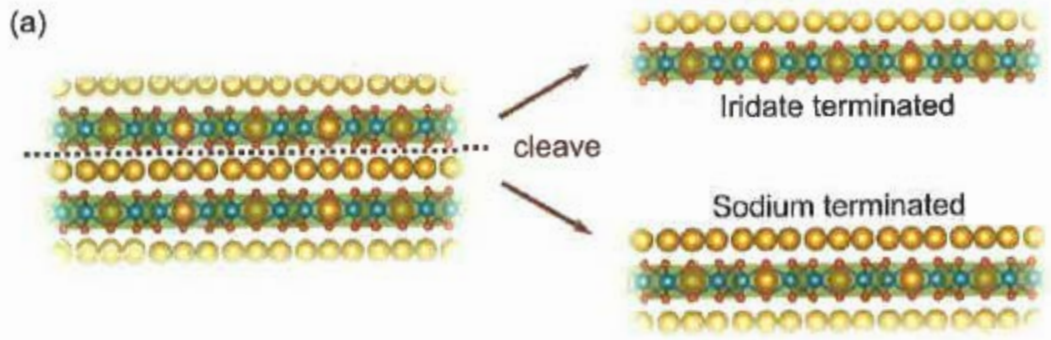


Charge counting→

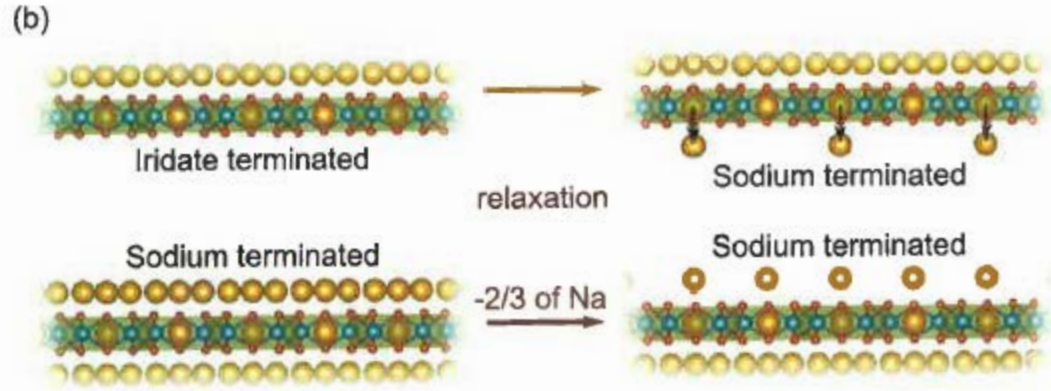
- Each Na donates 1 el
- Na layers donate ½ of their electrons to layers above and below, respectively
- All atoms of Na-layer positively charged → mobile

→ Cleavage should leave IrO_6 octahedra intact

- Experiment: in-situ cleaving at $p<10^{-10}$ mbar, immediate transfer to STM (77K)



Polar surfaces energetically instable

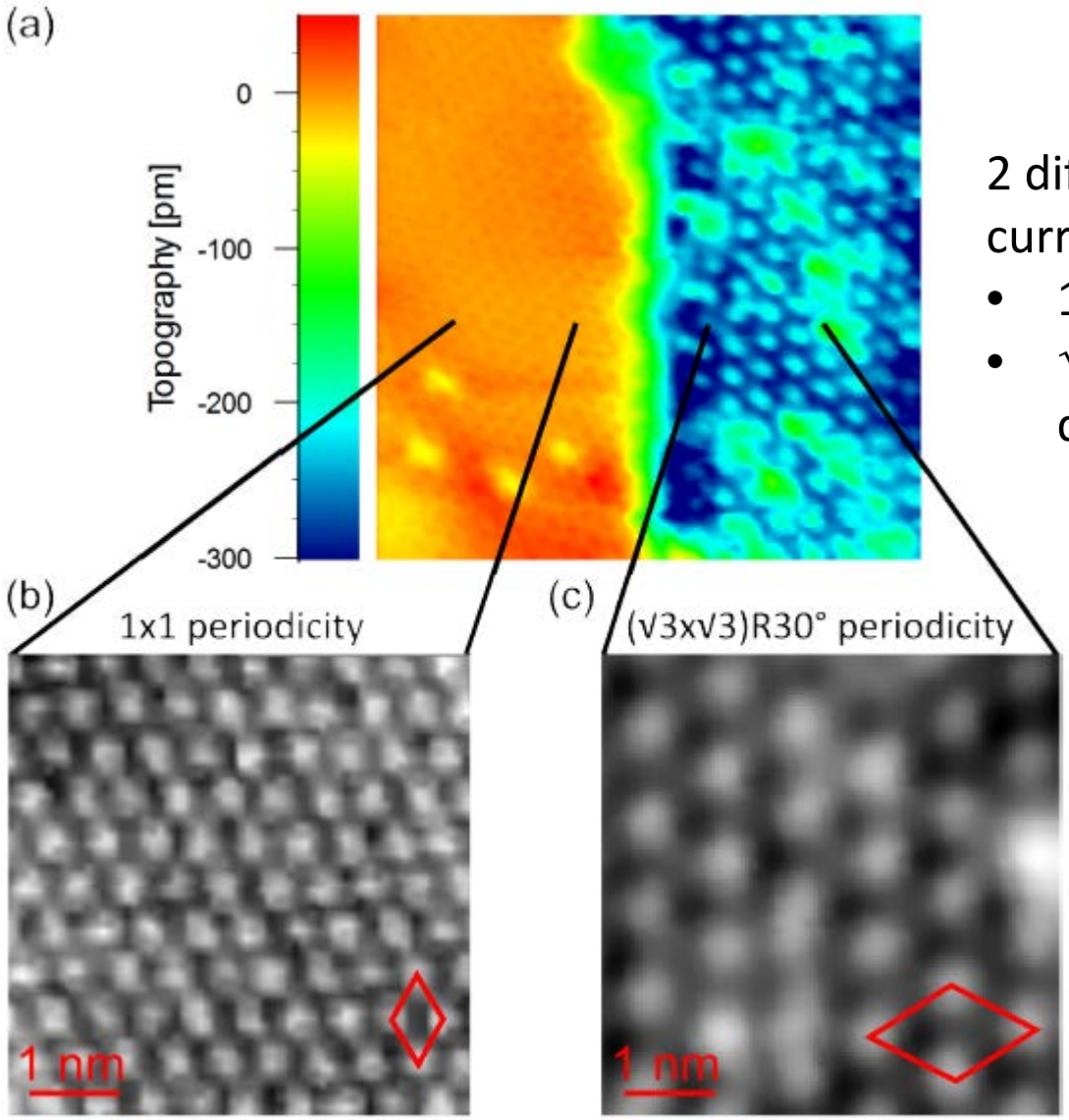


Surface relaxation suggested by DFT calculations and compatible with STM

Possible cleave leaving 50% Na on each side, incompatible with STM

F. Lüpke, Master Thesis 2013

STM on Na_2IrO_3



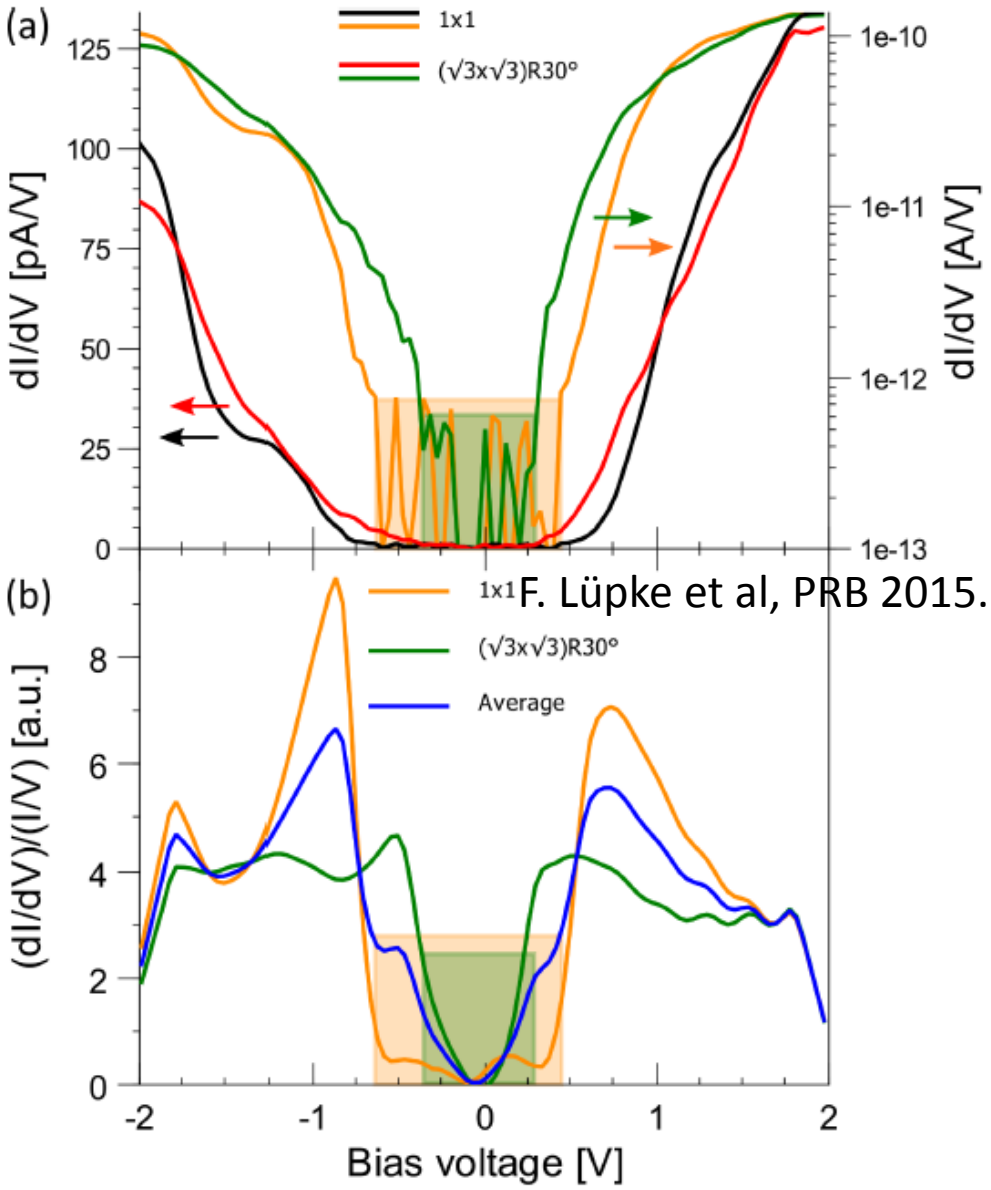
2 different surfaces in constant current images:

- 1x1 with nice periodicity
- $\sqrt{3}x\sqrt{3}$ reconstruction with defects

Very good match with total energy/force DFT calc.
→ 2/3 of Na-atoms are desorbed on both surfaces…

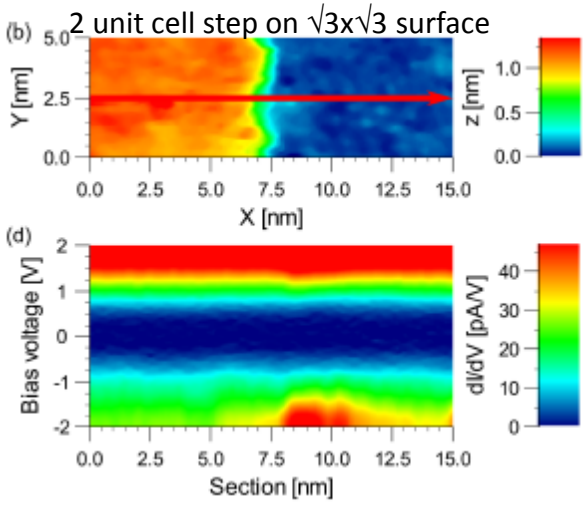
F. Lüpke, S. Manni, S.C. Erwin, I.I. Mazin, P. Gegenwart, M. Wenderoth, Phys. Rev. B 91 (2015) 041405(R).

Scanning tunneling spectroscopy



F. Lüpke et al, PRB 2015.

- Current detection limit (700 fA) indicated by shaded areas
- Surface gap ≈ 1 eV and 0.5 eV for 1x1 and √3x√3
- Due to relaxations, gap on surface different to bulk gap
- Gap maintained for steps either between similar or different surfaces→ no QSH effect



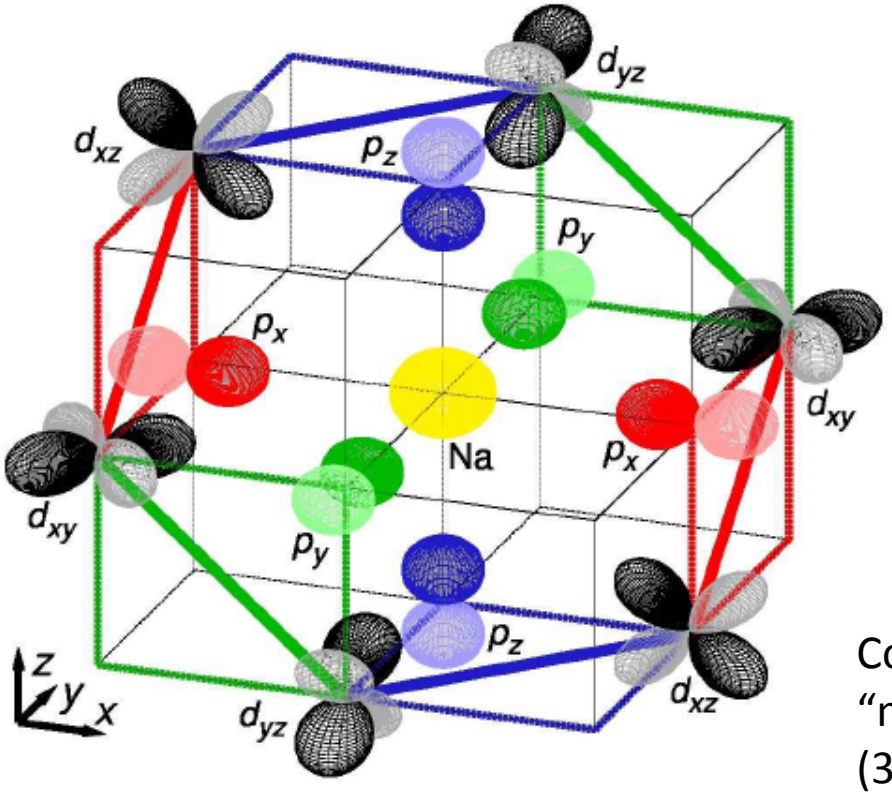
RIXS : H. Gretarsson et al. PRL 2013:

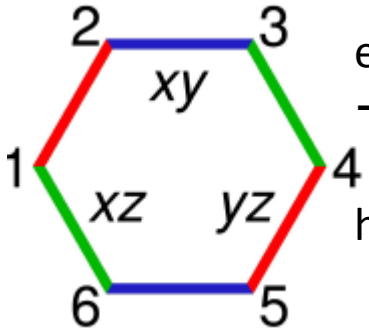
trigonal CEF splitting (~0.1 eV) smaller than SO coupling (0.4 eV)

→ Confirmation of j_{eff} = ½ Mott insulator picture

Itinerant scenario: Mazin, Jeschke, Foyevtsova, Valenti, Khomski, PRL 2012, Foyevtsova et al., PRB 2013

Exchange not necessarily short ranged, first-principle calc. suggest delocalization over Ir_6 hexagons

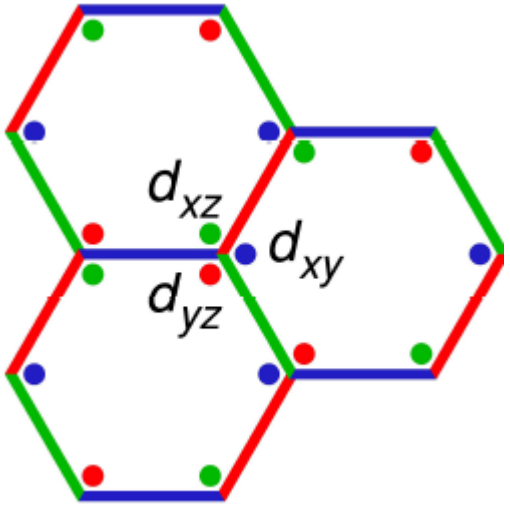




el loc. within hexagons

→ Quasi molecular orbits

highly anisotropic hopping

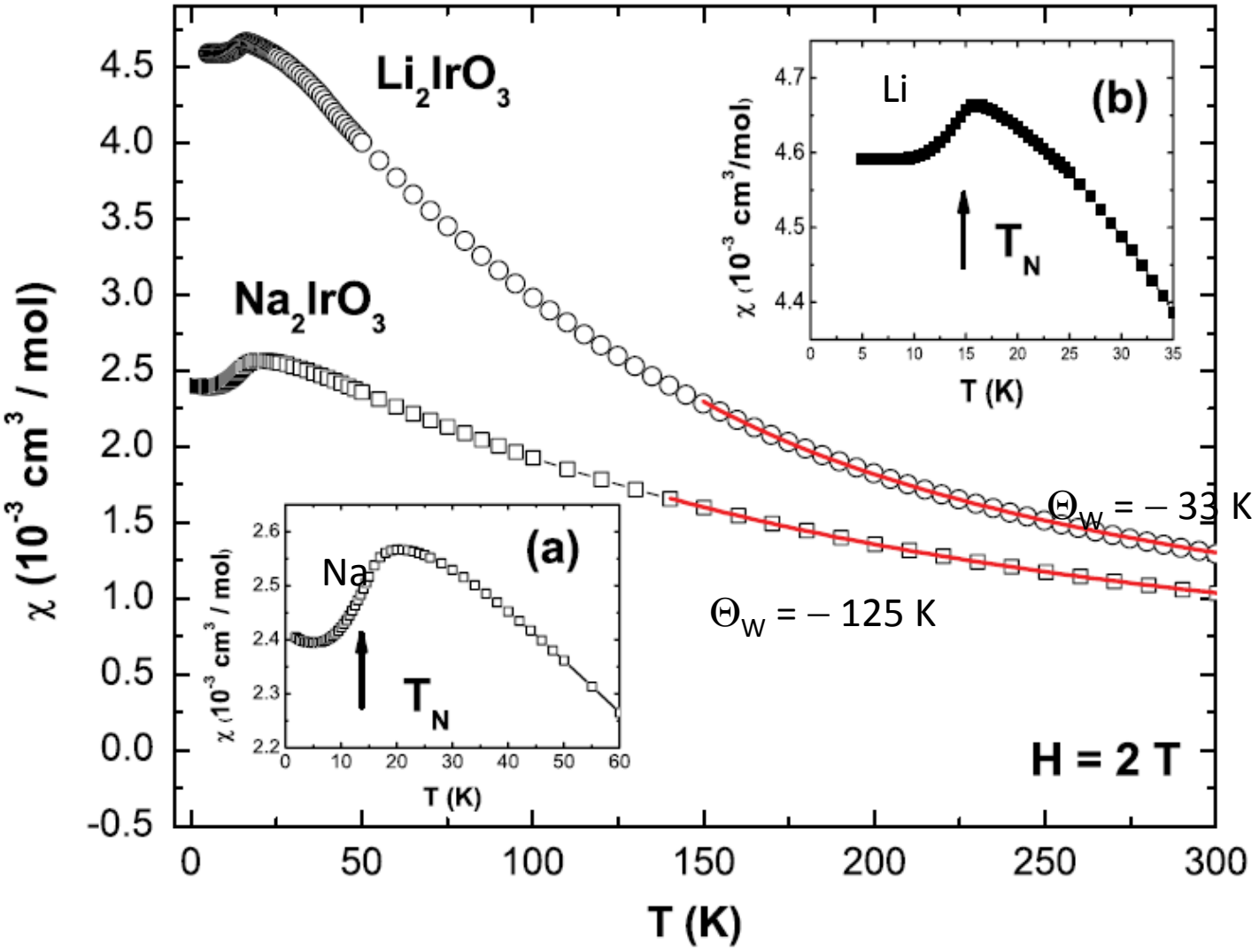


Connection of hexagon "molecules"

(3 t_{2g} orbitals belong to 3 different hexagons)

Magnetic properties

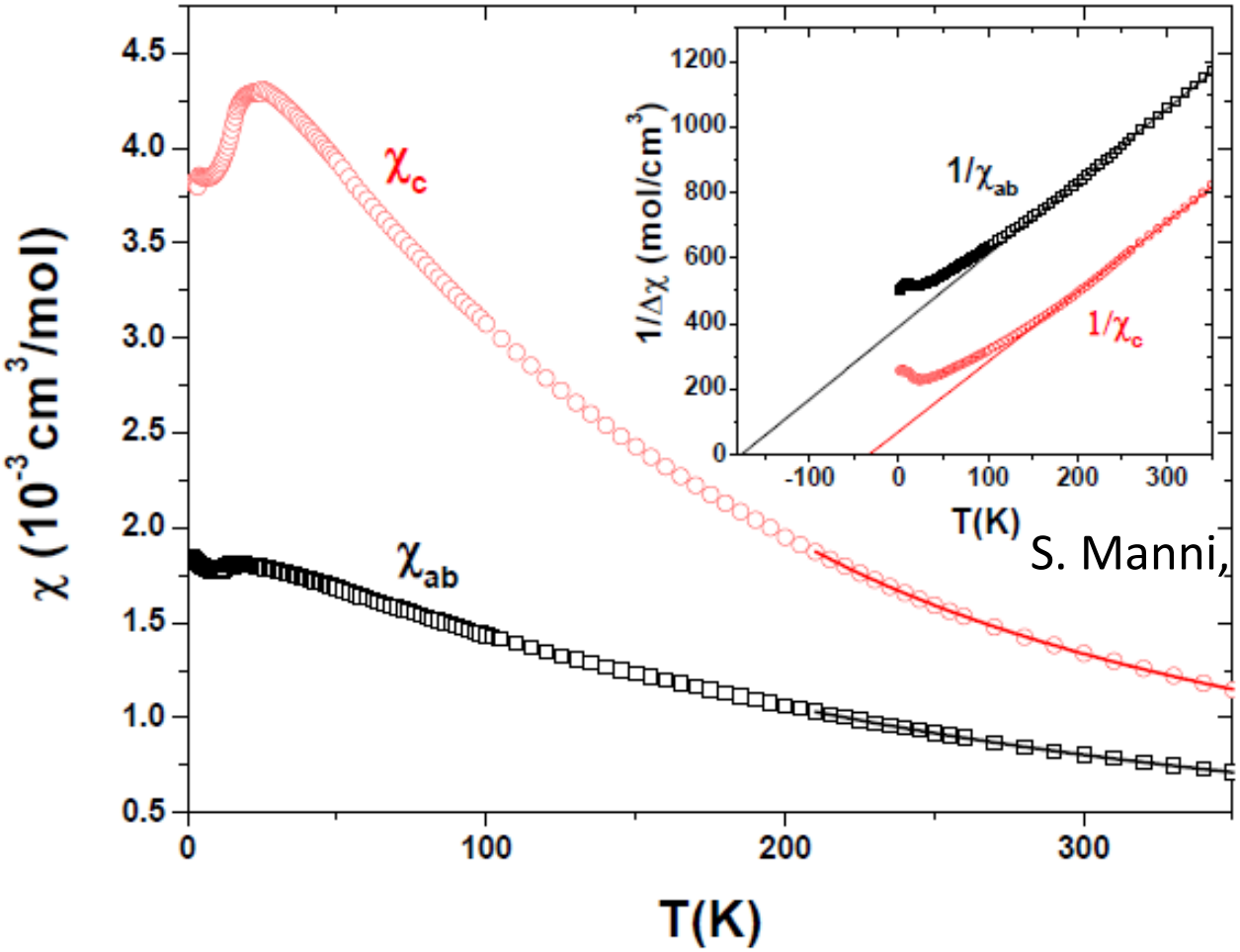
Magnetic susceptibility



Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst, P. Gegenwart, PRL **108** (2012) 127203

Na_2IrO_3 susceptibility anisotropy

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

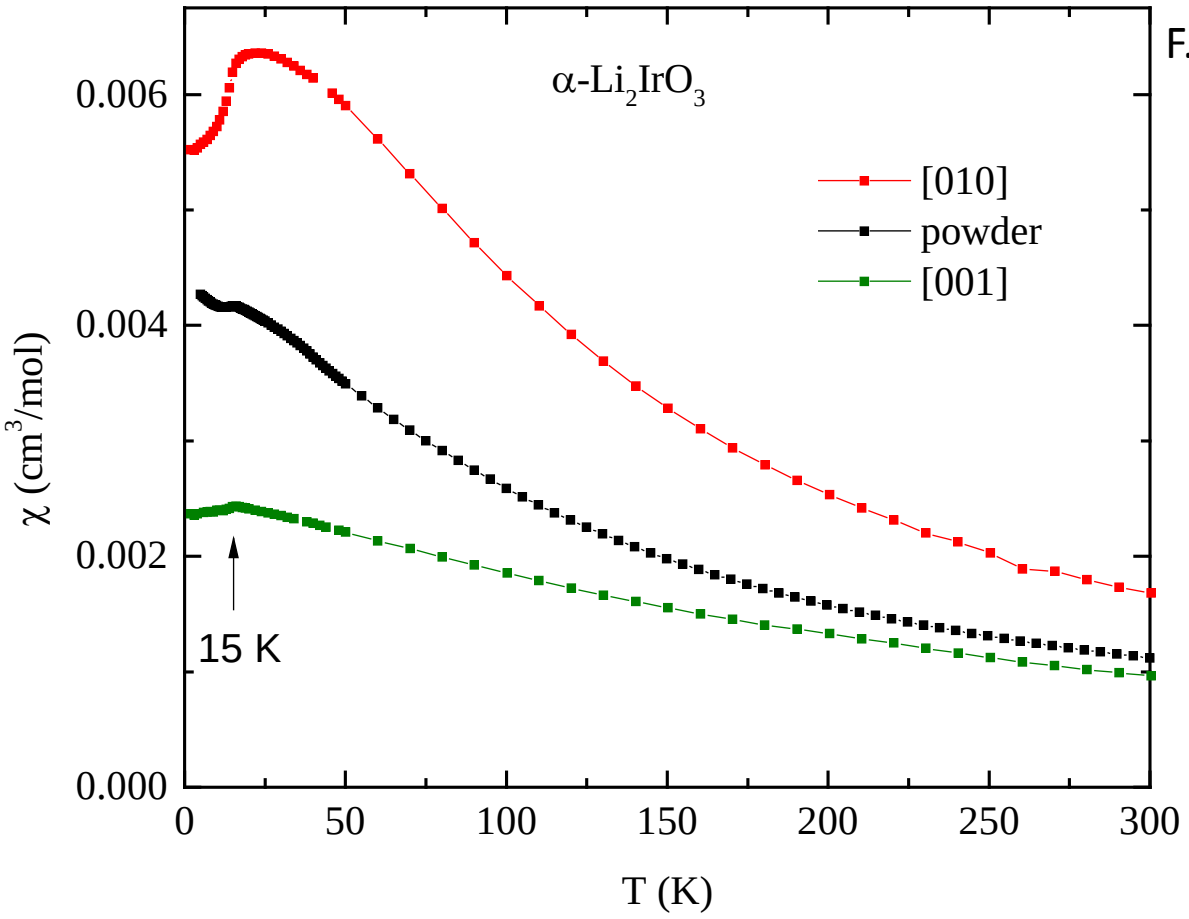


S. Manni, PhD 2014

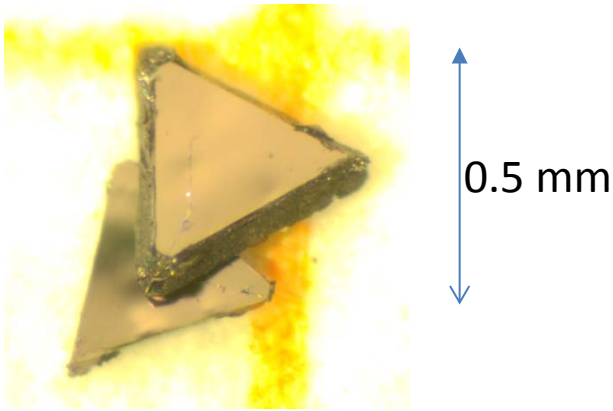
Anisotropic magnetic exchange + possible g-factor anisotropy due to trigonal distortion

Single crystalline α-Li_2IrO_3

Susceptibility of one 1.7 mg single crystal

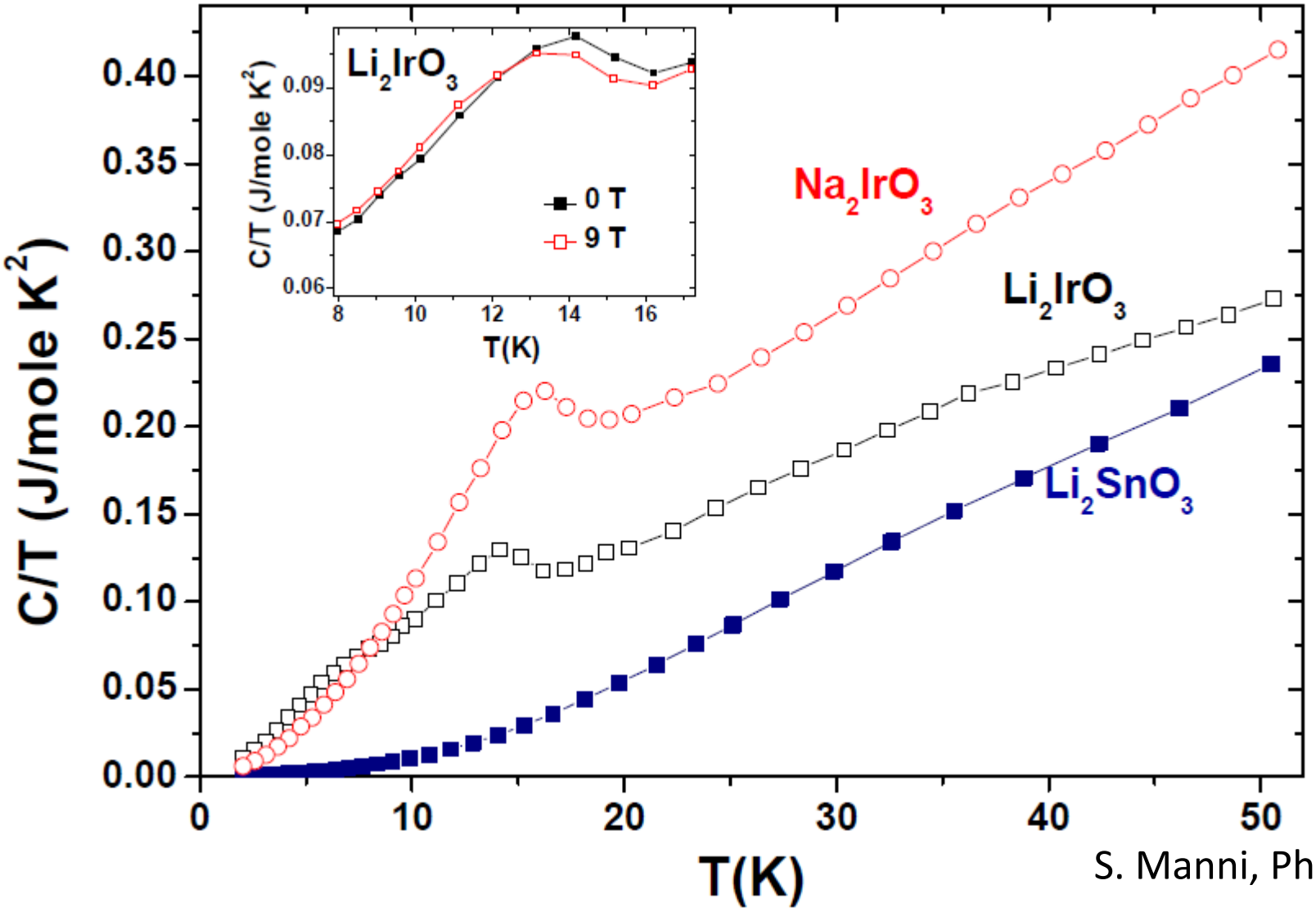


F. Freund and A. Jesche, unpublished



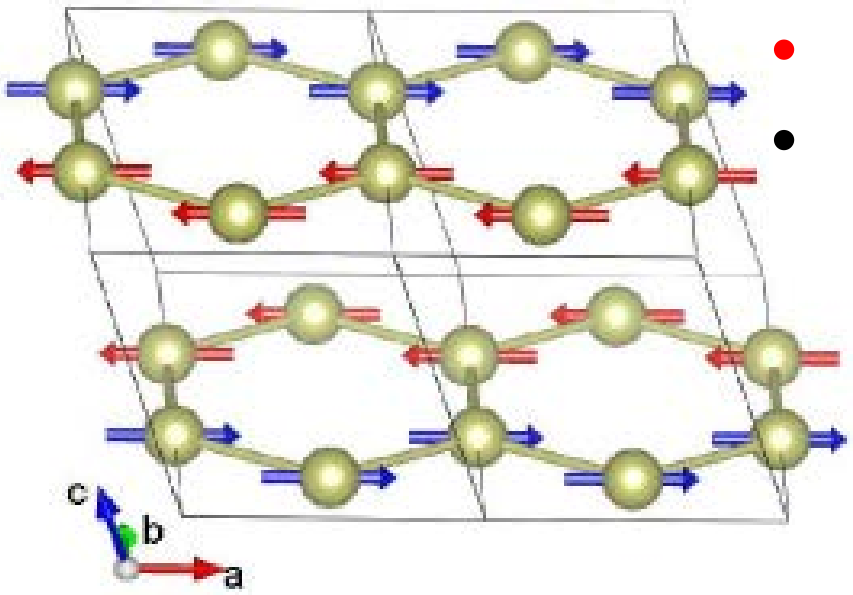
good quality in terms of sharp T_N but problem with twin domains

Specific heat

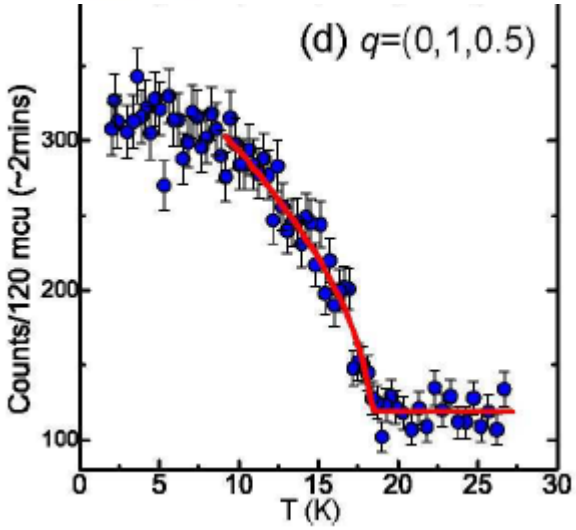


S. Manni, PhD 2014

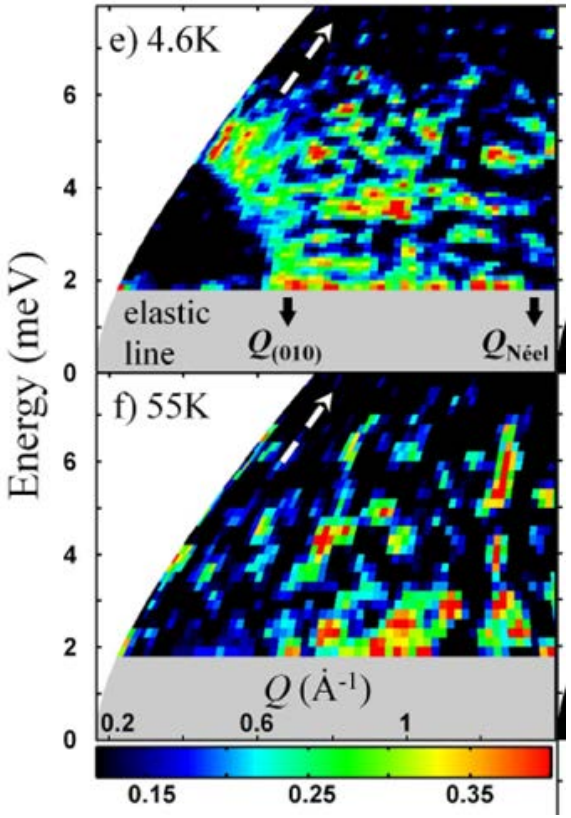
Na_2IrO_3 magnetic ordering



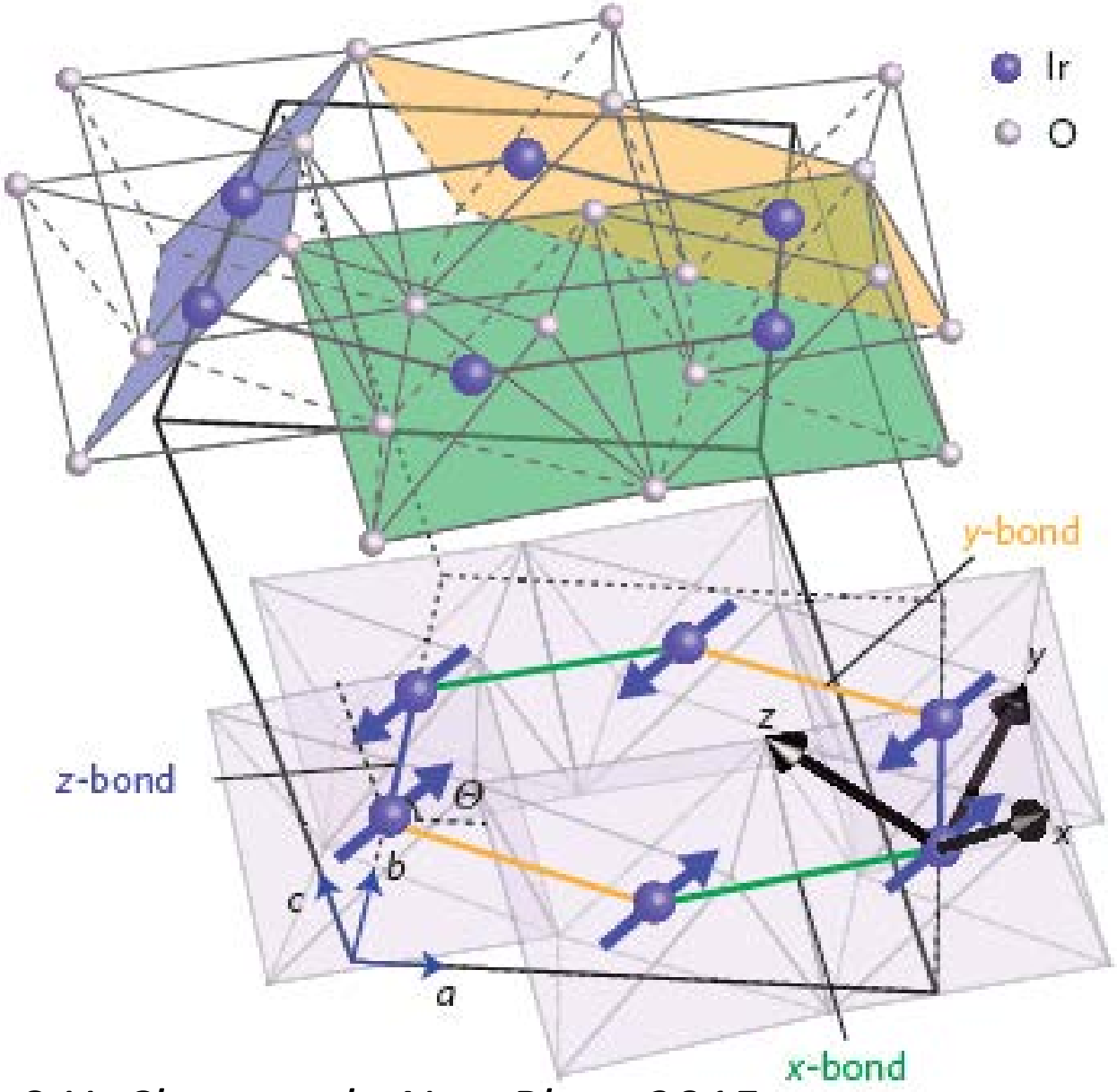
- Zigzag AF order stacked along c
- Ordered moment 0.22 μ_B

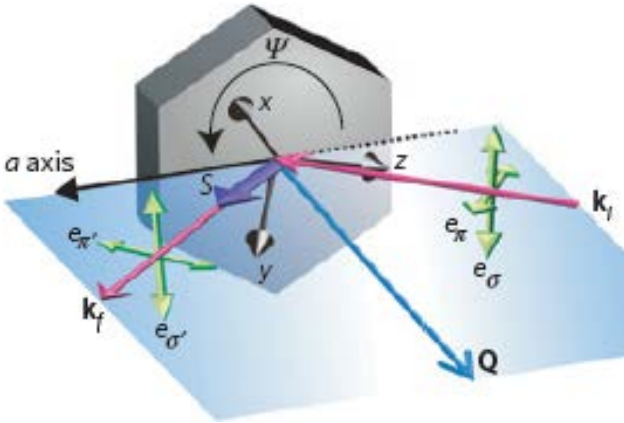


Magnons studied by INS on 10 g powder



Feng Ye at al. PRB **85** (2012) 180403(R), S.K. Choi et al., PRL **108** (2012) 127204





S.H. Chun et al., Nat. Phys. 2015

Magnetic X-ray scattering → moment orientation at $T<T_N$: ~(x+y)

~(a+c)

Modelling

J.G. Rau et al., PRL 2014 (next neighbor interactions only!)

$$H = \sum_{\langle ij \rangle \in \alpha\beta(\gamma)} [J\vec{S}_i \cdot \vec{S}_j + K S_i^\gamma S_j^\gamma + \Gamma(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)]$$

Heisenberg Kitaev generic off-diagonal exchange

Y. Yamaji et al., PRL 2014 (ab initio): J = +4.4 meV (AF), K = −34.5 meV, $\Gamma \sim 1$ meV
$\rightarrow$ Dominating Kitaev exchange

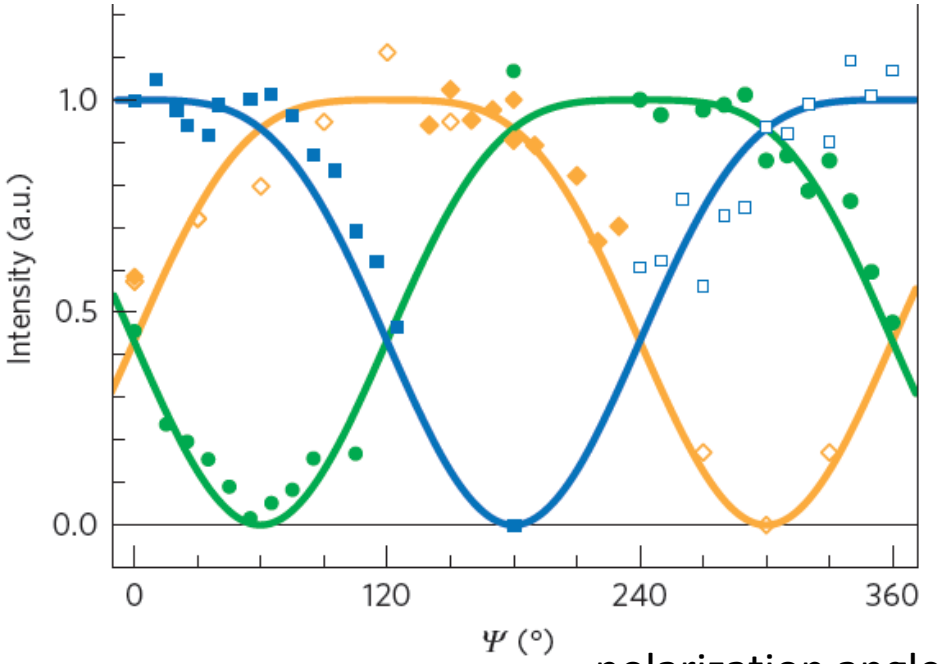
However: in addition also further neighbor interactions (Heisenberg and Kitaev)
e.g. N. Perkins et al. (2015): zigzag-state realized by K_1-K_2 (AF!) model

Kitaev spin-liquid correlations in fluctuating regime above T_N…
e.g. Raman signature predicted (Knolle PRL 2014)

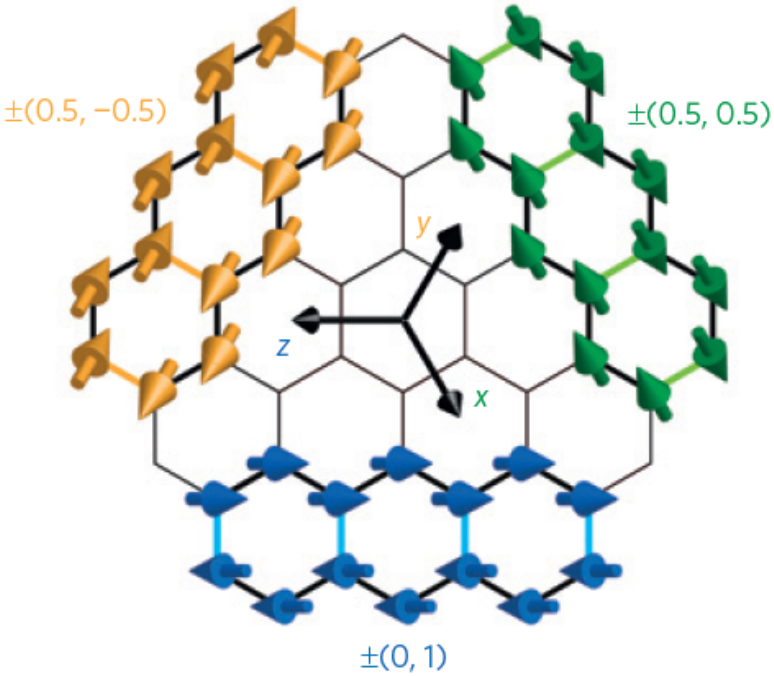
Spin space-real space entanglement in Na_2IrO_3

Diffuse magnetic scattering at $T>T_N$

colors represent different spin components



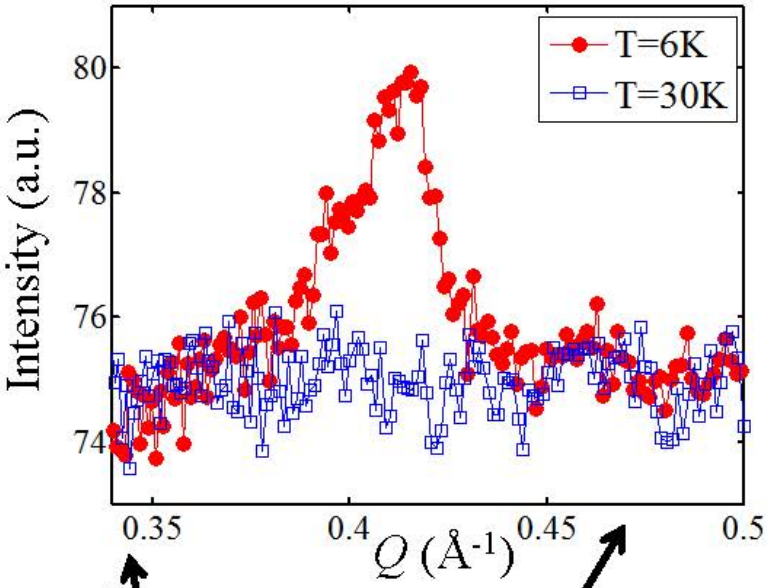
polarization angle

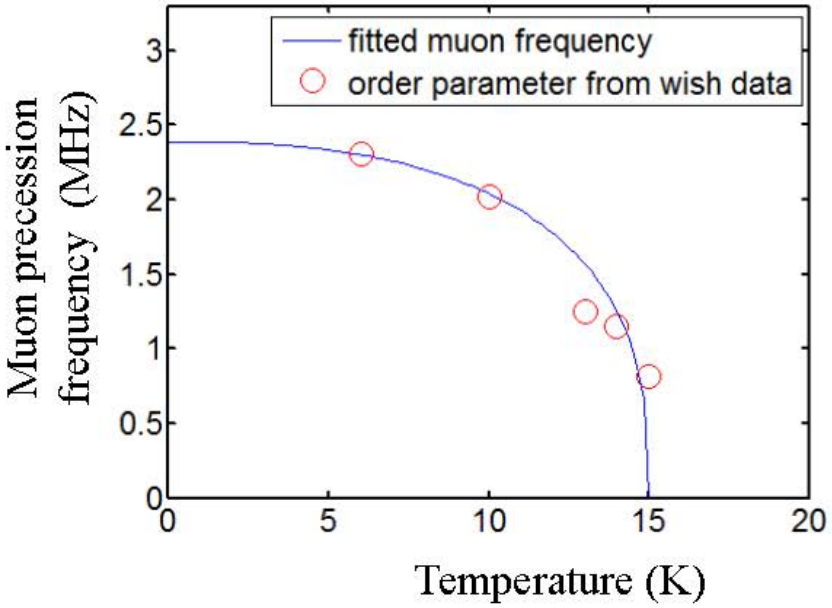


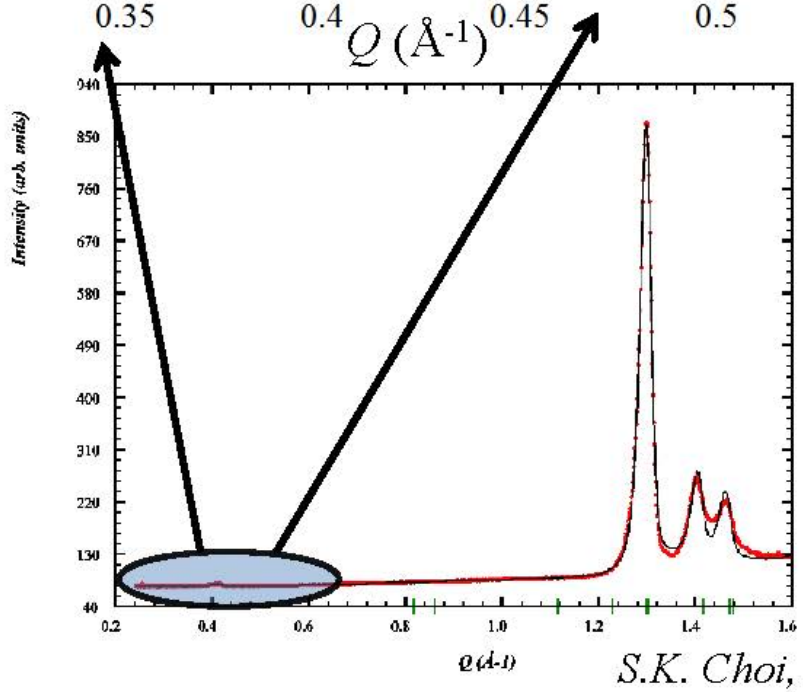
3 fluctuating zigzag clusters, seen in 3 respective spin components

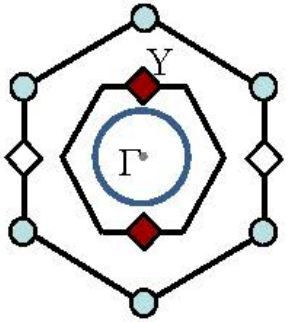
S. H. Chun, J.-W. Kim, J. Kim, H. Zheng, C. C. Stoumpos, C. D. Malliakas, J. F. Mitchell, K. Mehlawat, Y. Singh, Y. Choi, T. Gog, A. Al-Zein, M. M. Sala, M. Krisch, J. Chaloupka, G. Jackeli, G. Khaliullin, B. J. Kim, Nat. Phys. **11**, 462 (2015).

Magnetic neutron diffraction in Li_2IrO_3





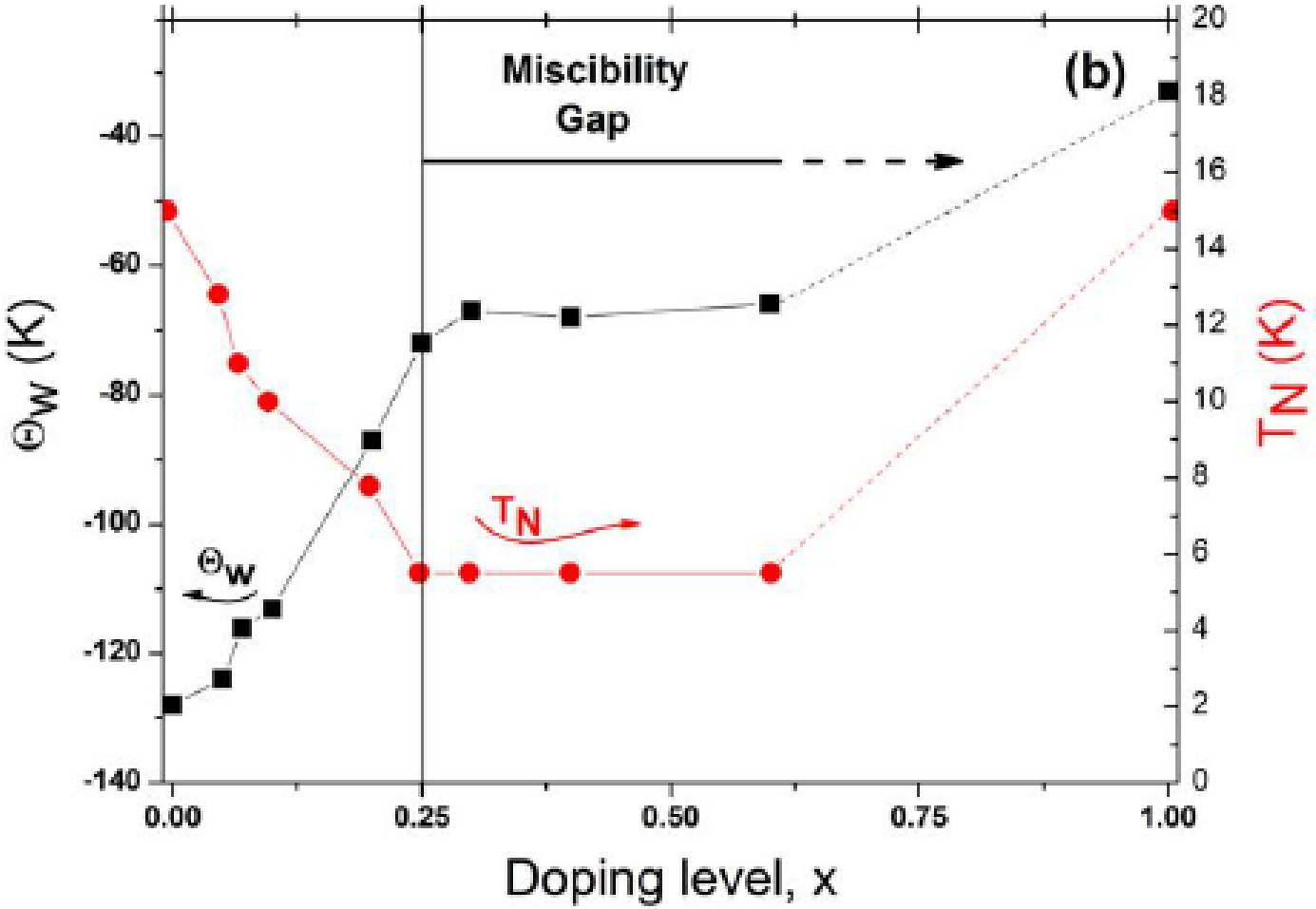




- small Q-vector, large supercell
- incommensurate spiral order

S.K. Choi, R. Coldea ...

Isoelectronic $(Na_{1-x}Li_x)_2IrO_3$

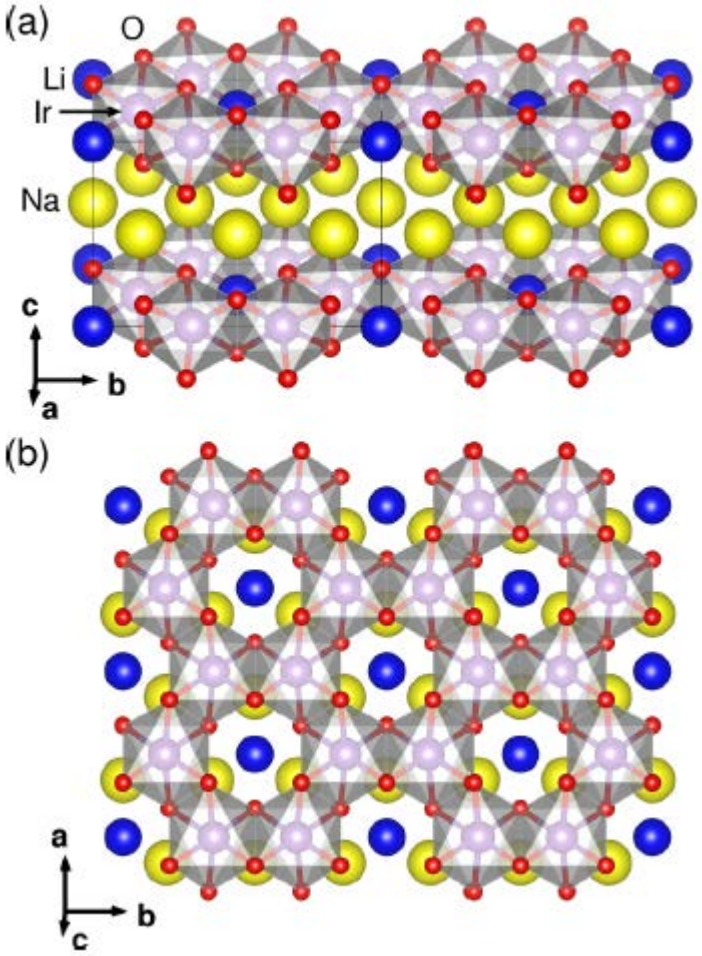


S. Manni, S. Choi, I.I. Mazin, R. Coldea, M. Altmeyer, H.O. Jeschke, R. Valenti, P. Gegenwart, Phys. Rev. B 89, 245113 (2014).

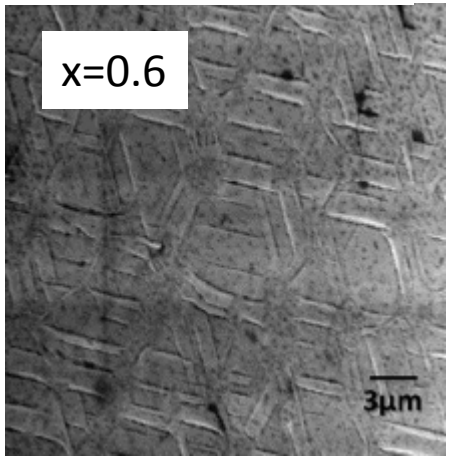
PHYSICAL REVIEW B 89, 245113 (2014)

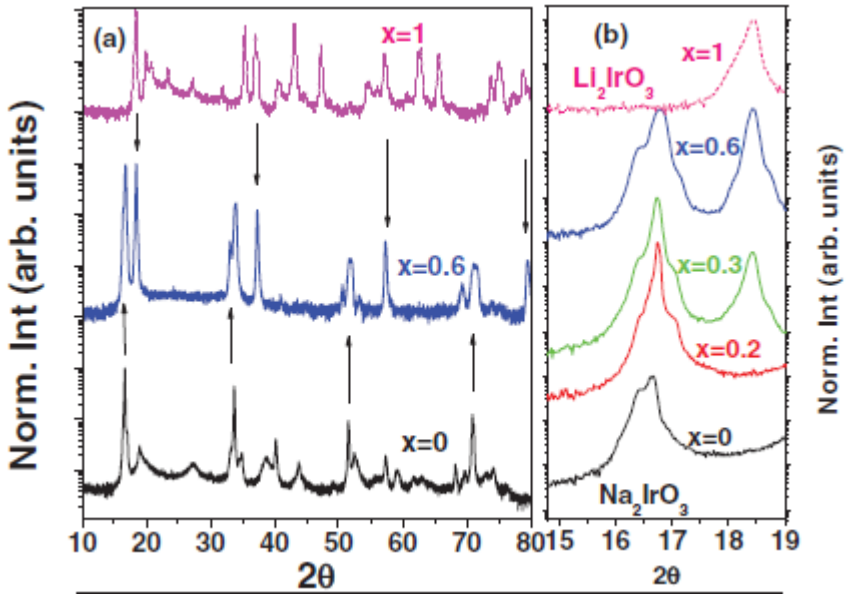
Effect of isoelectronic doping on the honeycomb-lattice iridate A_2IrO_3

S. Manni,[1] Sungkyun Choi,[2] I. I. Mazin,[3] R. Coldea,[2] Michaela Altmeyer,[4] Harald O. Jeschke,[4] Roser Valentí,[4] and P. Gegenwart[1,*]

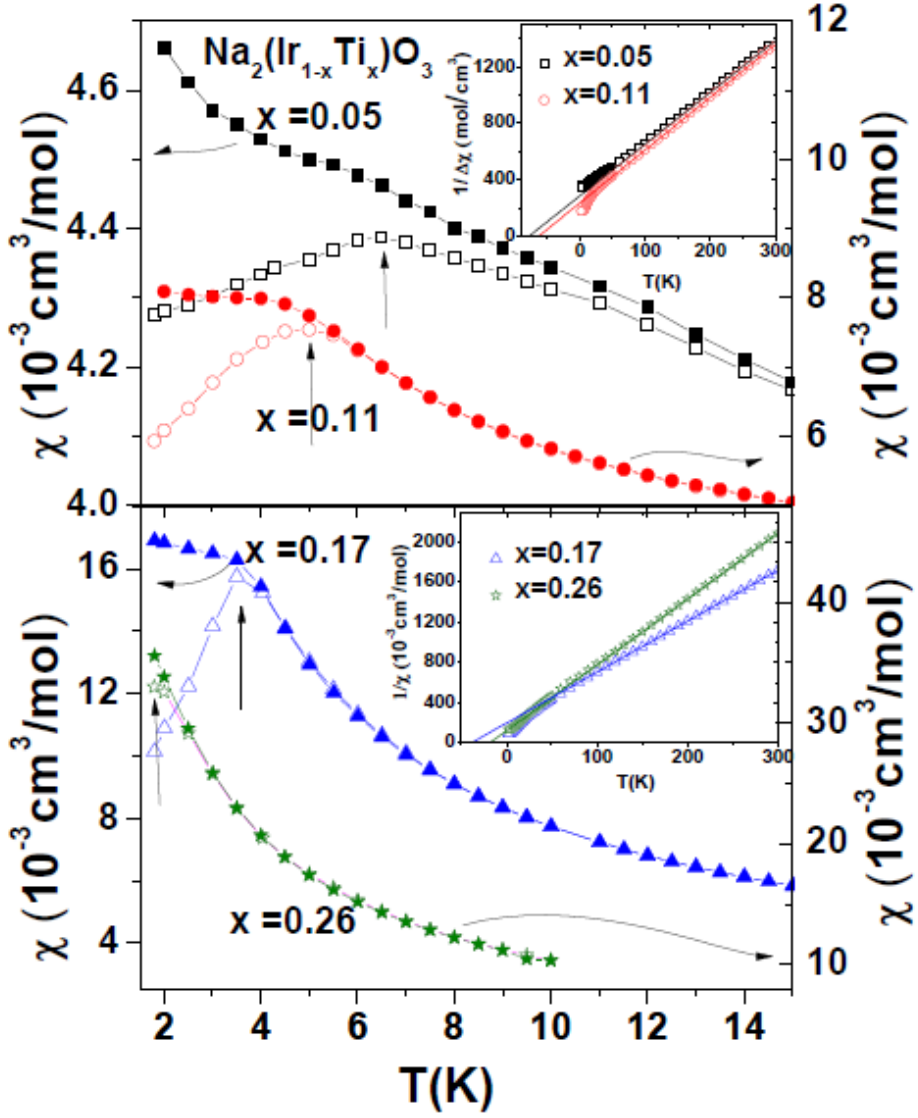


Ordered $Na_3LiIr_2O_6$





Magnetic depletion in $A_2(Ir_{1-x}Ti_x)O_3$

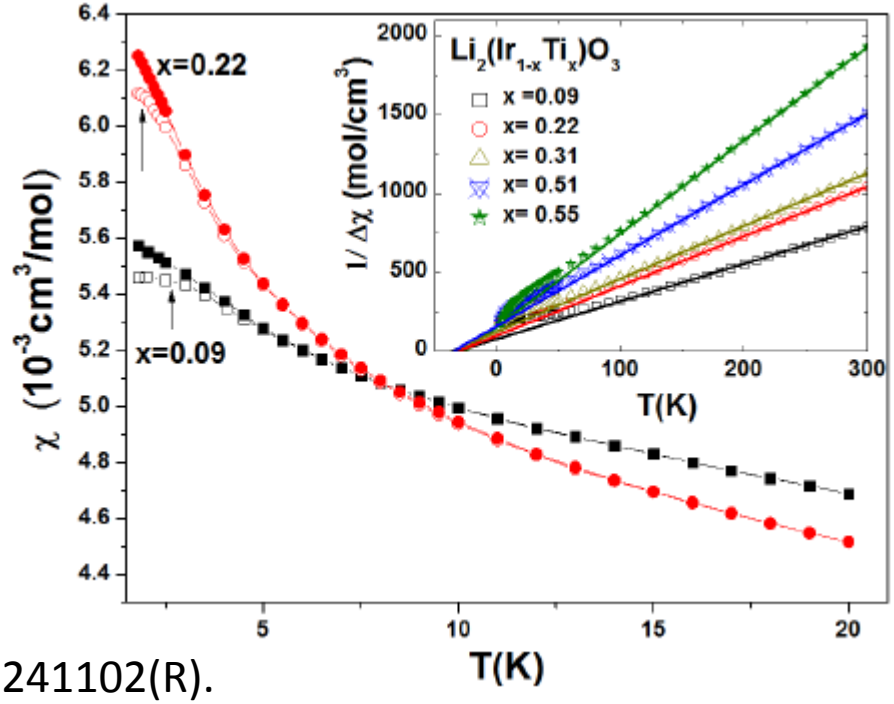


Na-system

- Spin glassy behavior beyond x=0.02
- Weiss temperature suppressed

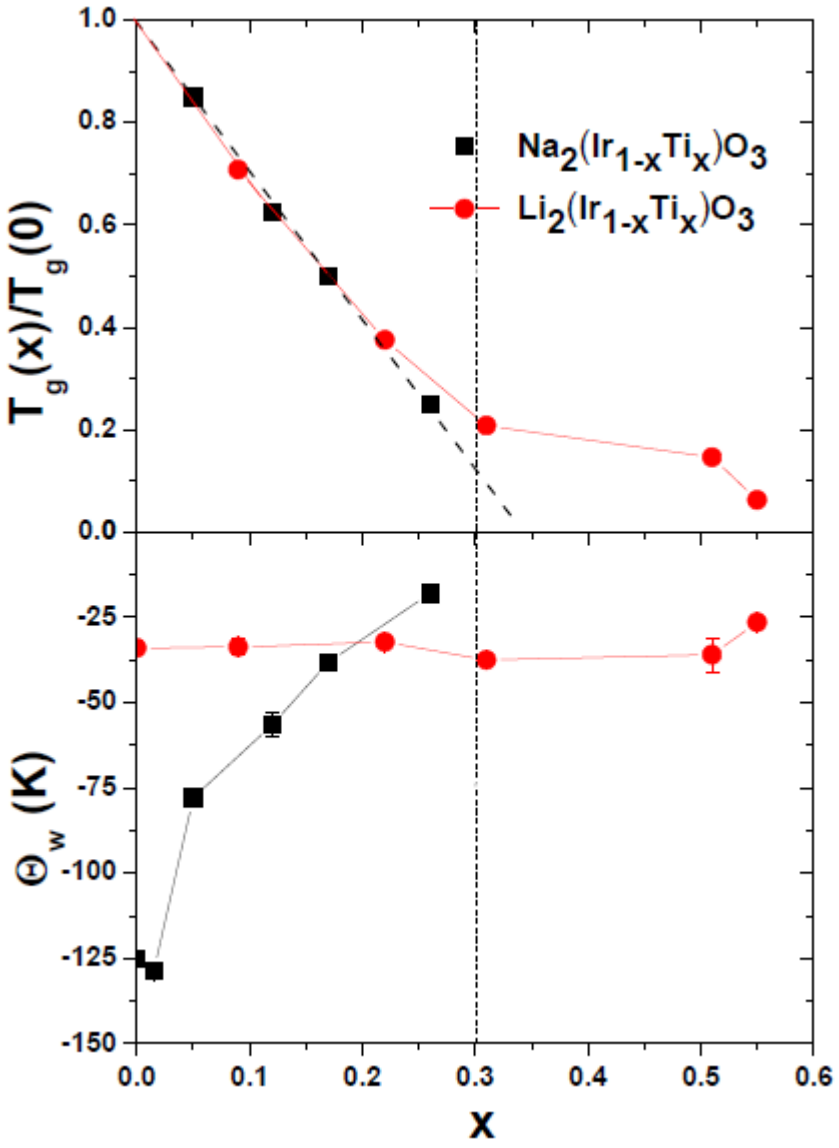
Li-system

- Spin glassy behavior
- Weiss temperature constant



S. Manni, Y. Tokiwa, P. Gegenwart, Phys. Rev. B 89, 241102(R).

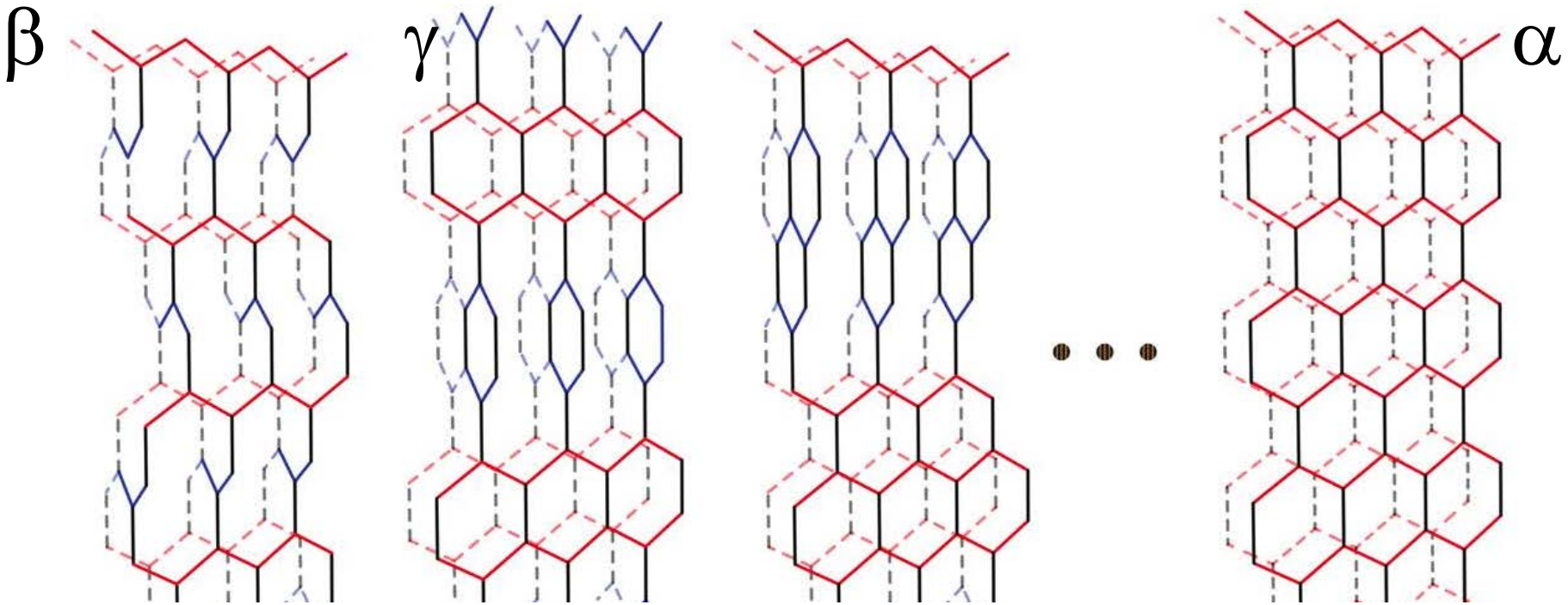
$A_2(Ir_{1-x}Ti_x)O_3$ Phase diagram



- Both systems substantially magnetically frustrated
- Li: no change in θ_W and SG persists well beyond percolation threshold
- Further neighbor couplings in Li system important…
- Na-system: dominating NN interaction

S. Manni, Y. Tokiwa, P. Gegenwart, Phys. Rev. B 89, 241102(R).

Structural variants of Li_2IrO_3

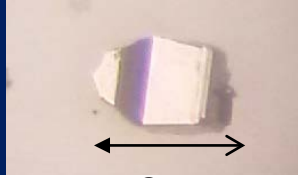


Hyper-Honeycomb Stripy-Honeycomb Honeycomb

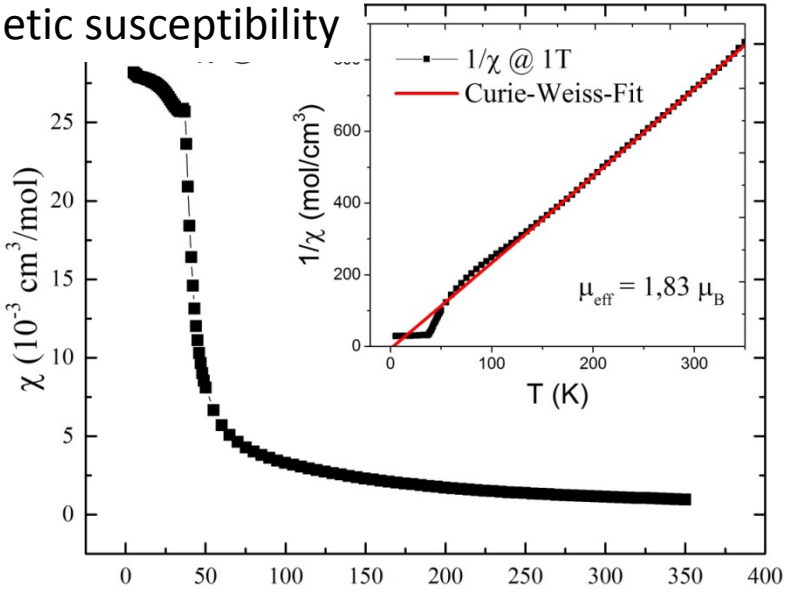
Similar local three-fold coordination of Ir and edge-shared IrO_6 octahedra → Possibility to realize Kitaev interaction in 3d!

Modic et al., Nature Comm. 2014, Takayama et al., PRL 2015, …

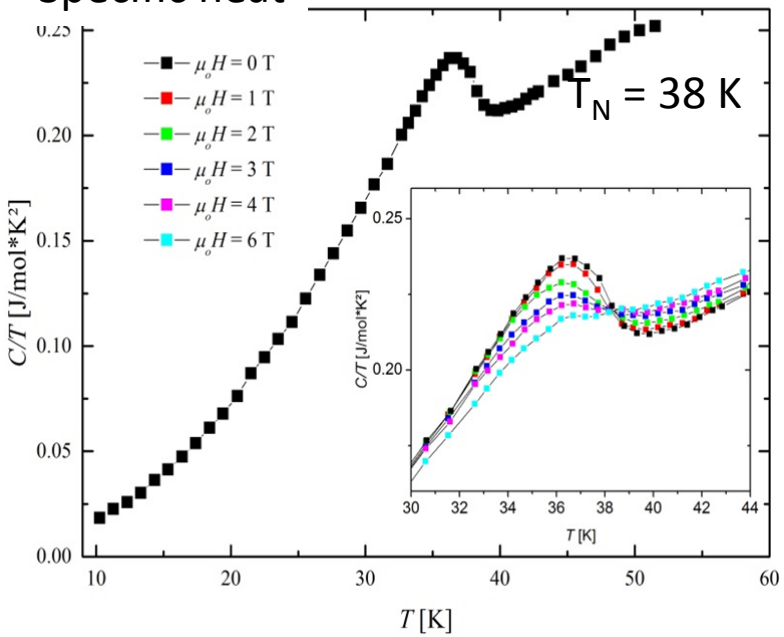
β-Li_2IrO_3 – bulk properties



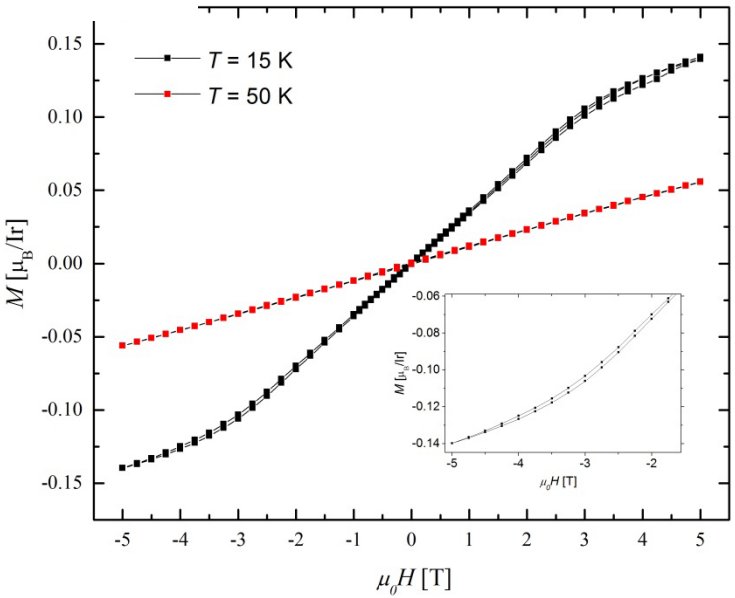
Magnetic susceptibility



Specific heat



Magnetization

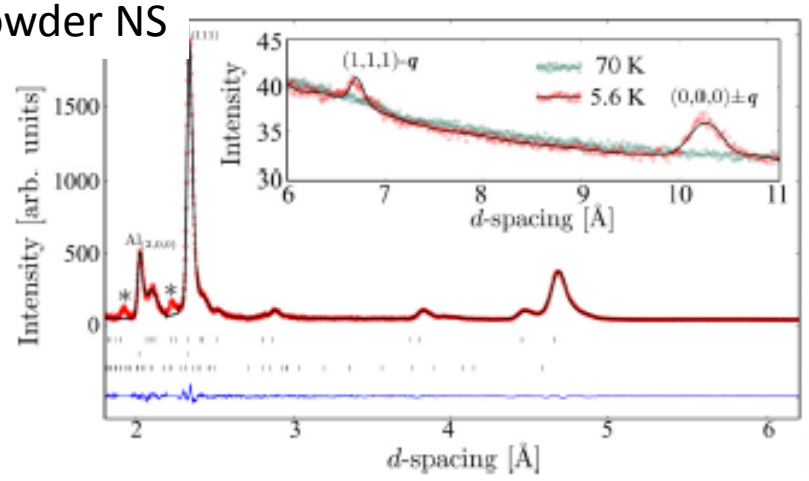


- Fluctuating j_{eff}=1/2 moments, Θ_W more FM
- T_N = 38 K, similar as for γ-Li_2IrO_3
- Partial polarization beyond 3 T

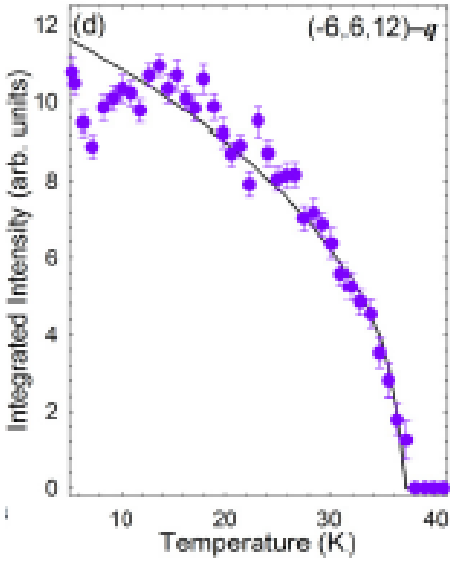
F. Freund, unpublished, A. Biffin et al., PRB 2014

Magnetic order in β-Li_2IrO_3

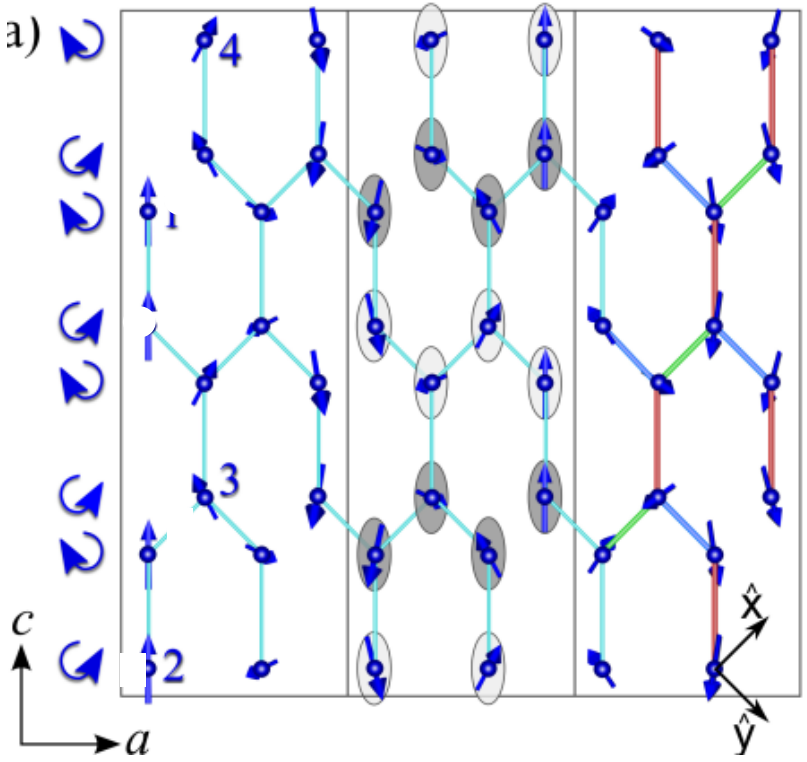
Powder NS



SC magnetic resonant x-ray diffraction



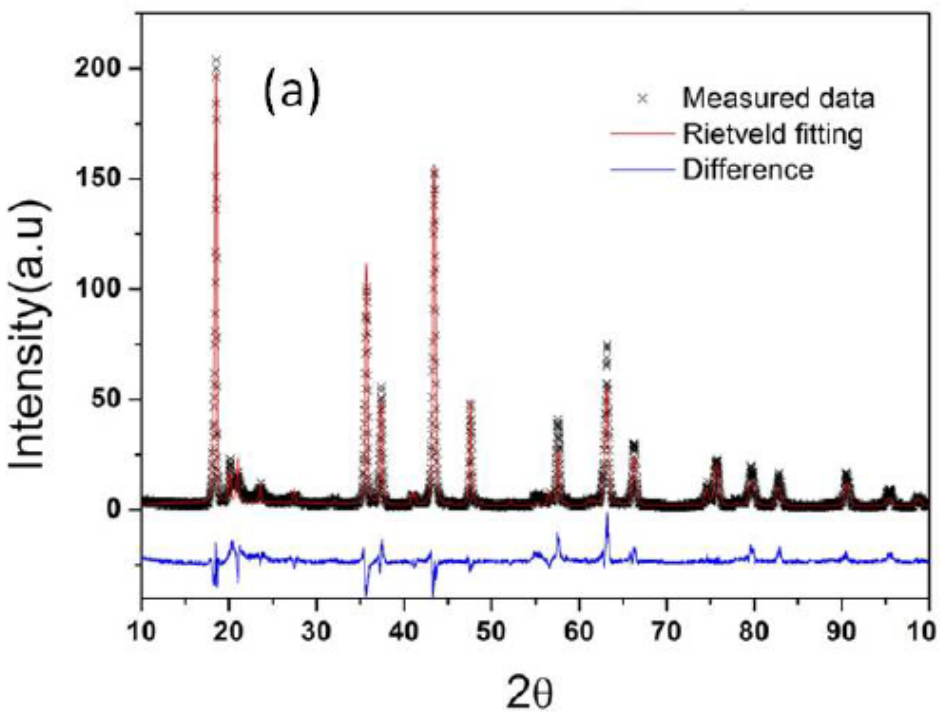
A. Biffin et al., PRB 2014

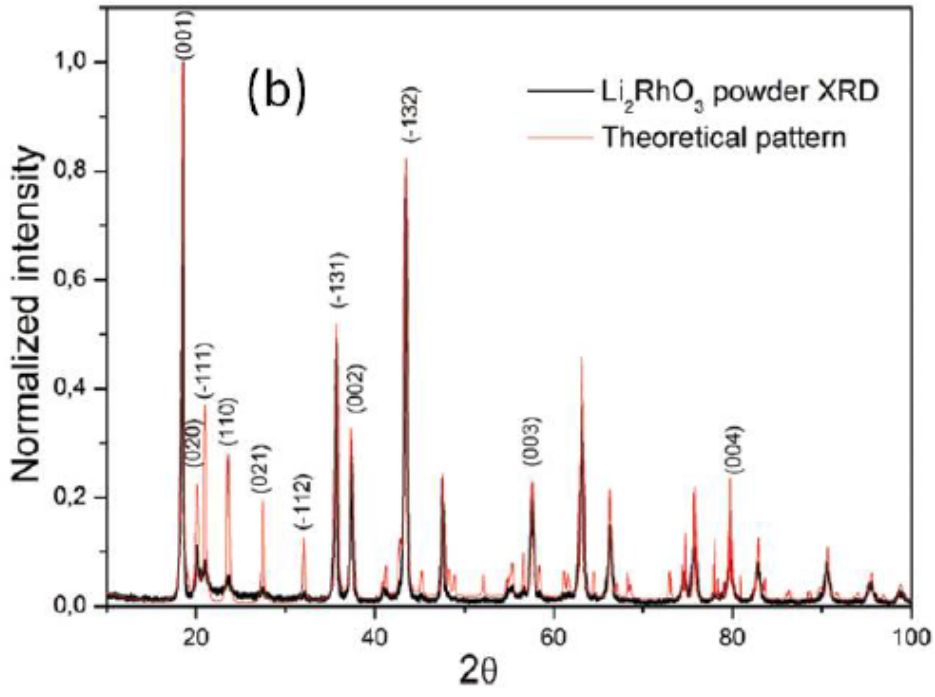


- Non-coplanar counter-rotating (on every NN bond along c) incomm. q=(0.57, 0,0) order
- T_N = 38 K, μ_{or}=0.47μ_B (similar as γ-Li_2IrO_3)
- Each Ir-Ir bond: FM coupling of comp. perp Ir-O_2-Ir planes (→ Kitaev!)

How about isoelectronic Li_2RhO_3?

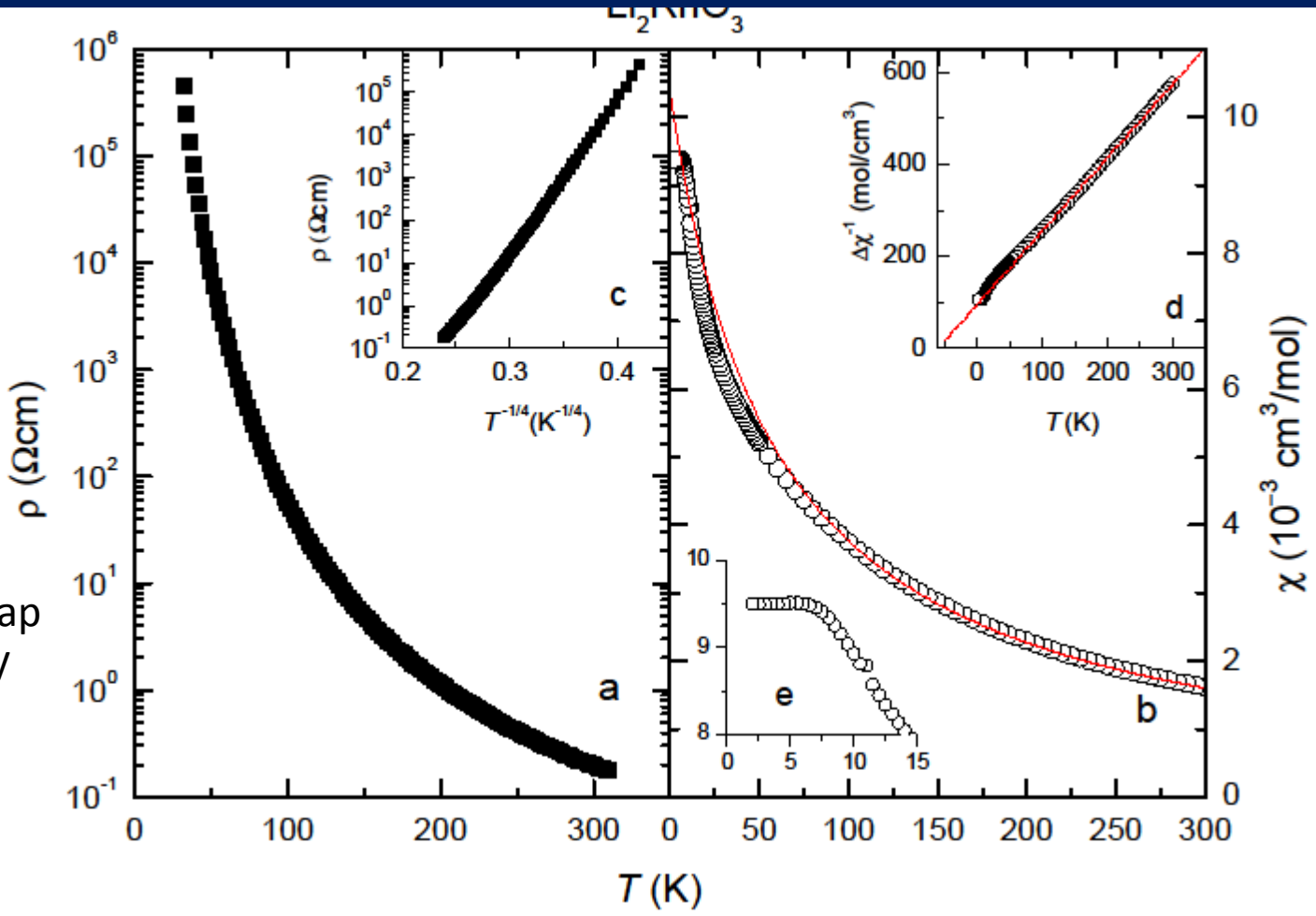
- Since preferred Rh valence is +3, to get +4 the synthesis was done in O_2 flow → polycrystals with honeycomb C2/m structure
- Powder refinement: stacking faults simulated by Rh/Ir site exchange (30% needed!)





S. Manni, PhD thesis

Mott insulating Li_2RhO_3

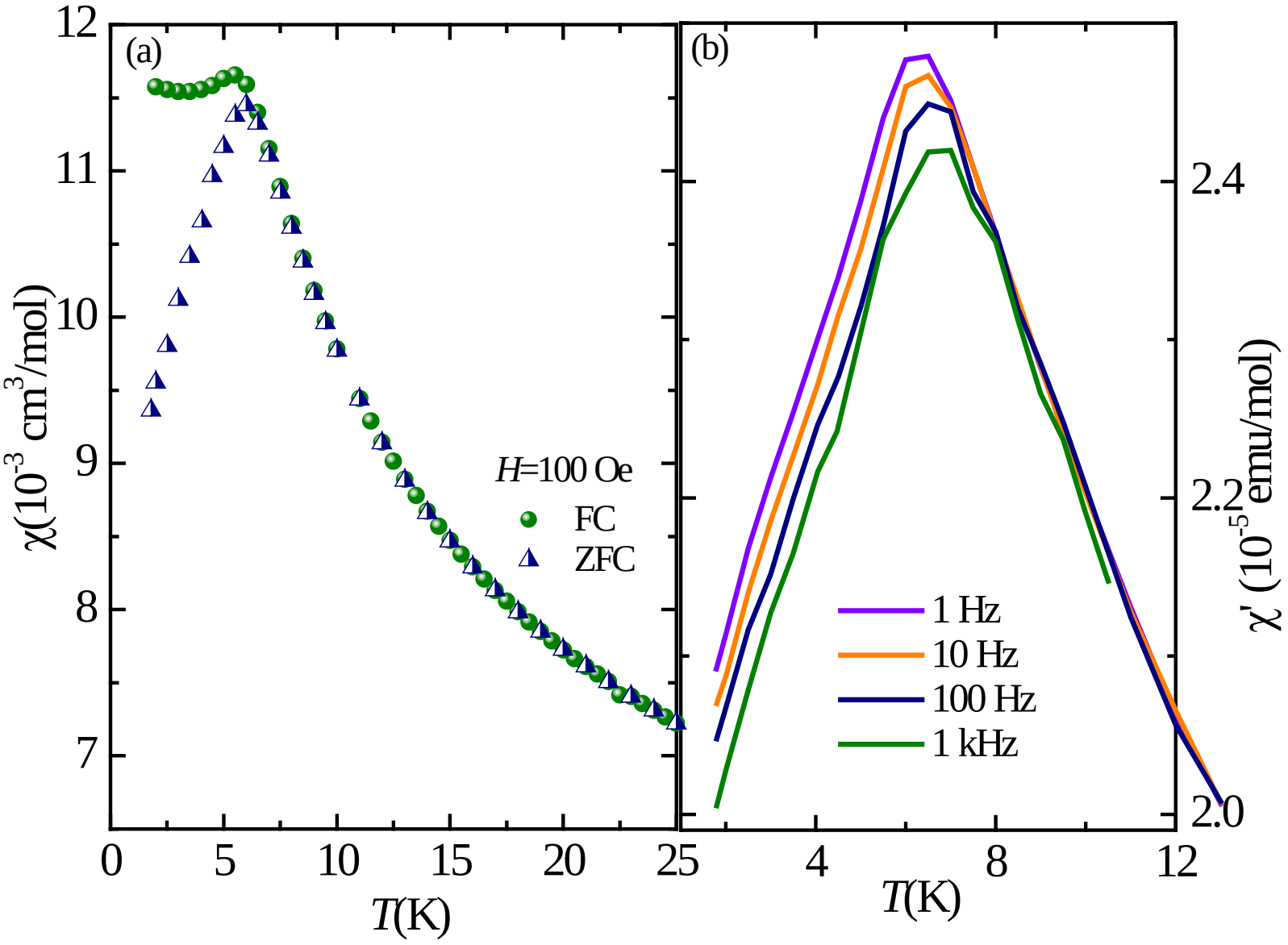


Charge gap
~ 85 meV

- Strong similarity to A_2IrO_3 despite larger U and smaller λ_{SO}

I. I. Mazin, S. Manni, K. Foyevtsova, H.O. Jeschke, P. Gegenwart, R. Valenti, PRB **88** (2013) 035115.

Li_2RhO_3: spin glassy behavior



P. Khuntia, S. Manni, F.R. Foronda, T. Lancaster, S.J. Blundell, P. Gegenwart, M. Baenitz, unpublished

Conclusion

- To realize Kitaev exchange, Spin-real space entanglement required $\rightarrow$ materials with large SO coupling
- Spin-orbit Mott insulating iridates (Ir^{4+} in octahedral O environment)
- Honeycomb Na_2IrO_3: zigzag order, stabilized by NN Kitaev, Heisenberg and anisotropic exchange
- Li_2IrO_3 polytypes: Ir-O-Ir bonding angles closer to 90°, incommensurate spiral orderings, indications for substantial further neighbor exchange
- Ongoing: study of single crystals of α-Li_2IrO_3 ($\rightarrow$magnetic structure)