The search and detection of quantum spin liquid in new materials with geometrically frustrated lattice

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NSF

U.S. DEPARTMENT OF ENERGY | Office of Science

Motivation:

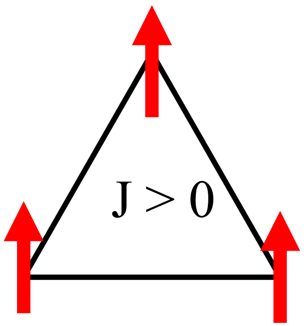
We must learn how the astonishing properties of quantum materials can be tailored to address our most pressing technological needs, and we must dramatically improve our ability to synthesize, characterize, and control quantum materials.

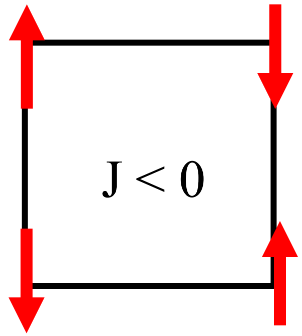
Grow single crystals

Search for quantum spin liquid state candidates (NSF)

Electronically detect spin states and magnetic excitations (DOE, collaboration with Jian Liu)

Non-frustrated magnets





$$H = -\sum_{ij} \mathrm{J}_{\mathrm{ij}} S_i \cdot S_j$$

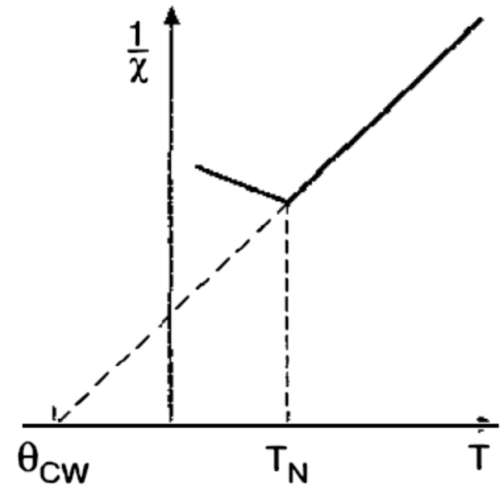
$$T_{\mathrm{N}} = \frac{zS(S+1)|\mathrm{J}|}{3k_B}$$

$$\chi = \frac{\mathrm{C}}{T - \theta_{\mathrm{CW}}}$$

Curie

Néel

Heisenberg



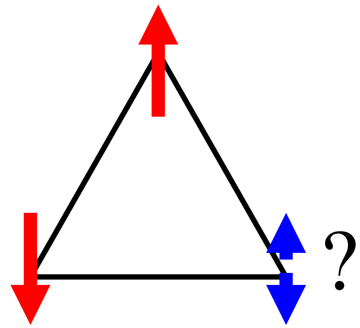
Non-frustrated $T_{\mathrm{N}} \sim \theta_{\mathrm{CW}}$

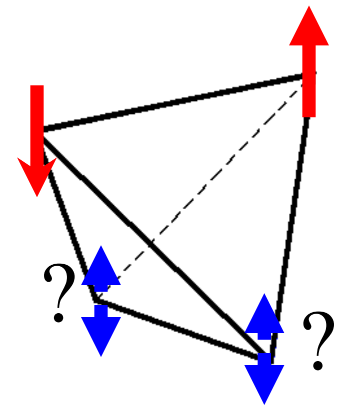
$z = 4$ nearest neighbor number

$\mathrm{S} = 1$

$T_{\mathrm{N}} \sim 2.7\ \mathrm{J}$

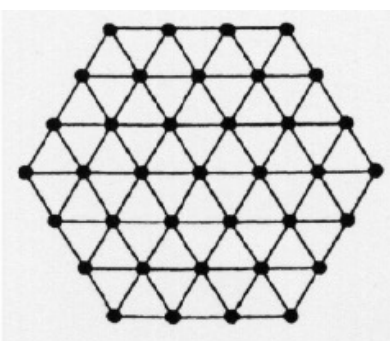
Geometrically Frustrated Lattice



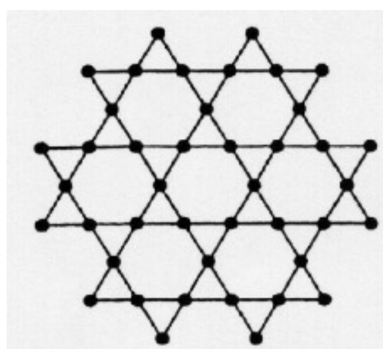


Interactions between magnetic degree of freedom in a lattice are incompatible with the underling crystal geometry ------Frustration

2D

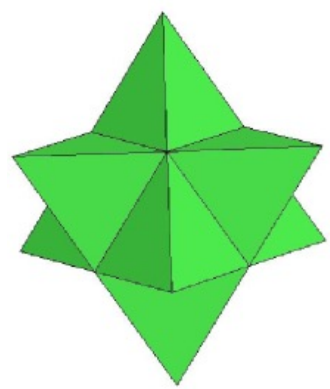


Triangular

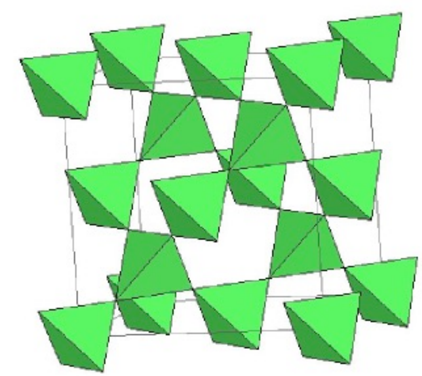


Kagome

3D

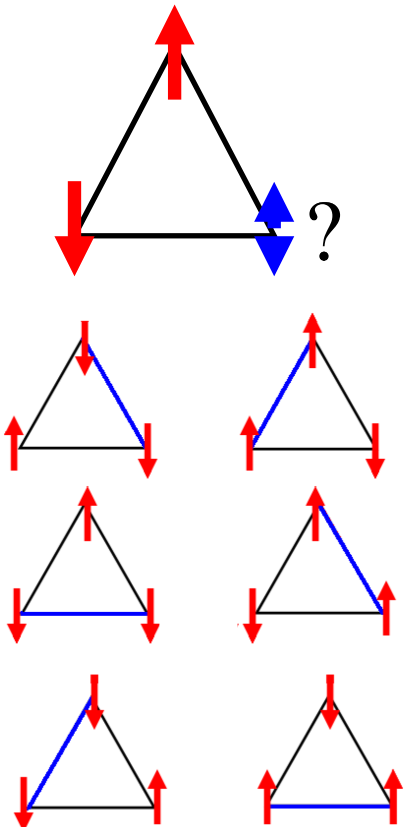


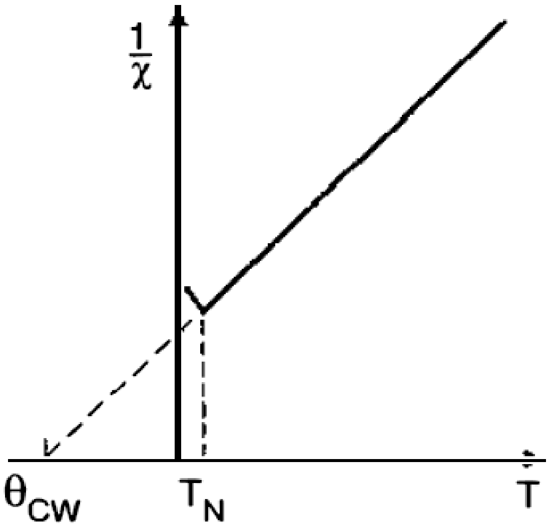
Face centered cubic



Pyrochlore

Degeneracy



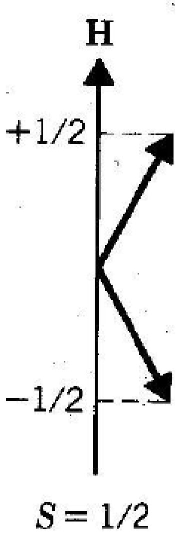


Frustrated $T_N << \theta_{CW}$

$$f = |\theta_{CW}|/T_N > 10$$

Frustration leads to degeneracy, which enhances spin fluctuations and suppresses magnetic ordering to *induce* ***exotic magnetism.***

Spin-1/2 Triangular lattice antiferromagnet (TLAF)

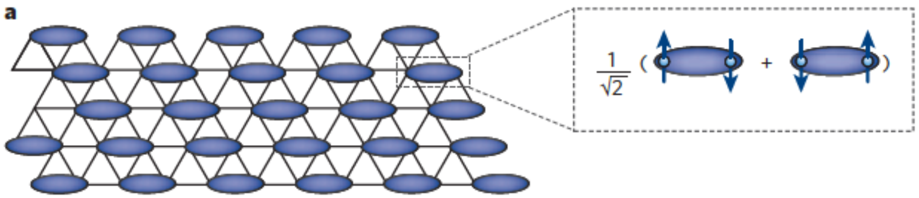


Strong quantum spin fluctuations

Quantum spin liquid

Quantum spin liquid (QSL) RARE!! No long range order down to 0 K; No symmetry breaking; Long range entanglement; Fractional excitation

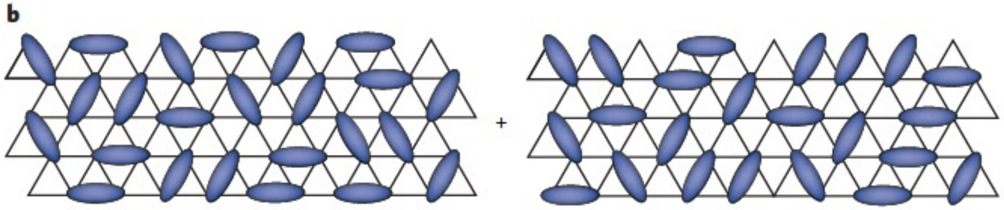
a



$$(i,j) = \frac{1}{\sqrt{2}}(|\uparrow_i\downarrow_j\rangle - |\downarrow_i\uparrow_j\rangle)$$

Valence-bond solid (VBS) state: a singlet dimer configuration dominates in the ground state.

b



$$+ \dots \quad |\Psi_{\mathrm{RVB}}\rangle = \sum_{i_1 j_1 \cdots i_n j_n} a_{(i_1 j_1 \cdots i_n j_n)} |(i_1, j_1) \cdots (i_n, j_n)\rangle,$$

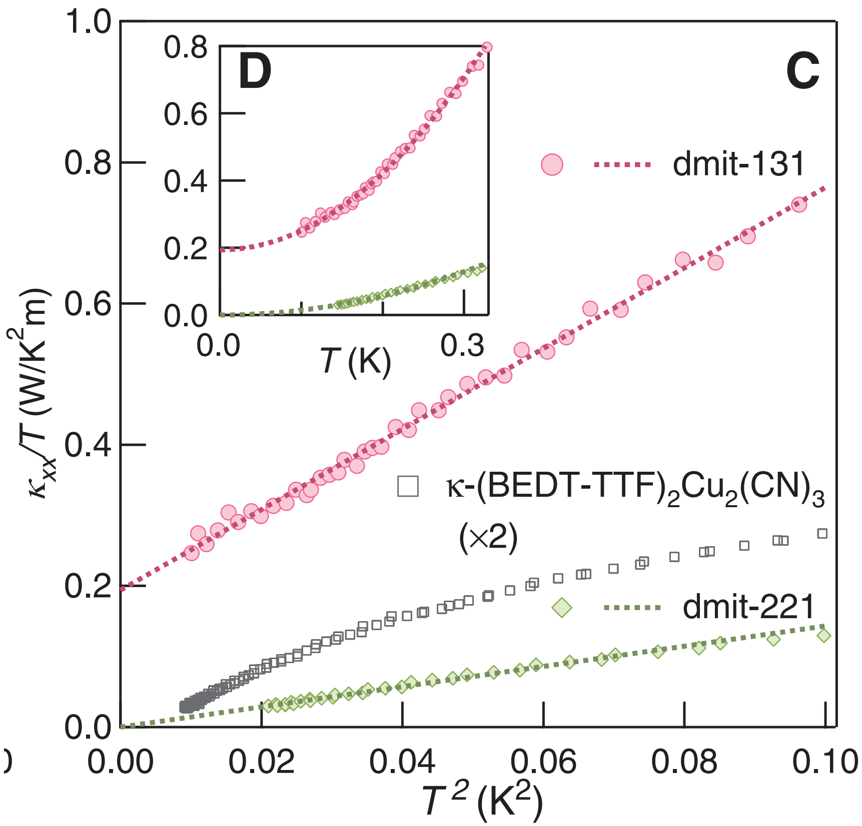
Resonant valence bond (RVB) state: The valence-bond pairs in the RVB construction are dominated by short-range pairs, resulting in liquid-like states with no long-range spin order.

P. W. Anderson, Mater. Res. Bull. ***8****, 153 (1973); Science* ***235*** *, 1196 (1987)*
L. Balents, Nature ***464,*** *199 (2010)*

Gapless QSL, itinerant spin excitations, residual k_0/T term

Organic molecular magnets: $EtMe_3Sb[Pd(dmit)_2]_2$, spin-1/2 TLAF

M. Yamashita et al., Science 4, 328 (2010).



Very rare to observe non-zero k_0/T approaching zero temperature in insulating magnets

Spin-1/2 geometrically frustrated magnets

Cu^{2+}, $3d^9$
$ZnCu_3(OH)_6Cl_2$, Herbertsmithite, kagome lattice, QSL
Cs_2CuBr_4, distorted triangular lattice, LRO with UUD

Ir^{4+}, $5d^5$
$Na_4Ir_3O_8$, hyper-kaogme, QSL

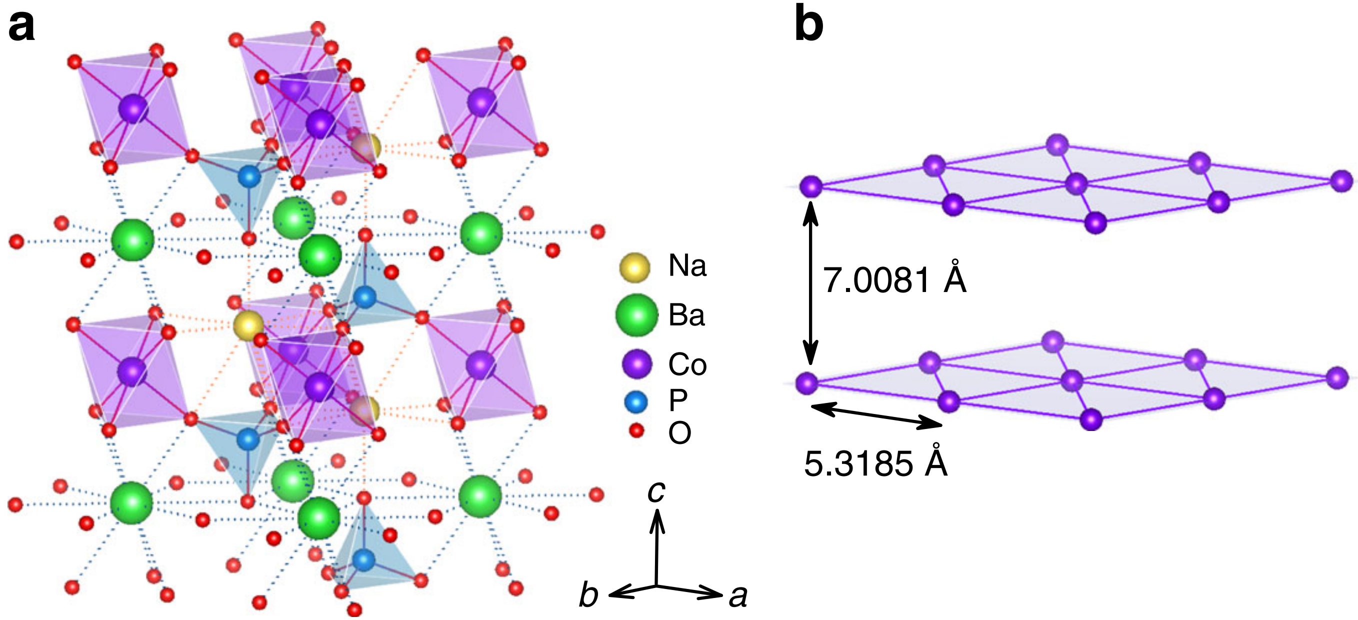
Co^{2+}, $3d^7$, effective spin 1/2
$Ba_3CoSb_2O_9$,
$B_3CoNb_2O_9$,
$Ba_8CoNb_6O_{24}$

Yb^{3+},$4f^{13}$, effective spin 1/2
$Yb_2Ti_2O_7$, pyrochlore, QSL

Ru_2O_9 dimer
$Ba_3ARu_2O_9$ (A = Y^{3+}, In^{3+}, Lu^{3+})

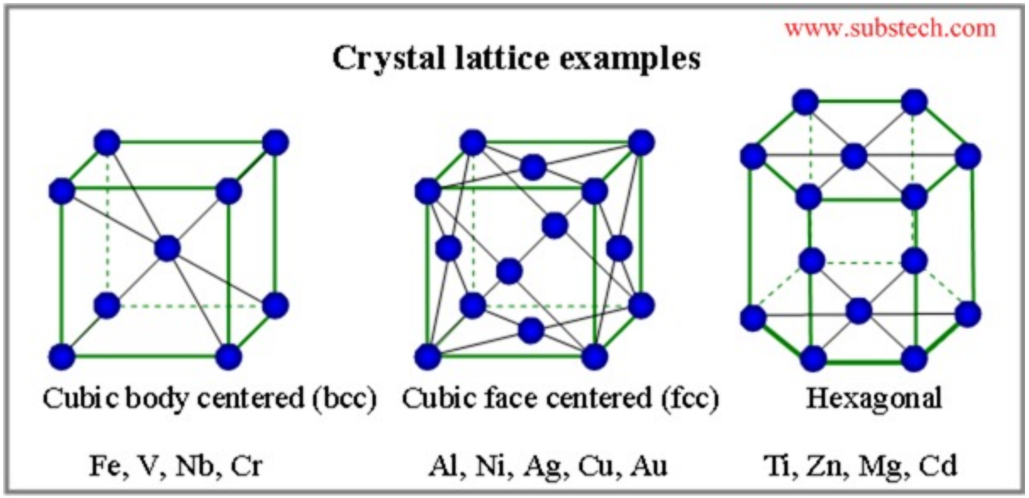
Mo_3O_{13} clusters
$LiZn_2Mo_3O_8$, distorted Kagome lattice QSL
$Li_2In_{1-x}Sc_xMo_3O_8$

$Na_2BaCo(PO_4)_2$, spin-1/2 triangular lattice antiferromagnet



Single Crystal

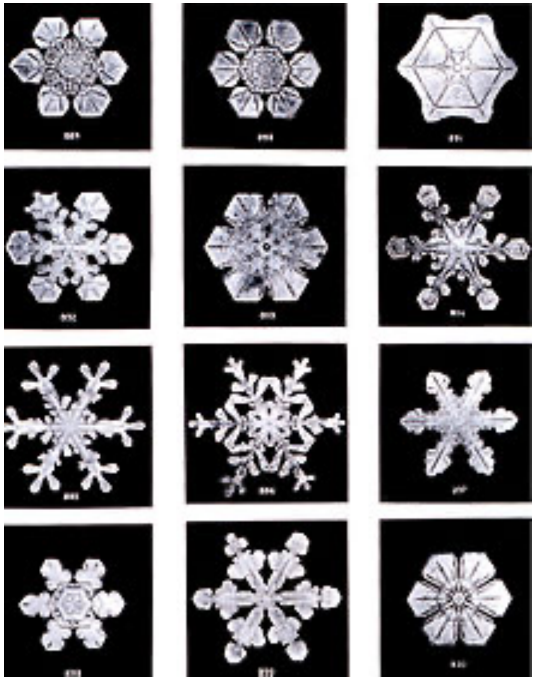
A **single crystal** is a material in which the crystal structure of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries.



Crystallization

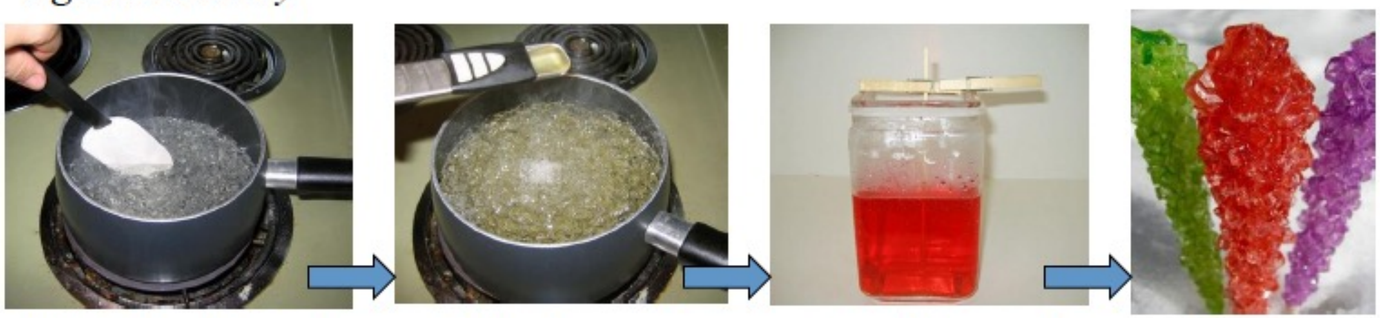
Nucleation is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region)

The *crystal growth* is the subsequent growth of the nuclei that succeed in achieving the critical cluster size.

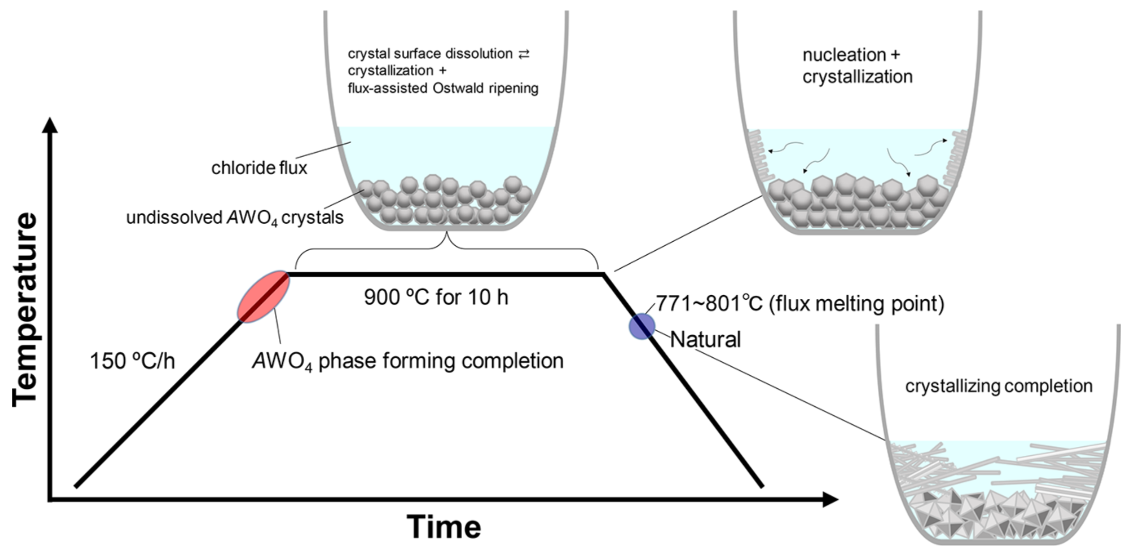


Flux growth

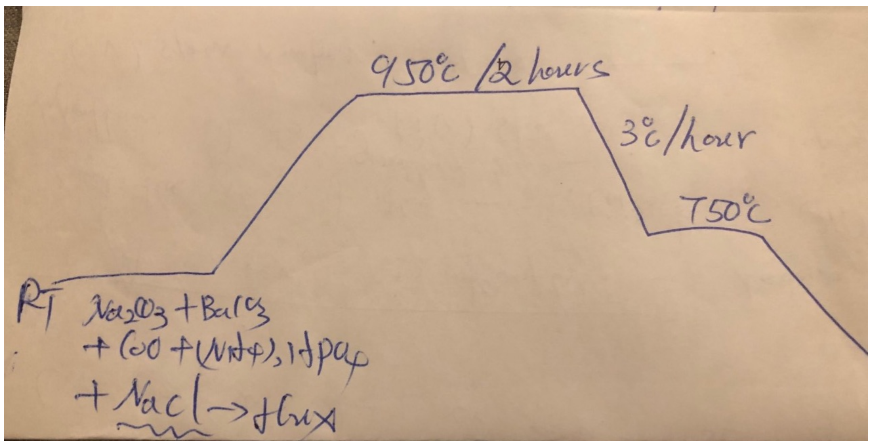
e.g. Rock candy



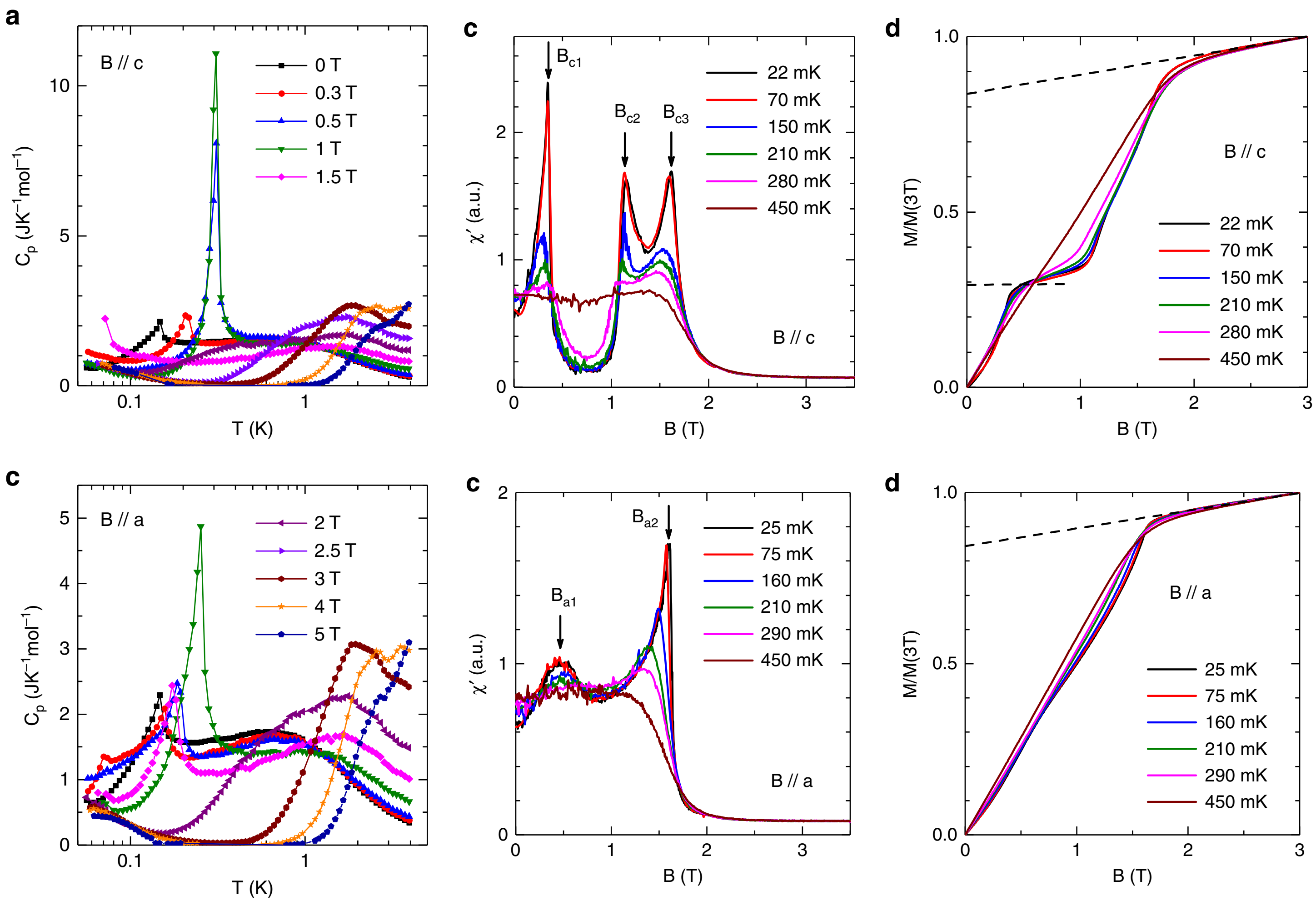
- *Find the right solvent and dissolve the starting materials*
- *Crystallize with time and temperature*



Flux growth

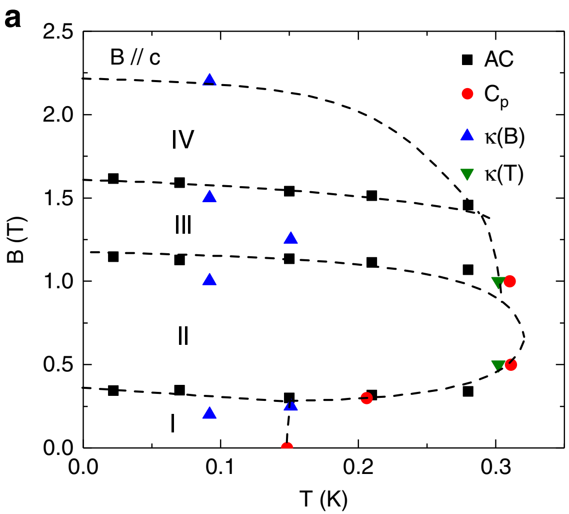


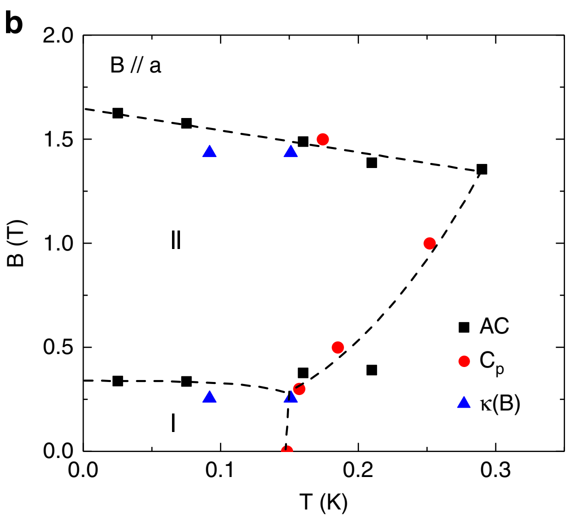
$Na_2BaCo(PO_4)_2$, T_N = 0.15 K, field induced spin state transitions



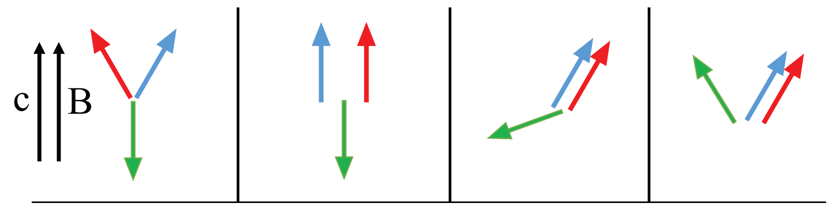
*N. Li,, H. D. Zhou et al., Nature Communications **11**, 4216 (2020).*

$Na_2BaCo(PO_4)_2$, magnetic phase diagram

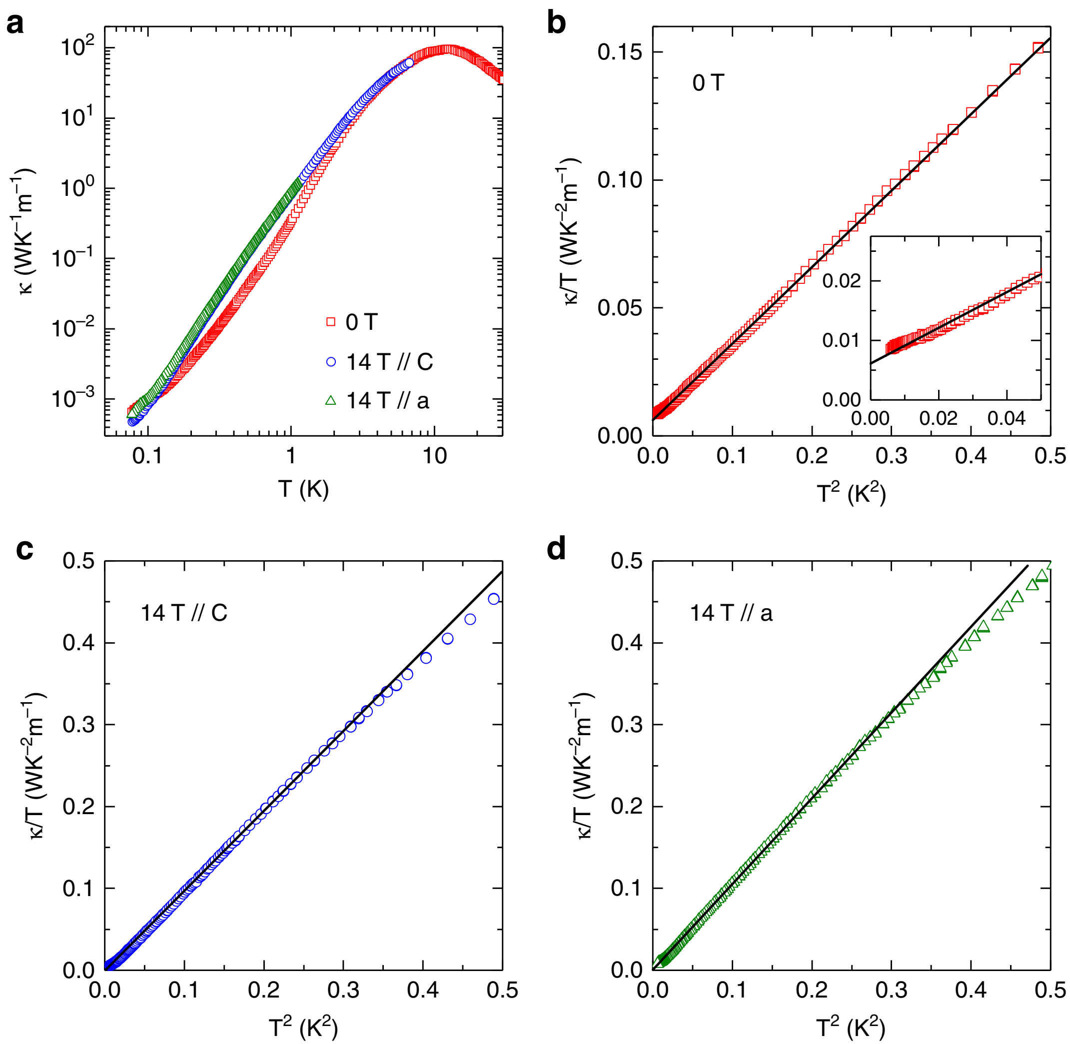




the UUD phase only survives for B // c, which strongly suggests its easy axis anisotropy.



$Na_2BaCo(PO_4)_2$ behaves as a gapless QSL above T_N



$$\frac{\kappa_0}{T} = \frac{\pi k_B^2}{9\hbar}\frac{l_s}{ad} = \frac{\pi}{9}\left(\frac{k_B}{\hbar}\right)^2 \frac{J}{d}\tau_s$$

a ~ 5.32 Å and d ~ 7.01 Å are nearest-neighbor and interlayer spin distance, respectively.

From the observed κ_0/T = 0.0062 $WK^{-2}m^{-1}$, the l_s (mean free path) is obtained as 36.6 Å, indicating that the excitations (spinons) are mobile to a distance seven times as long as the inter-spin distance without being scattered.

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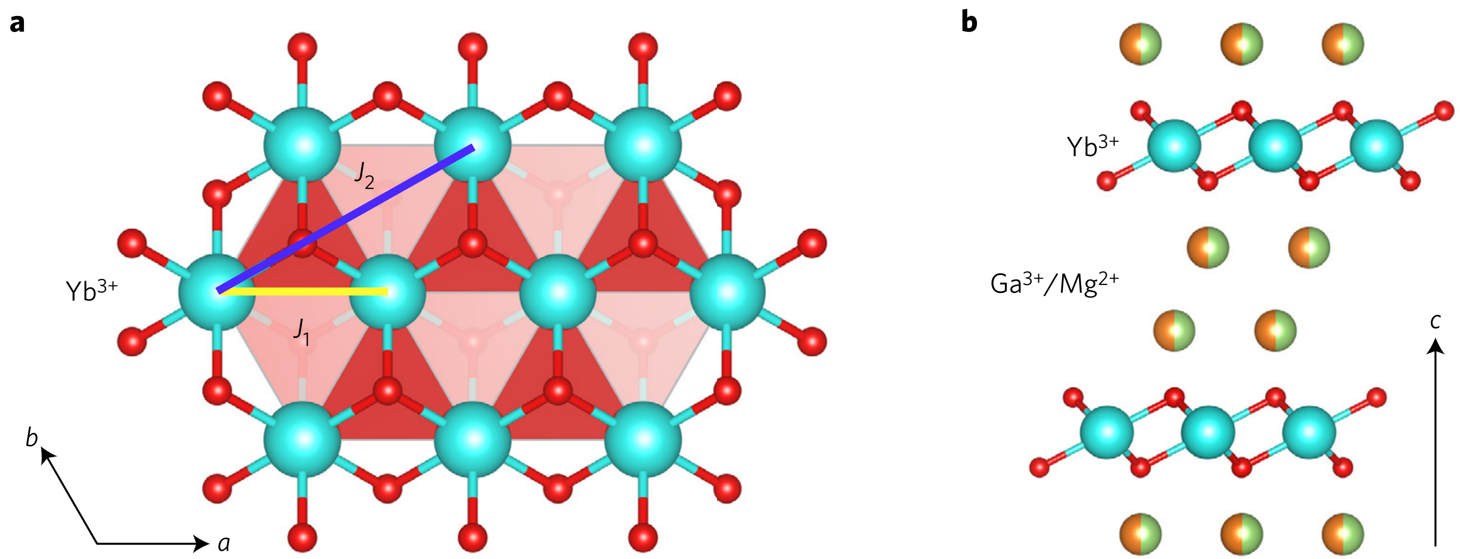
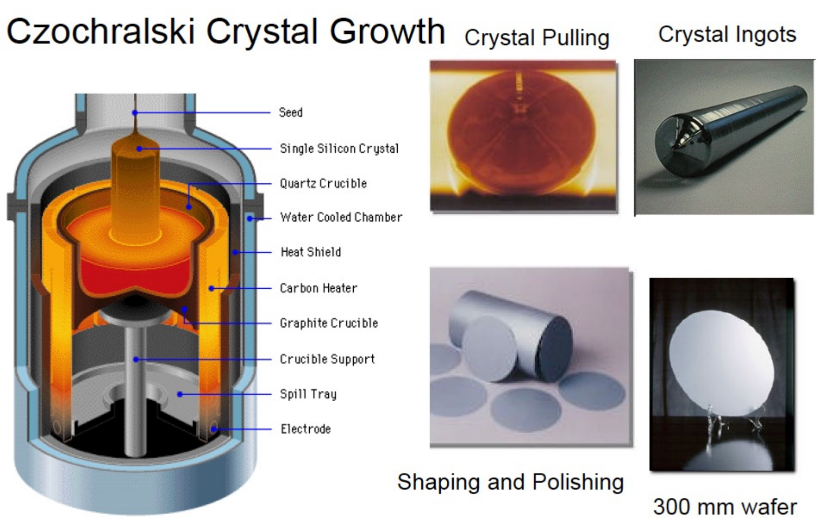
$YbMgGaO_4$, spin-1/2 triangular lattice antiferromagnet



Melting Growth

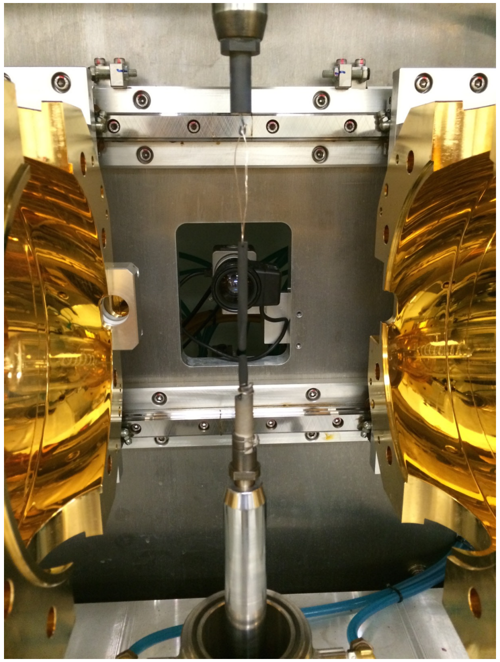
Bi Crystals grown in kitchen



Si crystal growth

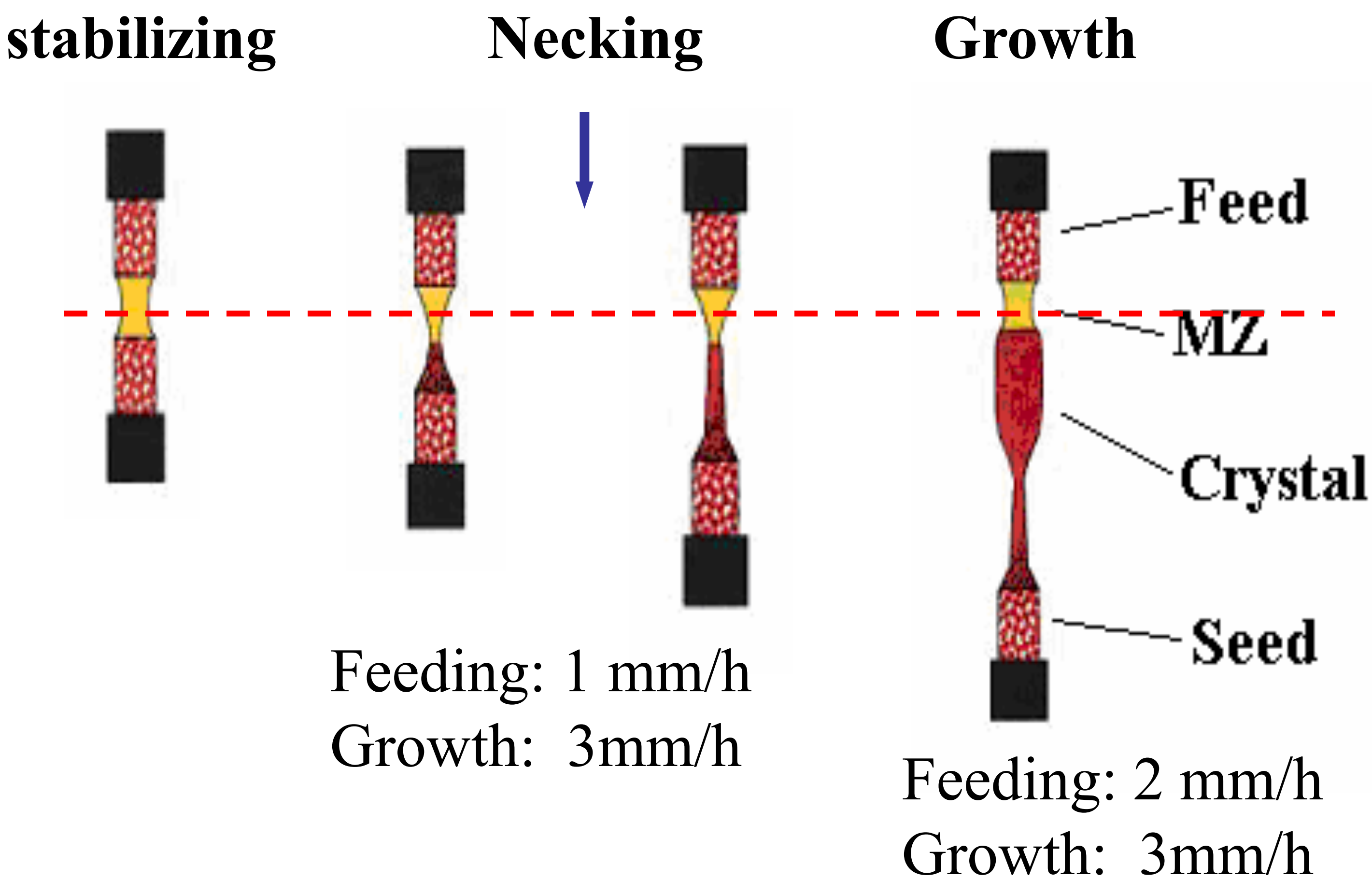
Image Furnaces

Two mirrors Image Furnace

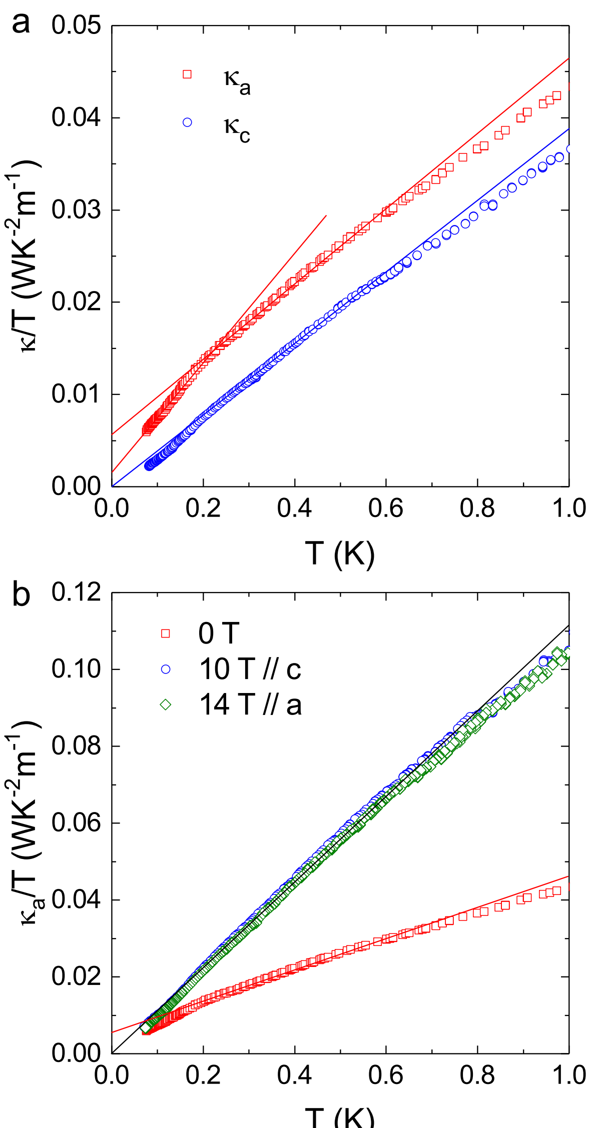


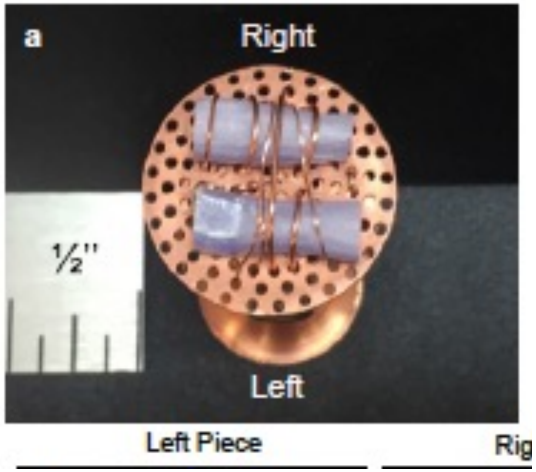
2200 Celsius degree

Crystal growth, floating zone technique



$YbMgGaO_4$, residual k_0/T term



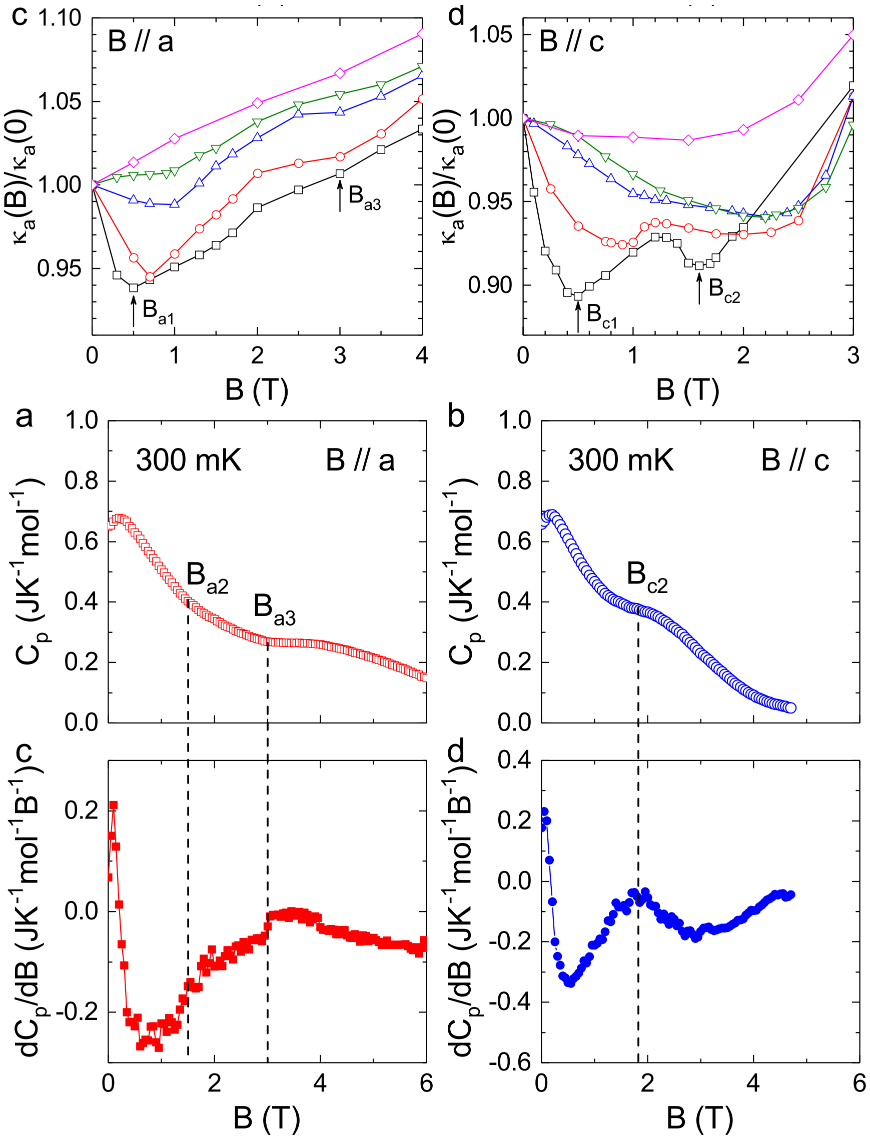


From the observed κ_0/T = 0.0058 WK^{-2}m^{-1}, the l_s (mean free path) is obtained as 78.4 Å, indicating that the excitations (spinons) are mobile to a distance 23 times as long as the inter-spin distance without being scattered.

The gapless QSL with itinerant excitations survives with Mg/Ga disorder

X. Rao, H. D. Zhou et al., Nature Communications ***12****, 4949 (2021).*

$YbMgGaO_4$, field induced spin state transitions



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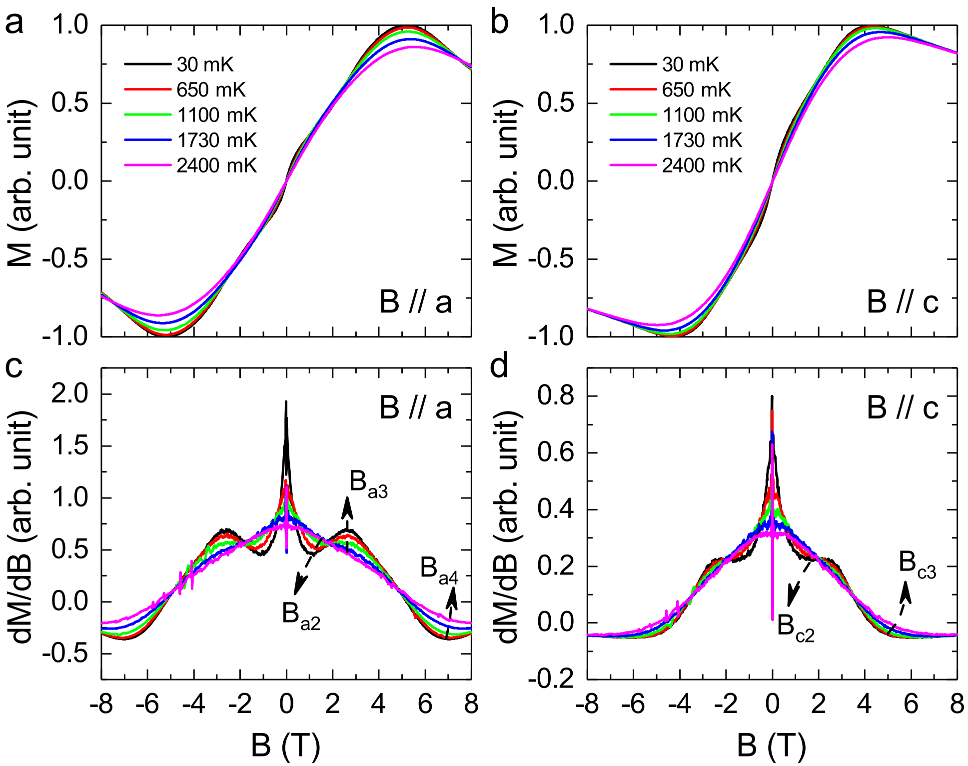
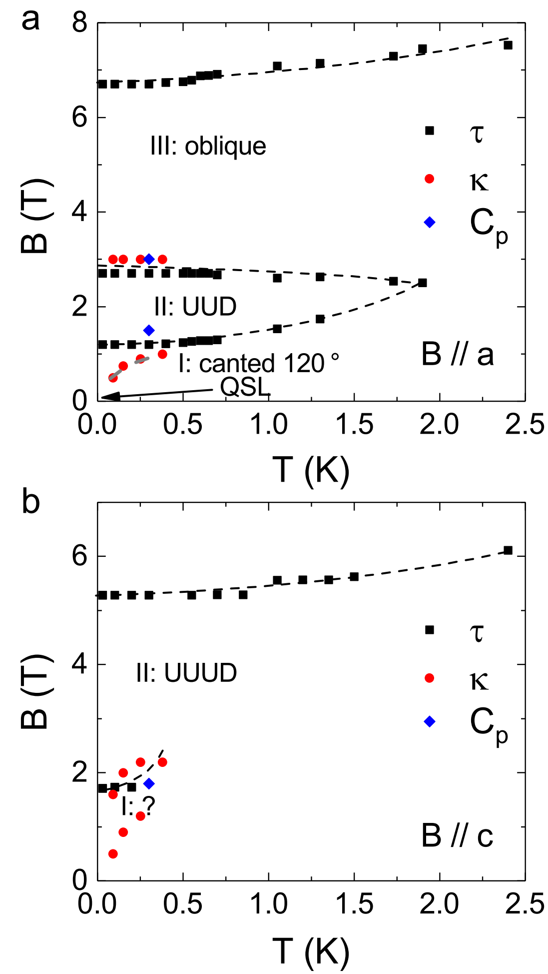
$YbMgGaO_4$, field induced spin state transitions





UUD phase with B // a
UUUD phase with B // c

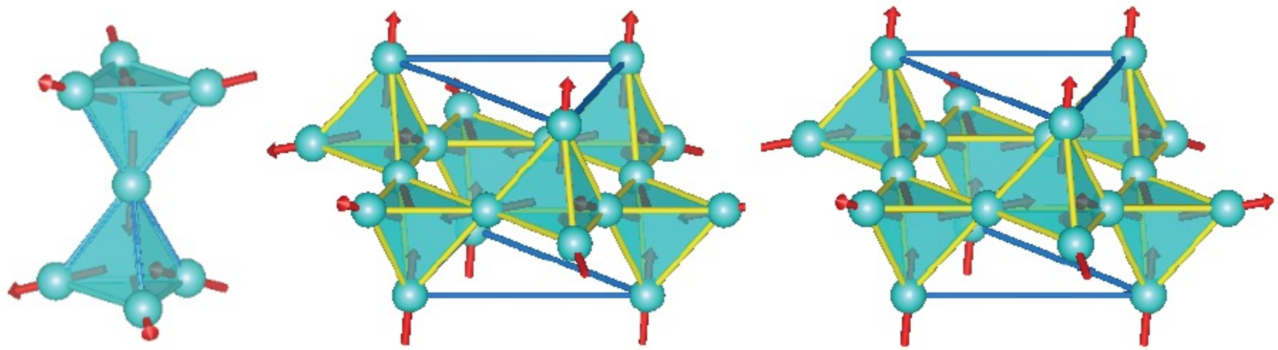
Magnetization plateau feature is weak due to disorder

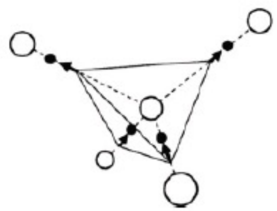
Pyrochlore heterostructure

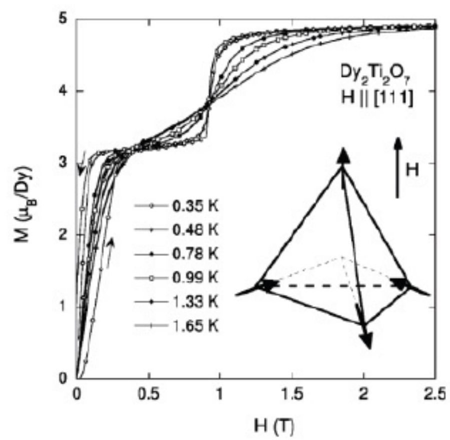
To explore a new route towards "metallization of quantum magnet" or electronically detect spin states and magnetic excitations

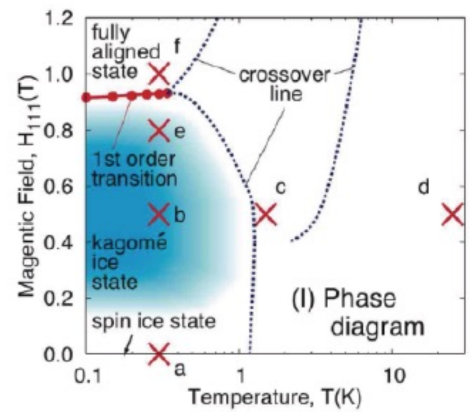
The hypothesis of the proposed approach is that, *when combined to form a heterostructure, the interfacial coupling between the magnetic degree of freedom in an insulating geometrically frustrated quantum magnet (GFQM) and the electronic degree of freedom in a spin-orbit-entangled correlated metal necessarily leads to electronic transport signatures that are characteristic of the unusual spin states and their elementary excitations*

Select Pyrochlore $Dy_2Ti_2O_7$ (DTO) as the GFQM





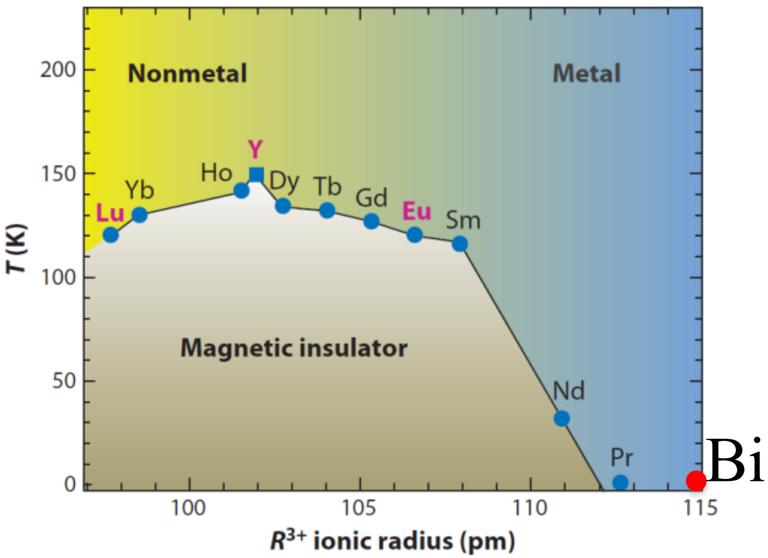


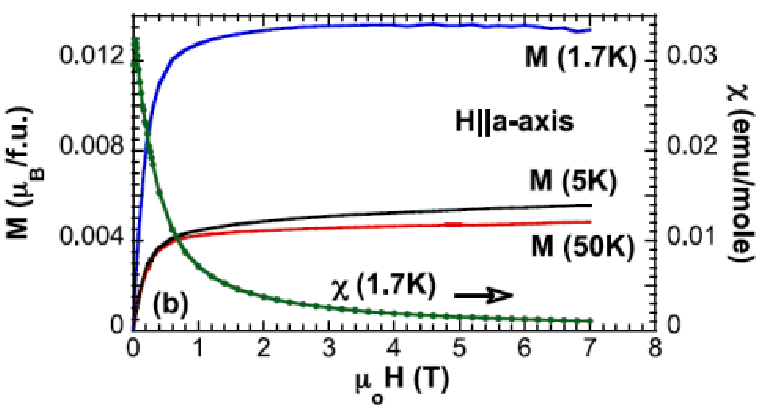


With applied field along the [111] axis, the spin ice (two in two out) state transforms to kagome spin ice and then three in one out state

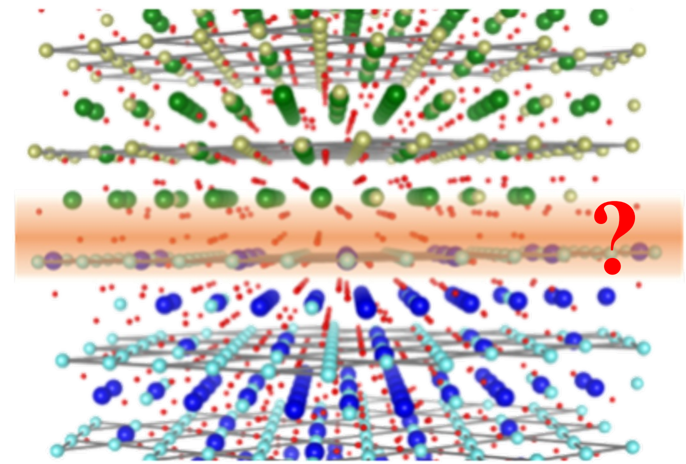
Sakakibara, T. et al Phys. Rev. Lett. ***90,*** *207205 (2003).*
Tabata, Y et al., Phys. Rev. Lett. ***97,*** *257205 (2006).*

Select Pyrochlore $Bi_2Ir_2O_7$ (BIO) as the Correlated Metal





Paramagnetic metal BIO



Spin Ice DTO

T. F. Qi et al., J. Phys. Condens. Matter ***24****, 345601 (2012);*
W. Witczak-Krempa et al., Annual Review of Condensed Matter Physics ***5****, 57 (2014).*

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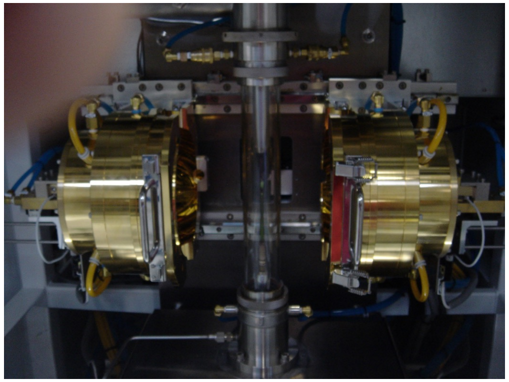
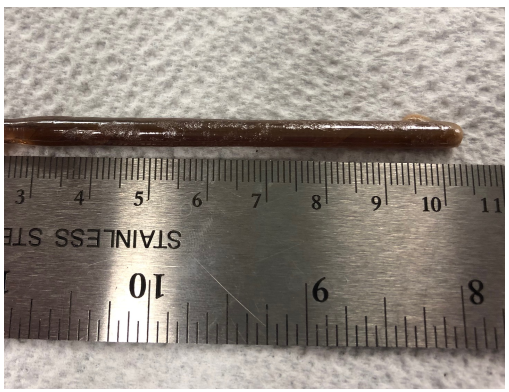
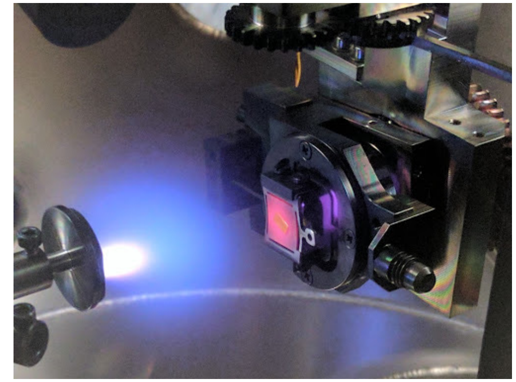
Growth (I): BIO film on DTO single crystal

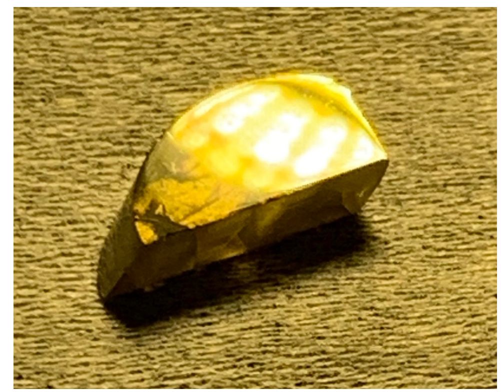
Floating Zone





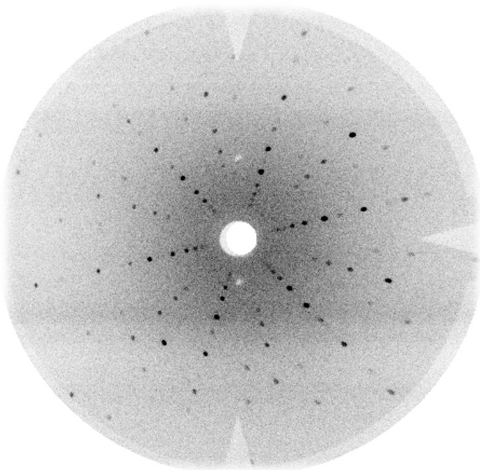
Pulsed Laser Deposition

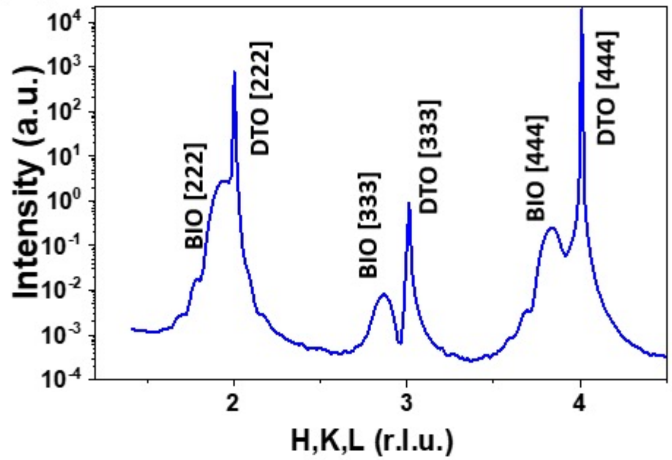


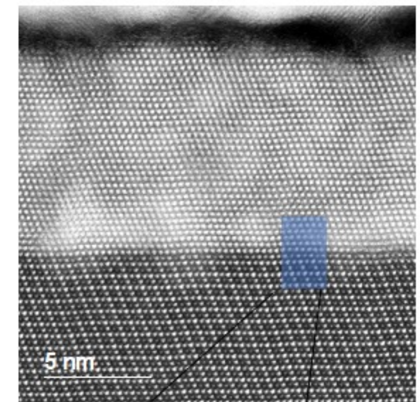


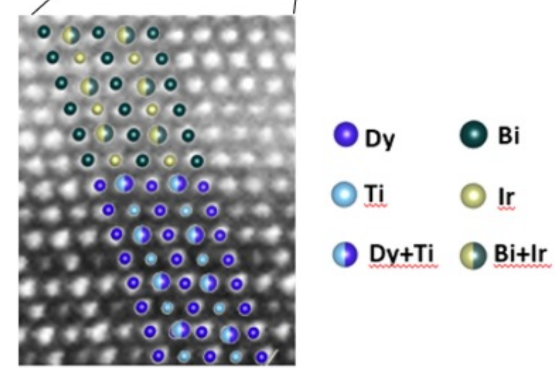
A combination of optical floating zone crystal growth and pulsed laser deposition is used to synthesize the DTO/BIO heterostructures along the [111] direction.

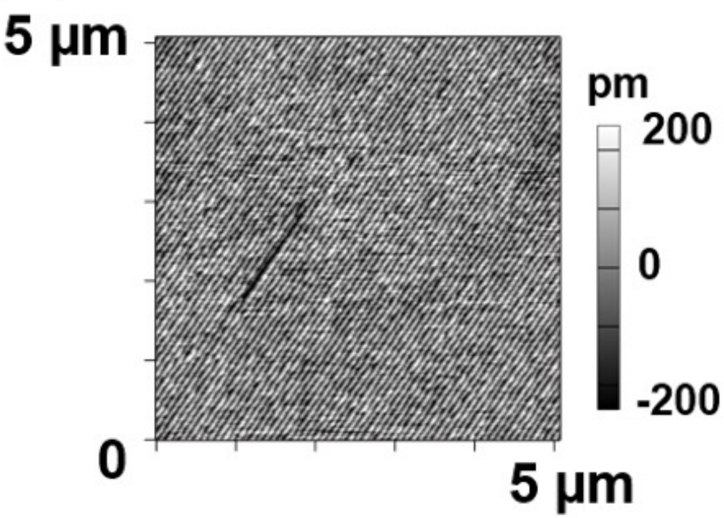
Growth (II): Orientation, Polish, Film, Interface

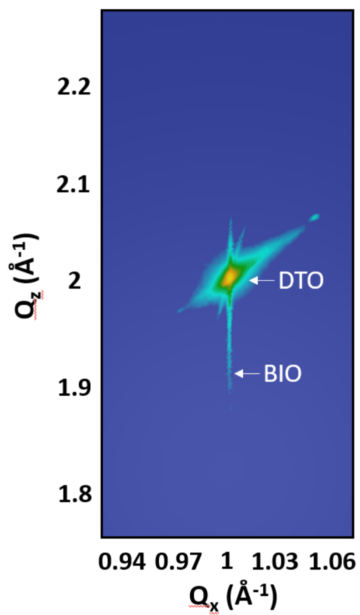












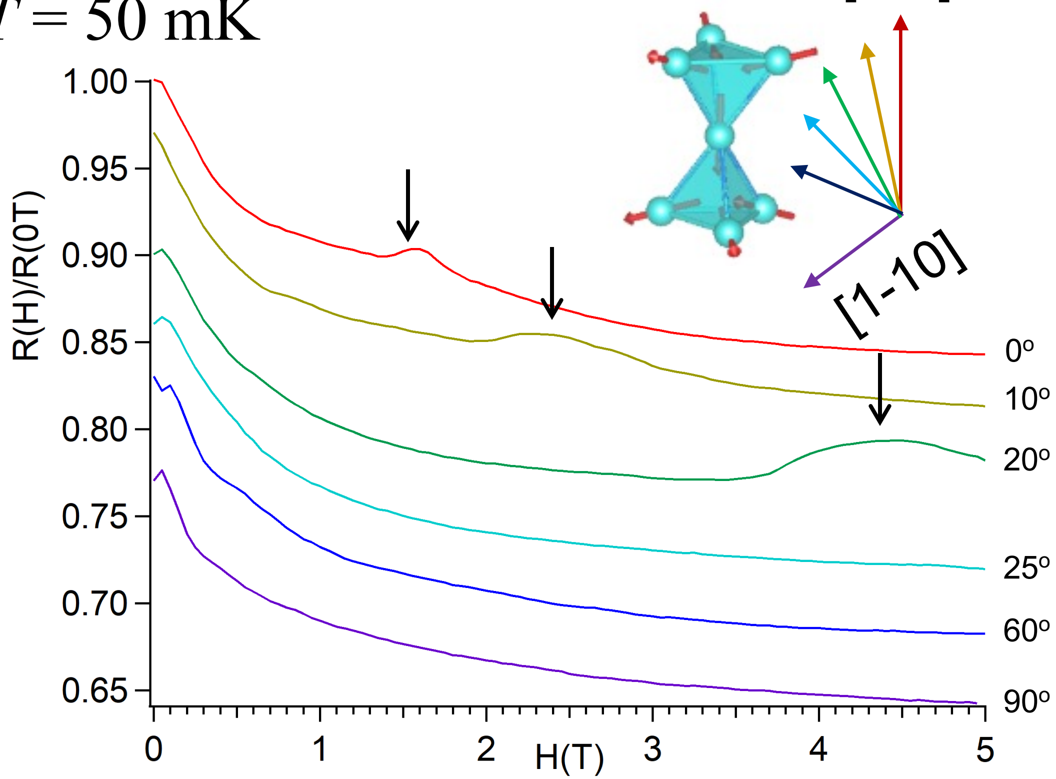
TEM, uniform interface

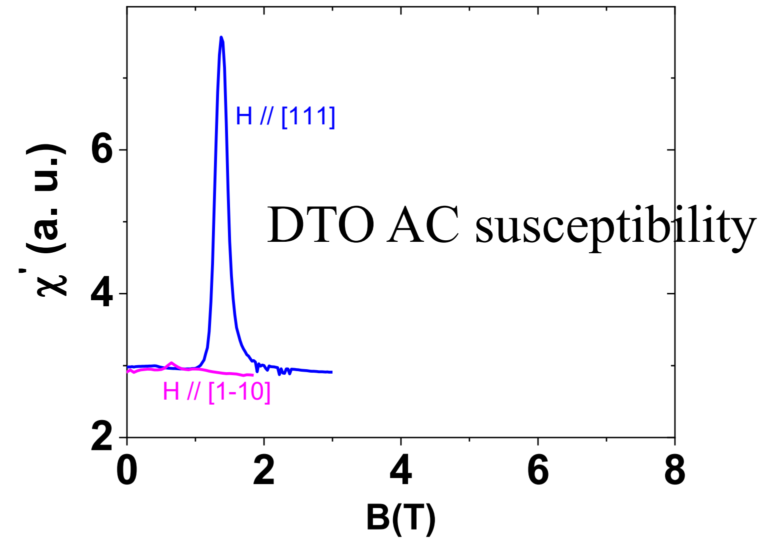
AFM, $R_s \sim 1.21$ Å

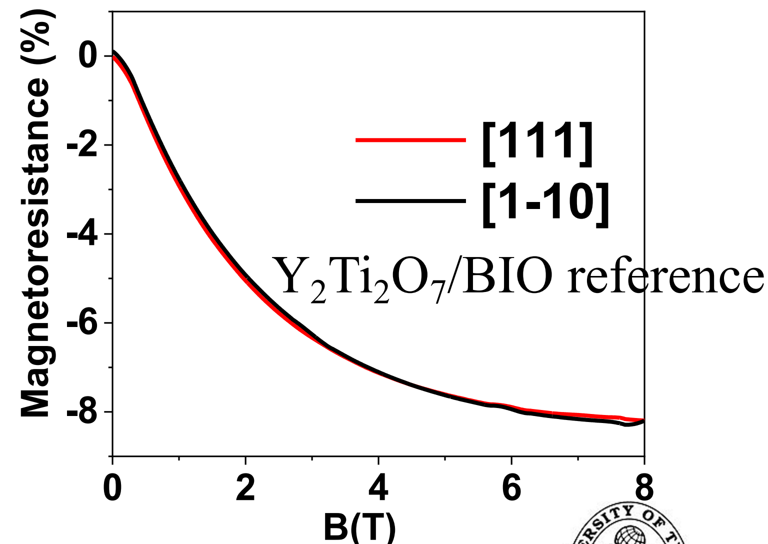
RSM, fully strained

Anomalous MR related to the ice-rule breaking

3 – 5 nm BIO film on DTO
$T = 50$ mK







MR feature occurs while DTO enters the three in one out state

H. Zhan, H.D. Zhou, J. Liu et al., arXiv:2011.09048

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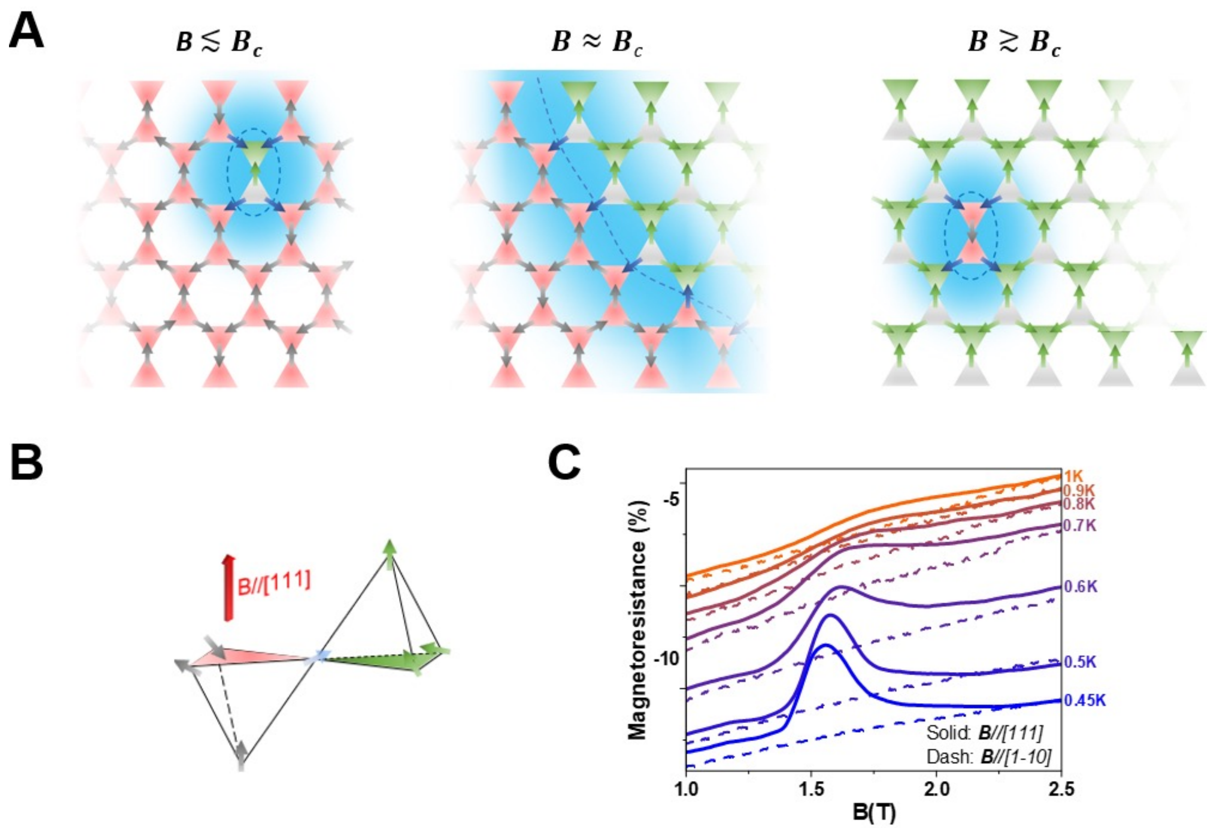
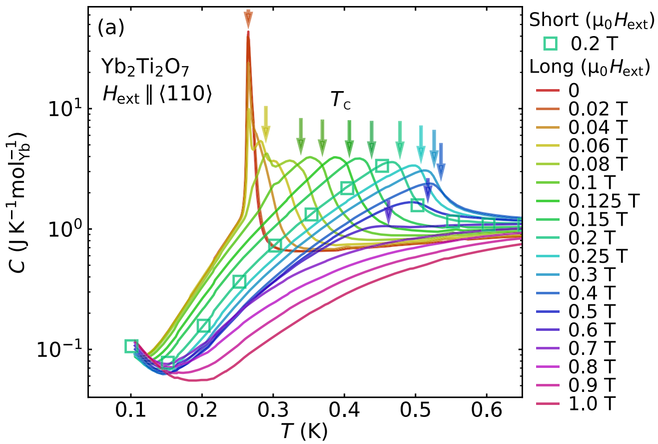
Anomalous MR (II): Temperature dependence

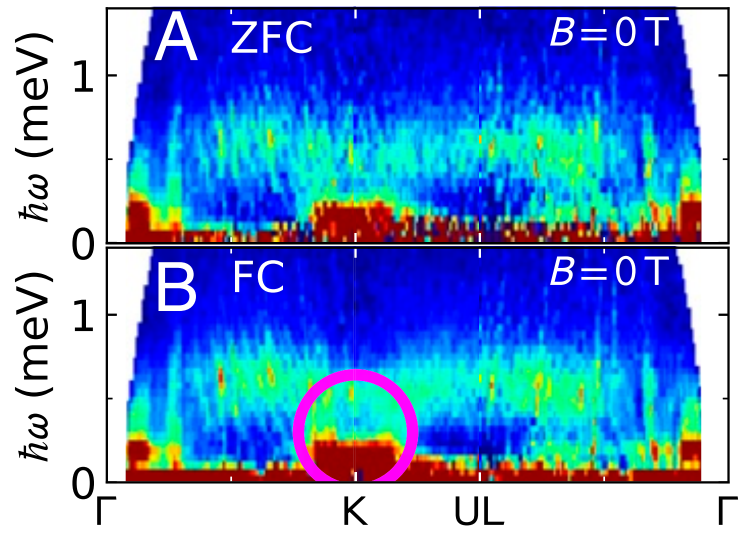


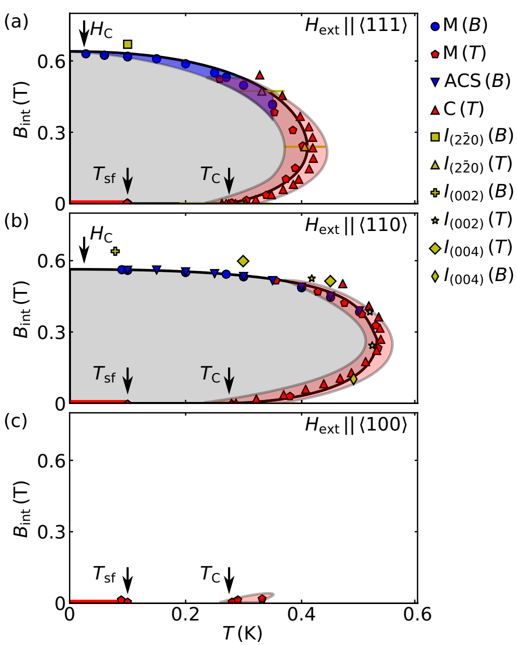
MR feature disappears above spin ice temperature

The anomalous MR responses can be depicted with the coexistence of the two spin states in the Kagome plane perpendicular to the field

$Yb_2Ti_2O_7/Bi_2Ir_2O_7$ heterostructure





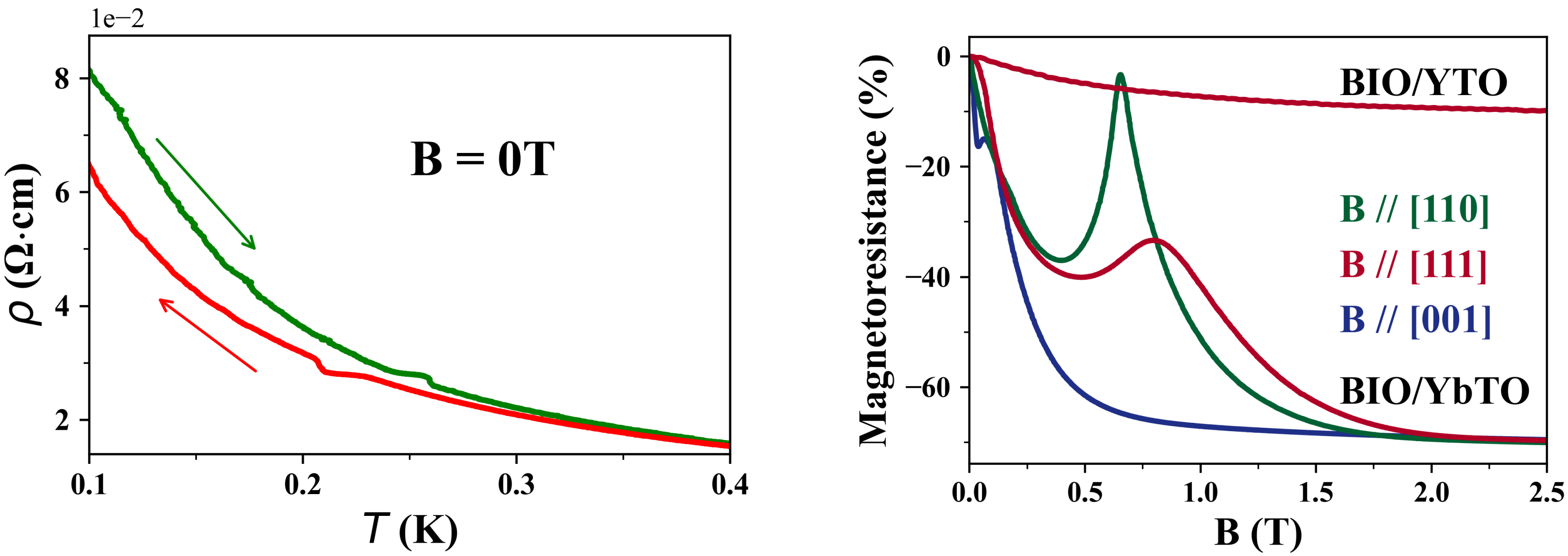


$Yb_2Ti_2O_7$: a ferromagnetic ordering at 0.28 K with strong quantum spin fluctuations

Ideal system to detect quantum spin fluctuations electronically

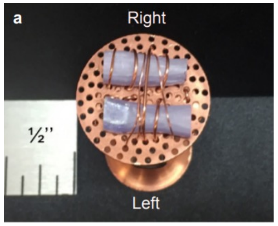
*A. Scheie et al., PNAS **117**, 27245 (2020).*
*S. Saubert et al., Physical Review B **101**, 174434 (2020).*

$Yb_2Ti_2O_7/Bi_2Ir_2O_7$ heterostructure



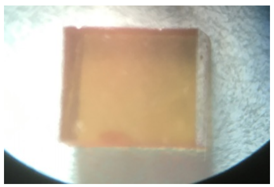
MR anomalies are related to strong quantum spin fluctuations at zero field, and the field dependence of the low energy excitation

Image Furnace

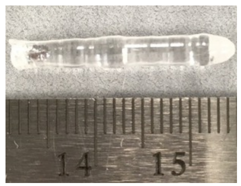


$YbMgGaO_4$
TLAF QSL

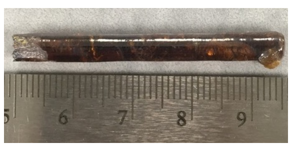
$Ba_3CoSb_2O_9$
TLAF QMP



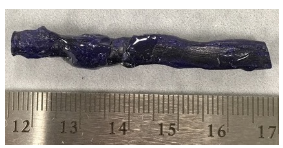
$Dy_2Ti_2O_7$
Pyrochlore Spin ice



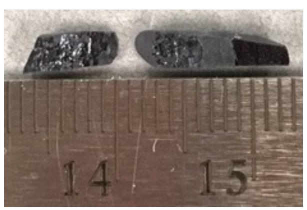
$Yb_3Ga_5O_{12}$
Garnet



$CaTiO_3$
Substrate



$SrCu_2(BO_3)_2$
Magnetization Plateau

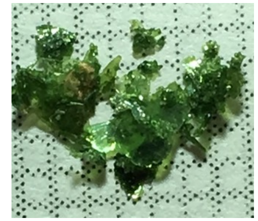


Sr_2RuO_4
SC

MnO
Magneto-structural coupling

Chemical Vapor Transport

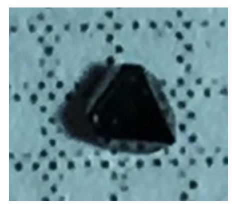
Cu_2OSeO_3
Skyrmion



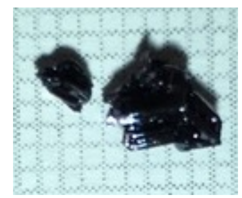
$MnPS_3$
2D magnet

MnP
SC under pressure

NbP
Weyl semimetal



$ZnCr_2Se_4$
spinel



RuO_2
Itinerant magnet

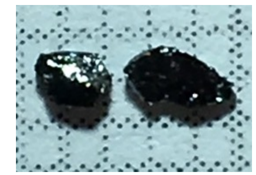
$CoNb_2S_6$
Anomalous Hall Eff.

FeS
MI transition

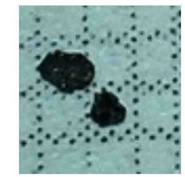
Flux

$NiTe_2$
Topological phase?

$Er_2Si_2O_7$
Honeycomb

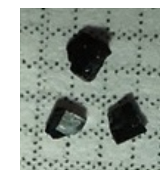


MnB_4
MI transition?

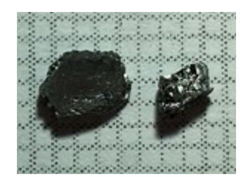


WB_2
Hexagonal?

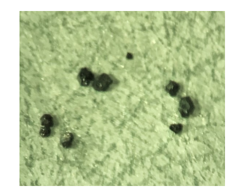
$CuCrO_2$
TLAF multiferroic



$GaFeO_3$
Multiferroic?



$Co_3Sn_2S_2$
Magnetic Weyl



Ba_2YIrO_6
Double Perov.

Summary

Geometrically frustrated lattice, magnetic ordering at extremely low temperatures, disorder, and spin-1/2, are good ingredients for QSL

Demonstrate a new route to electronically probe the exotic dynamics of geometrically frustrated quantum magnets through epitaxial interfaces.

Crystals = hard work + FedEx

Thank You