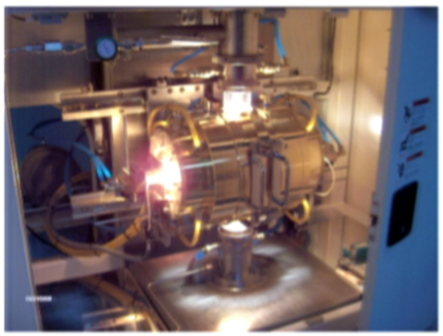
Title: Quantum Materials Discovery: The Synthesis of Geometrically Frustrated Magnets

Date: Jun 03, 2012 10:30 AM

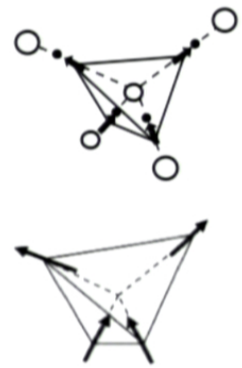
URL: http://pirsa.org/12060032

Abstract: In the last few decades, there has been a marked rise in the diversity of compounds studied with frustrated networks of spins. This was clearly not the case in the early days of this field, where only a handful of â€œmodelâ€• systems were being studied (ie. in two dimensions, the triangular or kagome lattices, and in three dimensions, the pyrochlore lattice). Solid state chemists have played a major role in not only the identification of new geometrically frustrated materials, but also in the synthesis of high quality crystals with low degrees of chemical disorder that are essential for direct comparisons to theory. In this tutorial, strategies for the discovery of new frustrated materials and their synthesis will be reviewed, with an emphasis on recent advances in the literature.

Quantum Materials Discovery: Synthesis of Frustrated Magnets



Professor Chris Wiebe
University of Winnipeg
University of Manitoba



THE UNIVERSITY OF WINNIPEG

UNIVERSITY OF MANITOBA

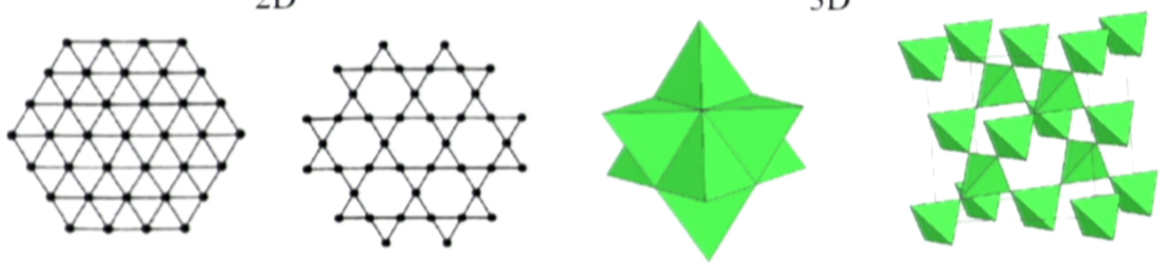
Solid state chemistry of frustrated magnets

- Outline:
- (1) Lattice types (targets for synthesis)
- (2) Synthesis methods
- (3) Crystal growth methods

Geometric Frustration

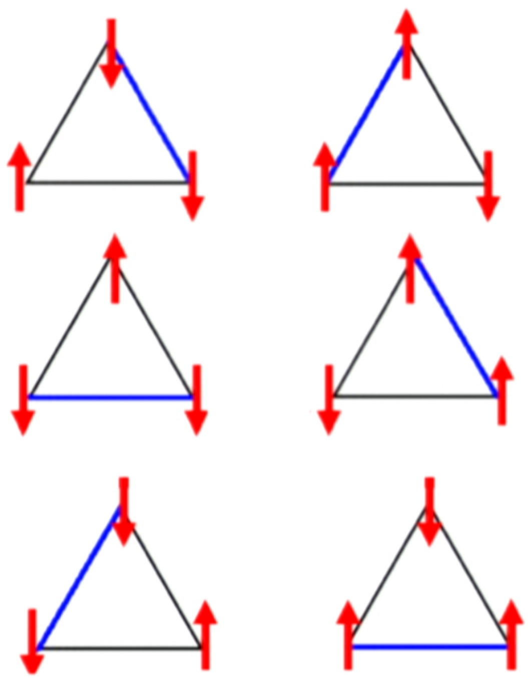
The inability of the magnetic spins to satisfy local ordering constraints------Frustration

2D 3D



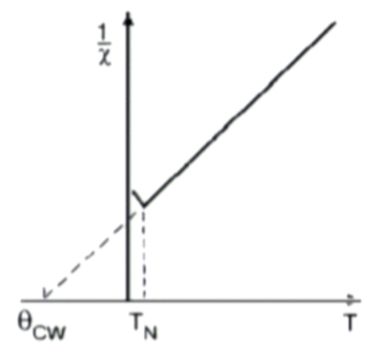
Triangular Kagome Face centered cubic Pyrochlore

Frustration and degeneracy



Degeneracies can persist.
When they do:

1. Spin fluctuations are enhanced.
2. Magnetic ordering is suppressed.

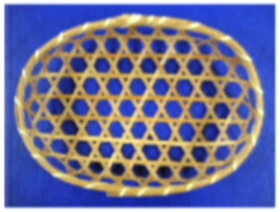


Frustrated $T_N << \theta_{CW}$

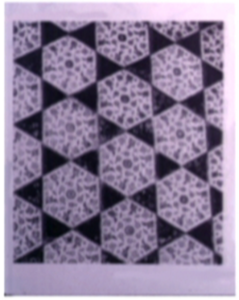
Ramirez introduced $f = |\theta_{CW}|/T_N > 10$

Inspirations for solid state chemistry

"Let no one destitute of geometry enter my doors."
Plato (c. 427 - 347 B.C.E.)



Kagome: eyes in the basket



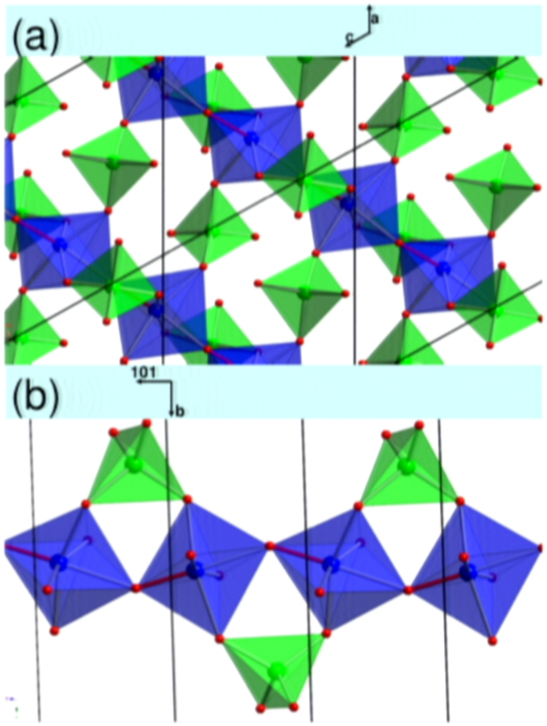
Islamic tiling pattern

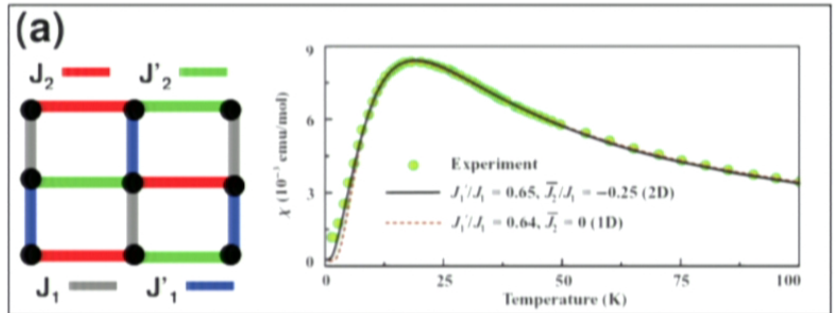
Frustration and dimensionality

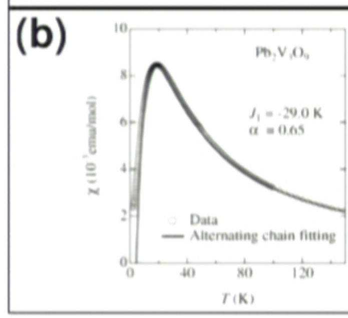
- Frustration in 1D: alternating antiferromagnetic/ferromagnetic exchange in spin chains
- Frustration in 2D: triangular lattice, kagomé lattice, square lattice
- Frustration in 3D: Spinel lattice, pyrochlore lattice, hyperkagomé, FCC

Frustration in 1D

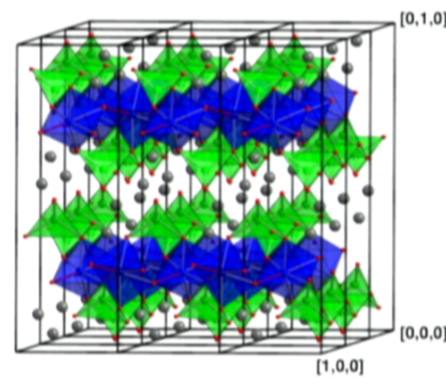
Alternating chain compound: S=1/2 $Pb_2V_3O_9$ (no order in zero field!)





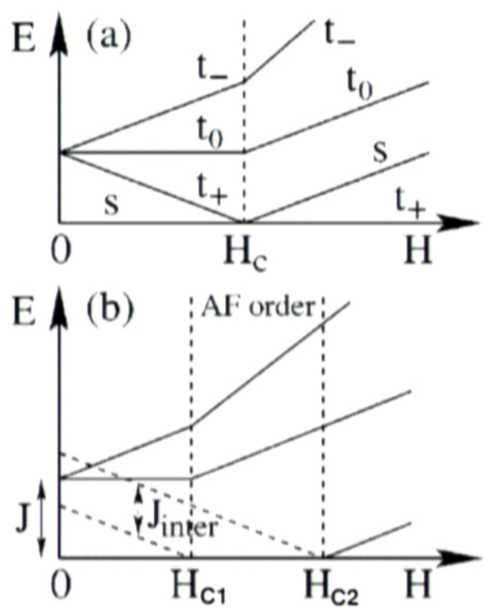


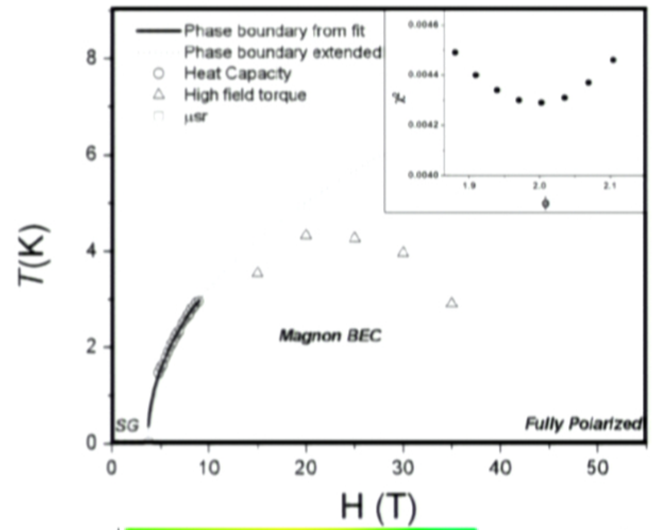
V^{4+}: blue
V^{5+}: green

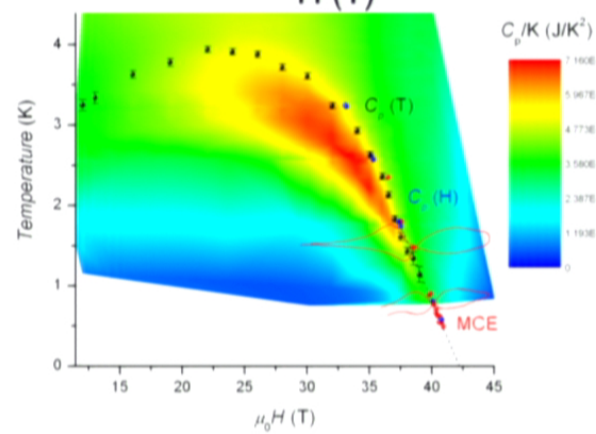


BEC of magnons?

In applied fields, a Zeeman splitting of the excited triplet state leads to a BEC of magnons!

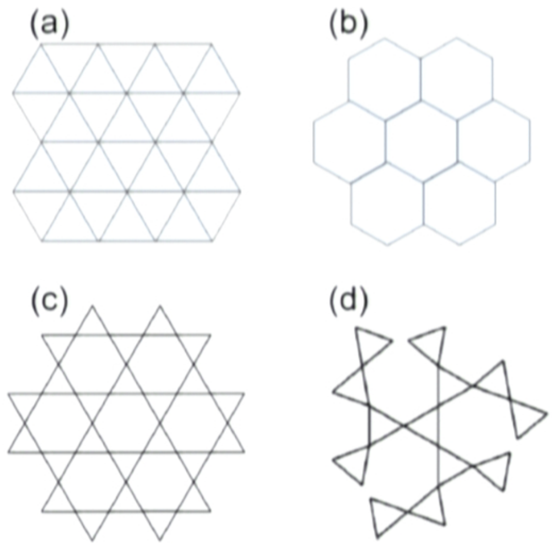




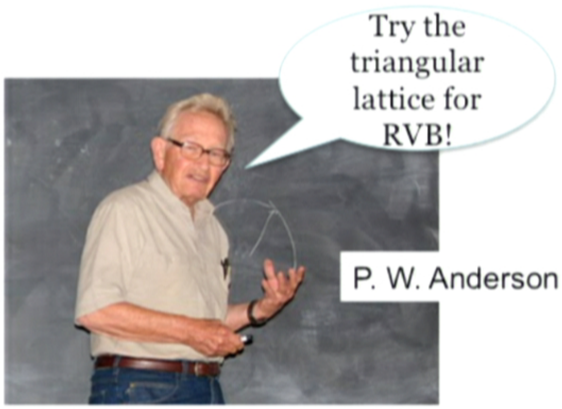


Frustration in 2D

Many ways of introducing two dimensionality on a magnetic sublattice.
Which compounds can we synthesize which have these motifs?



Frustration in the (a) triangular lattice (b) honeycomb lattice, (c) kagome lattice and (d) Bethe lattice



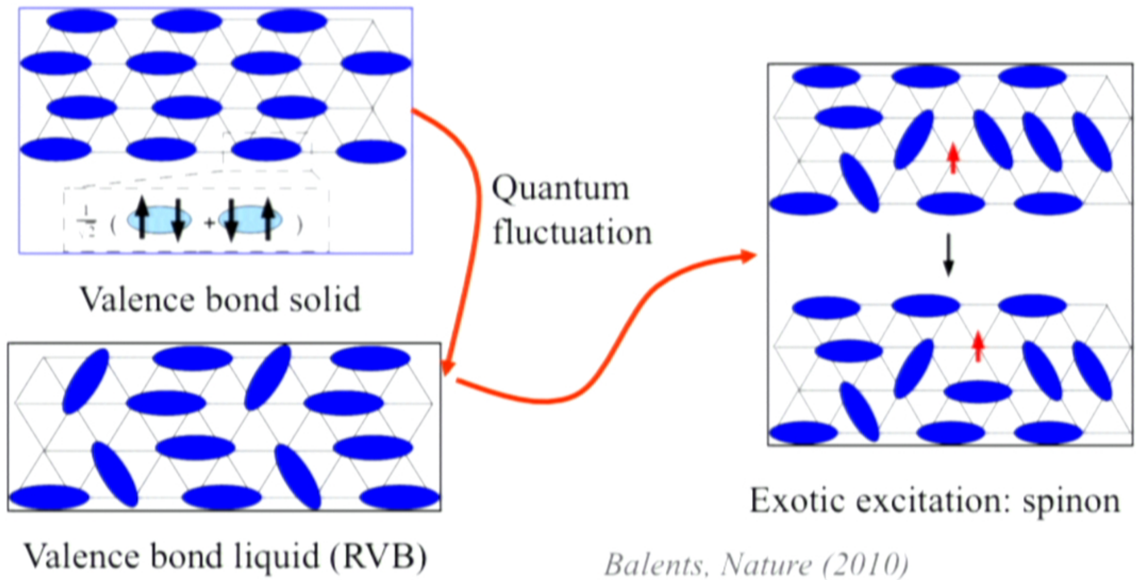
Triangular lattice

Quantum Spin Liquid (QSL)

Quantum fluctuations destabilize the ordered state

Resonating valence bond (RVB) state

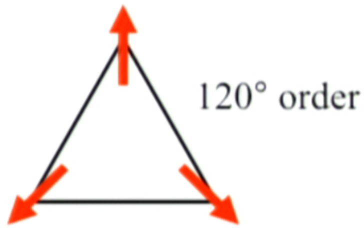
Anderson Mater. Res. Bull. (1973)

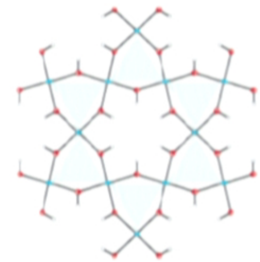


Balents, Nature (2010)

Néel vs. QSL

Néel states usually win... but not always!





"An end to the drought of QSL"
Patrick A. Lee, Science (2008)

κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

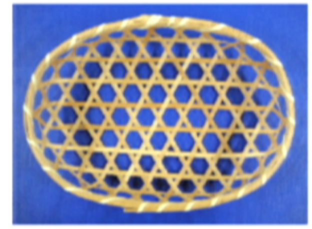
$ZnCu_3(OH)_6Cl_2$

Table 1 | Some experimental materials studied in the search for QSLs

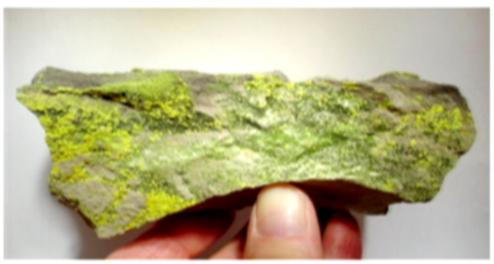
Material	Lattice	S	Θ_{CW} (K)	R*	Status or explanation
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$	Triangular†	½	−375‡	1.8	Possible QSL
$EtMe_3Sb[Pd(dmit)_2]_2$	Triangular†	½	−(375–325)‡	?	Possible QSL
$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ (volborthite)	Kagomé†	½	−115	6	Magnetic
$ZnCu_3(OH)_6Cl_2$ (herbertsmithite)	Kagomé	½	−241	?	Possible QSL
$BaCu_3V_2O_8(OH)_2$ (vesignieite)	Kagomé†	½	−77	4	Possible QSL
$Na_4Ir_3O_8$	Hyperkagomé	½	−650	70	Possible QSL
Cs_2CuCl_4	Triangular†	½	−4	0	Dimensional reduction
$FeSc_2S_4$	Diamond	2	−45	230	Quantum criticality

Balents Nature (2010)

Kagomé lattice

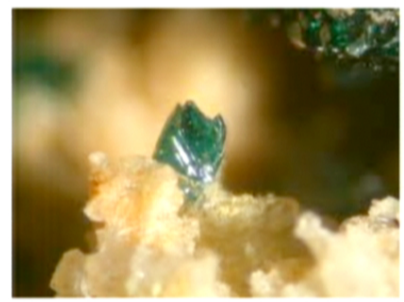


- Different lattice topology than triangular lattice, but still a candidate for quantum spin liquid states.
- Many naturally occurring minerals contain the kagomé magnetic sublattice, such as volborthite, jarosite, and herbertsmithite.
- These can be grown by hydrothermal methods (more on this later).



Volborthite (Cu kagomé sublattice)

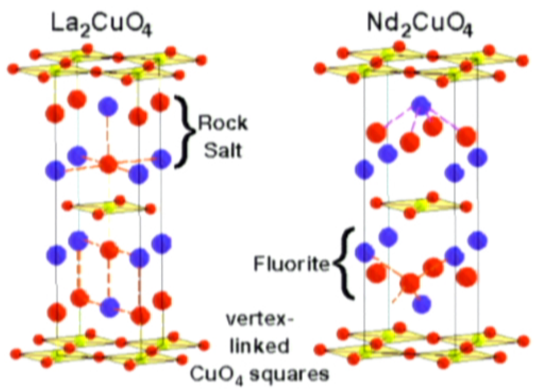
Iron Jarosite

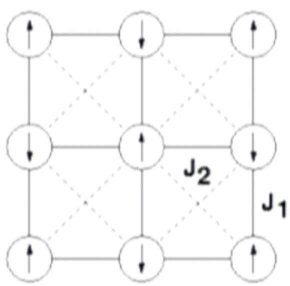


Herbertsmithite (Cu sublattice)

Square lattice

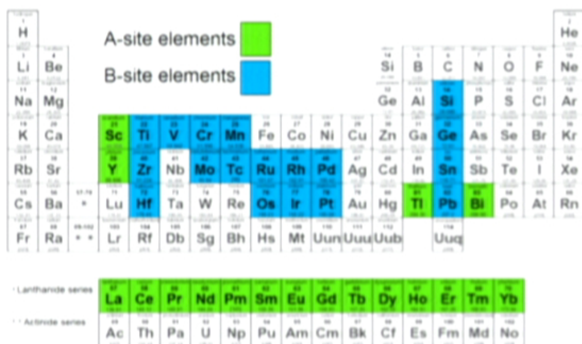
- At a first glance, a conventional Néel state can be formed in the 2D square lattice for nearest neighbour antiferromagnetic exchange (J_1)
- However, for next nearest neighbour antiferromagnetic exchange, the lattice is frustrated (J_2)
- This underlying frustration is important for the physics of the cuprates and related compounds.

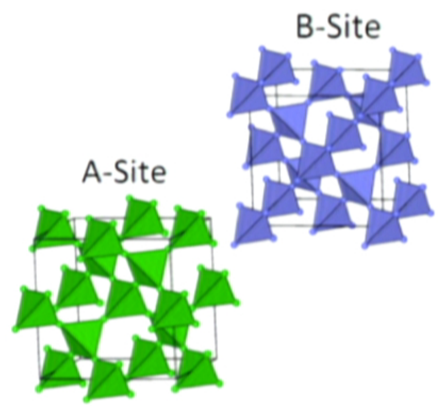




Frustration in 3D: Pyrochlore structure

- The pyrochlore lattice, of general form $A_2B_2O_7$, has two interpenetrating networks of corner shared tetrahedra on the A and B cubic sublattices.
- Typically, the A site is trivalent and the B site is tetravalent.
- Enormous variety of ground states! Spin liquids, spin ices, exotic magnetic ordering, strange metallic behaviour, spin glasses.... (See Gardner, Gingras and Greedan, Review of Modern Physics, 2010).

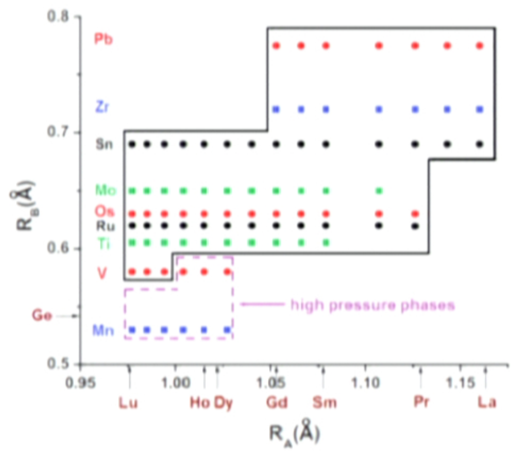




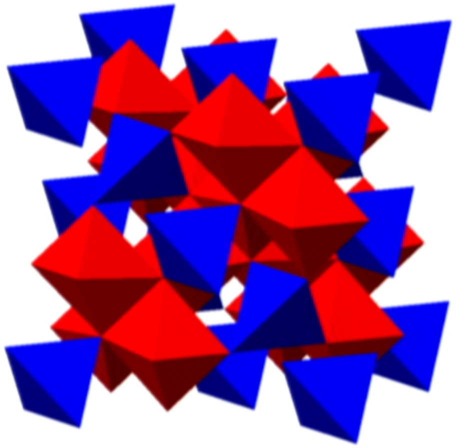
Pyrochlore structural stability

- The pyrochlores are naturally occurring minerals, so they are very stable.
- While flux growths are common, many pyrochlores can be grown in the image furnace (more on this later).
- The A site forms the framework for the lattice. If it is too small, the lattice will collapse to the fluorite structure or distorted monoclinic lattices.

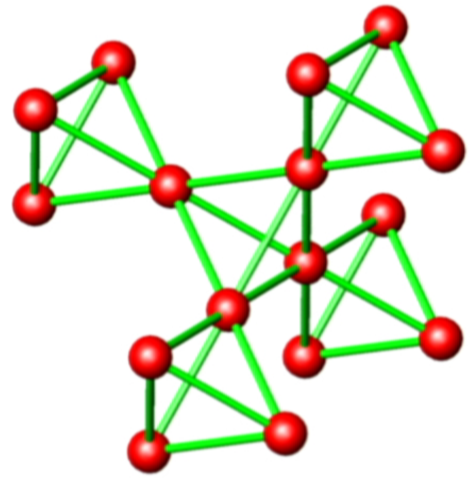
Pyrochlore found in Quebec!
$(Na,Ca)_2Nb_2O_6(OH,F)$



Spinel structure



$A[B_2]O_4$
AO_4 tetrahedron
BO_6 octahedron

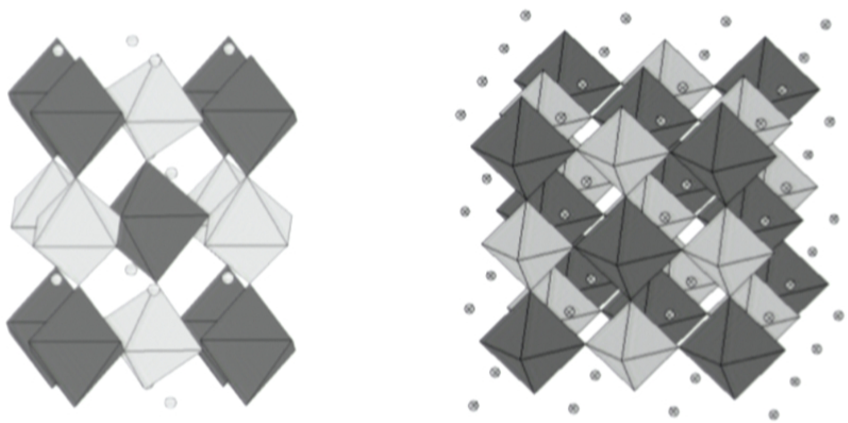


B ions form the three-dimensional network of corner-sharing tetrahedra.

Geometrically frustrated pyrochlore lattice

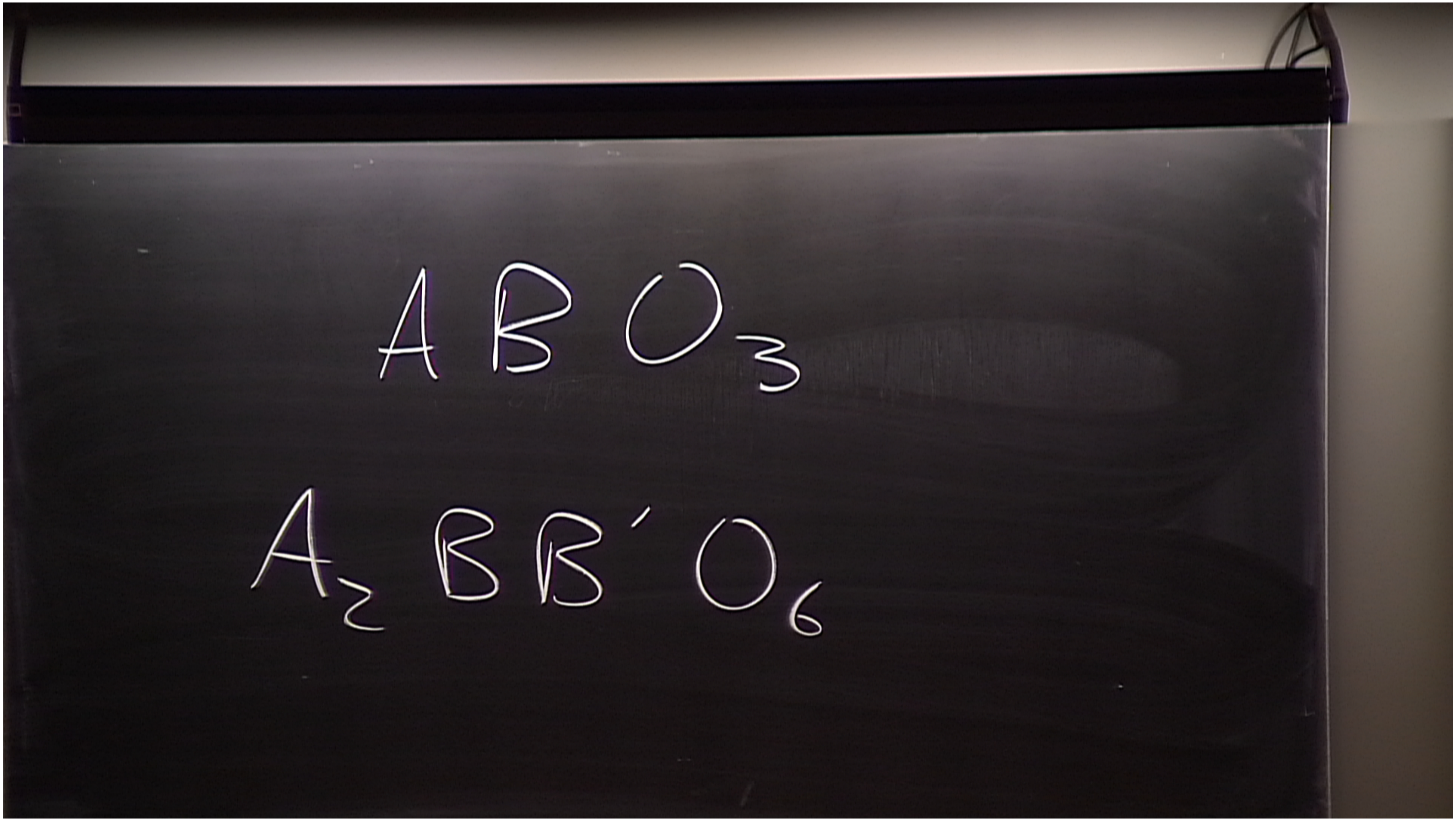
FCC structure

- The FCC lattice, which can be thought of as a network of edge-shared tetrahedra, is in principle frustrated for nearest-neighbour antiferromagnetic interactions.
- One of the routes to ordered FCC lattices is through the double perovskites of the form $A_2BB'O_6$, where B and B' are transition metal ions. Proper choices of B and B' will ensure cation ordering (ie. different charge/size).



Crystal structure of La_2LiMoO_6 (an exotic spin glass), with dark grey MoO_6 octahedra and light grey LiO_6 octahedra. Both of these form frustrated networks, with Mo^{5+} as the S=1/2 magnetic species.

Aharen, Wiebe *et al*, PRB, 2010


ABO_3
$A_2BB'O_6$

Synthesis techniques

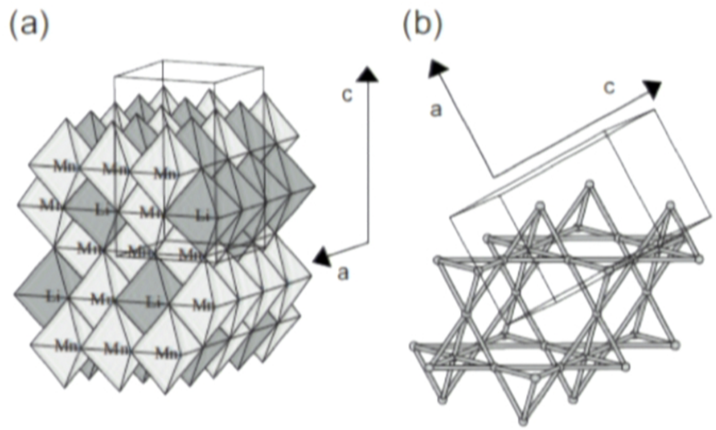
- Traditionally, solid state chemists have used "heat and beat" methods to synthesize samples - combining stoichiometric quantities of materials, pressing into pellets to improve kinetics, and then firing at high temperatures.
- Over the years, there has been a host of other methods that have become popular (too numerous to list here!), which includes intercalation techniques, high pressure synthesis, and sol-gel methods.

Intercalation methods

- The properties of some materials can be changed by intercalation of ions into the lattice without changing the frustrated topology. For example, in the spinel $LiMn_2O_4$, extra Li ions can be inserted with a reaction using butyl-Lithium at low temperatures in inert conditions:

$LiMn_2O_4$ + n-butyl-Li → butane + $Li_2Mn_2O_4$

(40 degrees C in dried hexane solution, Ar environment)



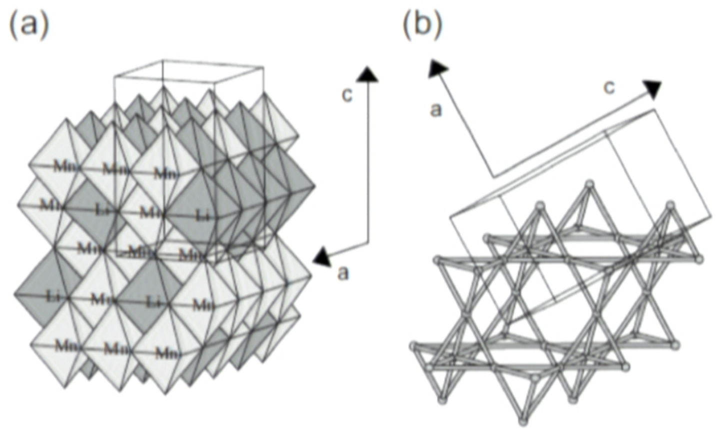
- $Li_2Mn_2O_4$ has the same spinel structure, but the oxidation state of Mn is now Mn^{3+} instead of mixed Mn^{3+}/Mn^{4+}. This leads to a 2D ordering in the compound in kagome layers that exist within the pyrochlore structure (Wiebe *et al*, JPCM, 2005).

Intercalation methods

- The properties of some materials can be changed by intercalation of ions into the lattice without changing the frustrated topology. For example, in the spinel $LiMn_2O_4$, extra Li ions can be inserted with a reaction using butyl-Lithium at low temperatures in inert conditions:

$LiMn_2O_4$ + n-butyl-Li → butane + $Li_2Mn_2O_4$

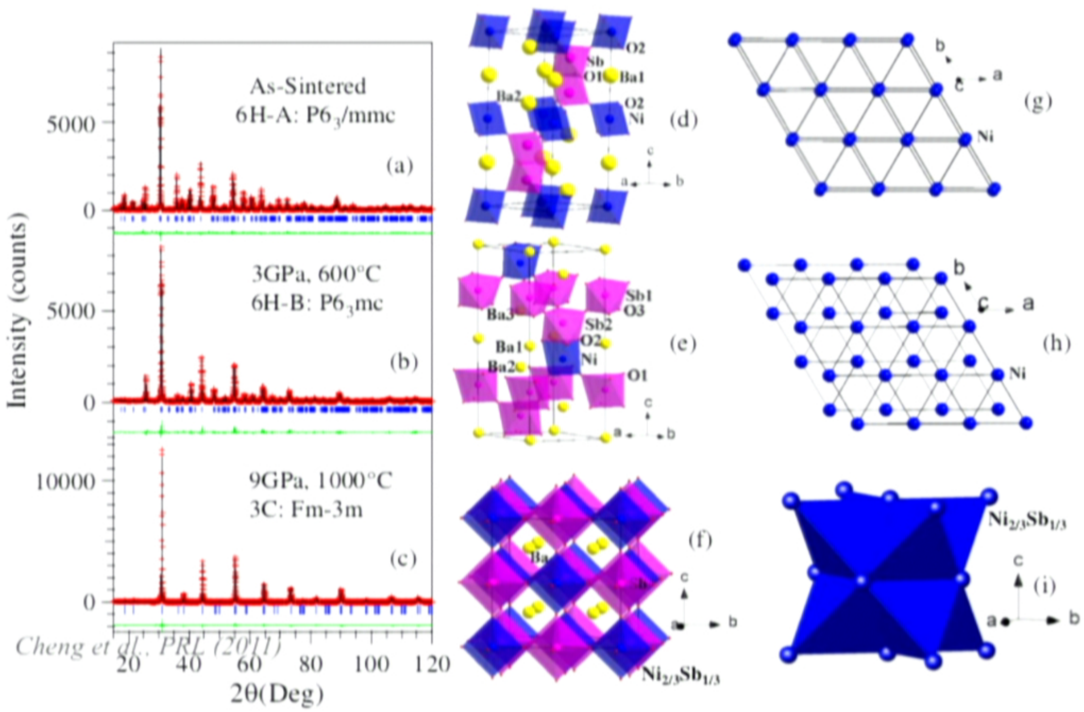
(40 degrees C in dried hexane solution, Ar environment)



- $Li_2Mn_2O_4$ has the same spinel structure, but the oxidation state of Mn is now Mn^{3+} instead of mixed Mn^{3+}/Mn^{4+}. This leads to a 2D ordering in the compound in kagome layers that exist within the pyrochlore structure (Wiebe *et al*, JPCM, 2005).

High pressure phases

High pressure reaction conditions can be used to attain quasistable phases!

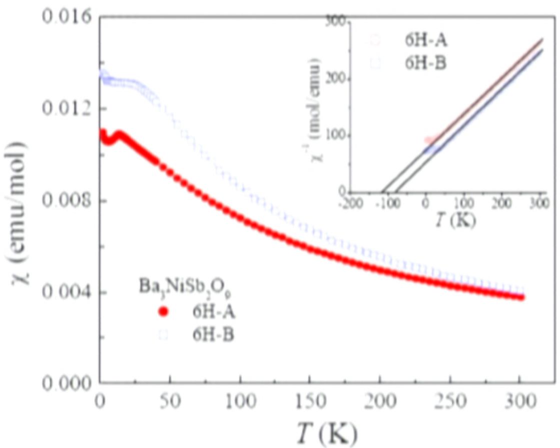


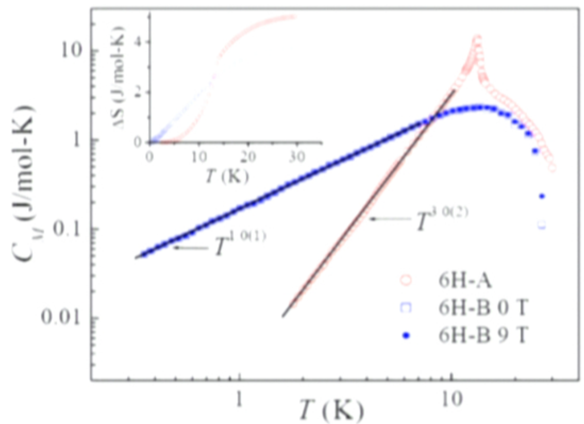
$Ba_3NiSb_2O_9$ high pressure phases.

Spin solid to spin liquid

Cheng, H. D. Zhou et al., PRL (2011)

QSL S =1?   3GPa 600 °C 6H-B phase $Ba_3NiSb_2O_9$



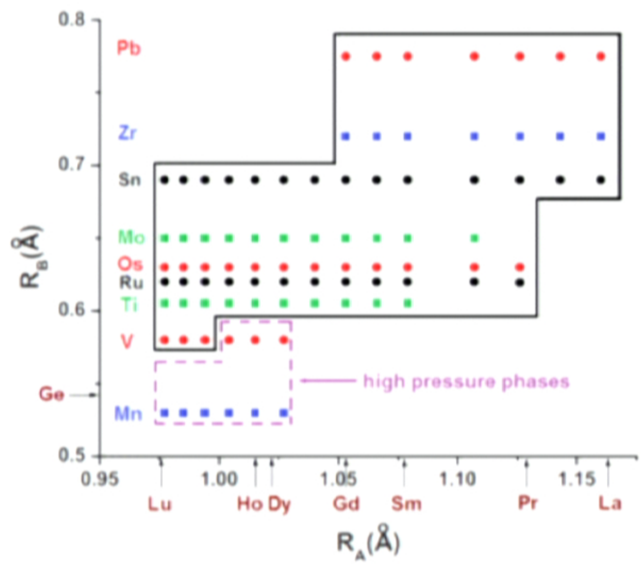


6H-A
T_N = 13 K
θ_{CW} = -117 K, f = 9
$C_M \sim T^3$, 3D AFM

6H-B
No ordering down to 0.35 K
θ_{CW} = -76 K, f > 217
χ_0 = 0.013 emu/mol
$C_M \sim \gamma T$, γ = 168 mJ/molK^2
R = 5.6

High pressure pyrochlores

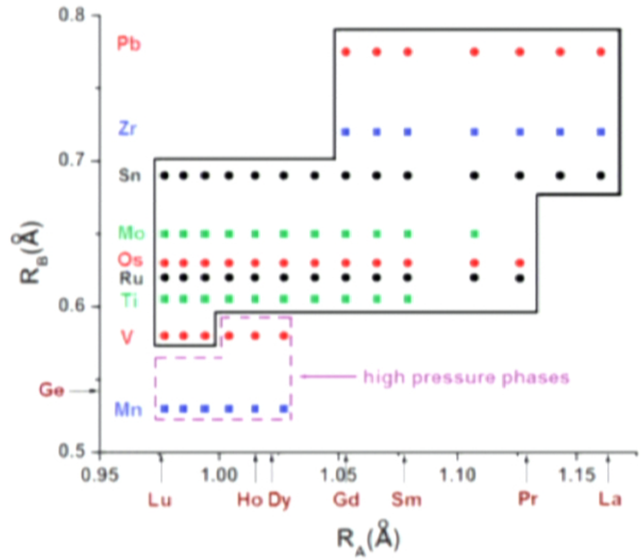
Within the stability field of the pyrochlores, there are some phases that can be synthesized under high pressure (dashed line). The Ge pyrochlores, fall into this category, in which many members of the rare earth series are quasistable. $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$ represent new spin ice phases, for example.



For more on this see Wiebe's talk (Monday) or Hallas' poster (Tuesday).

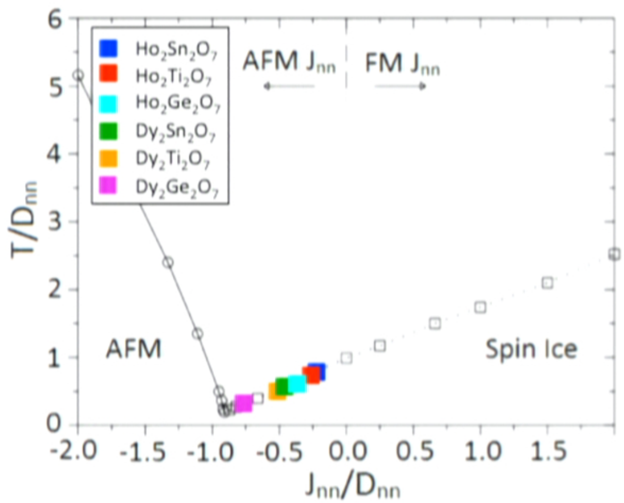
High pressure pyrochlores

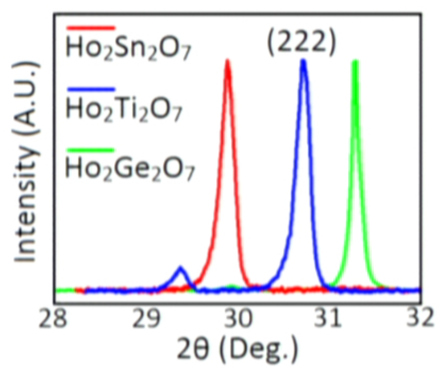
Within the stability field of the pyrochlores, there are some phases that can be synthesized under high pressure (dashed line). The Ge pyrochlores, fall into this category, in which many members of the rare earth series are quasistable. $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$ represent new spin ice phases, for example.

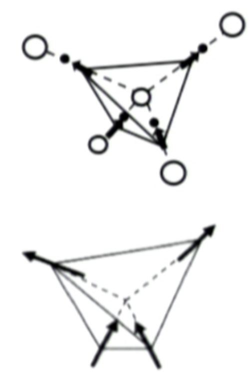


For more on this see Wiebe's talk (Monday) or Hallas' poster (Tuesday).

High pressure routes to new spin ices





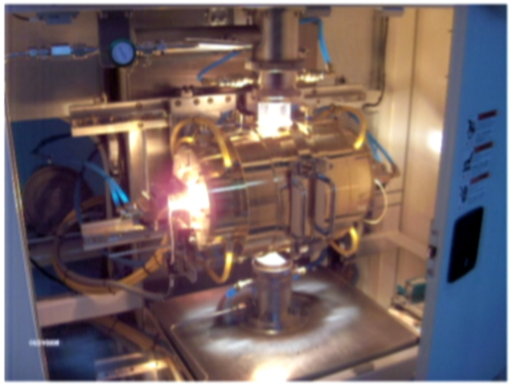


[4] H.D. Zhou, A.M. Hallas et al. Phys. Rev. Let. 108, 207206 (2012)

The Ge pyrochlores can be used to test the den Hertog/Gingras phase diagram for spin ices. For more on this see Wiebe's talk (Monday) or Hallas' poster (Tuesday).

Crystal growth

- Many methods for growing crystals, but popular ones include flux growth, vapour transport, hydrothermal and image furnace crystal growth.
- Image furnaces have completed changed how we think about sample preparation, especially for probes such as neutron scattering which require large, single crystals.



A floating zone image furnace, which uses light to grow crystals from polycrystalline feed rods.

Flux growth

Traditional method: Use of a solvent (flux) to bring down the temperature of the solute. As the temperature is lowered, crystals form, and the flux is removed.

ACr_2O_4
flux growth

Polycrystalline

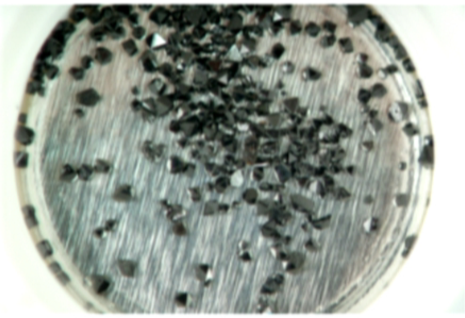
ZnONiO/CuO
$+Cr_2O_3$ in air

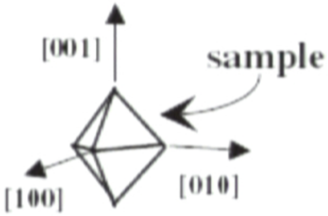
$MnO+Cr_2O_3$ in Ar

1000°C-1400°C

Bi_2O_3 flux
Mass ratio: ACr_2O_4:Bi_2O_3(1:8)
1250°C-2°C/hour-800°C in Pt crucible

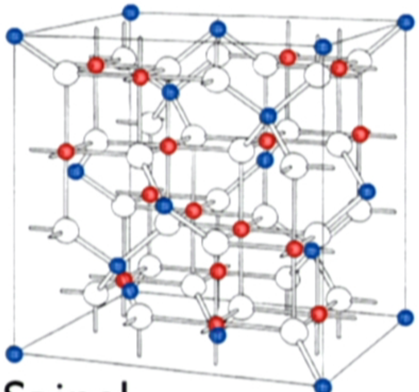
Bi_2O_3 is cleaned by HNO_3



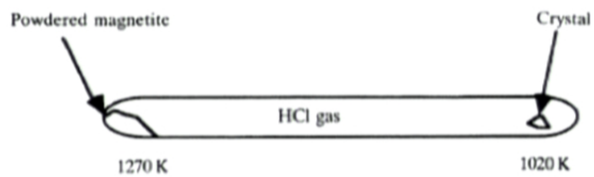


Vapour transport

$Fe_3O_4(s) + 8\ HCl(g) \rightarrow FeCl_2(g) + 2\ FeCl_3(g) + 4\ H_2O(g)$
Endothermic reaction - as T is increased, equilibrium is shifted to the right (results in Fe_3O_4 deposited at the cold end of the tube).



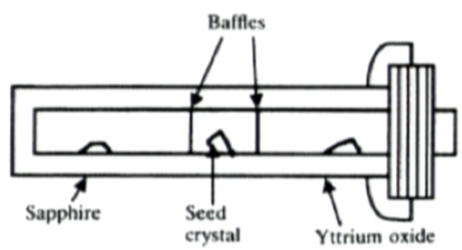
Spinel structure ($FeFe_2O_4$)



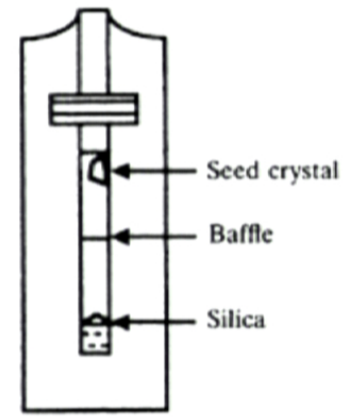
Magnetite crystal growth

Hydrothermal growth

Hydrothermal methods use pressure to grow crystals - heating up samples in a sealed tube with water. Under pressure, the water is super-heated above 100 degrees C, and stays a liquid at high pressure. Natural process - many minerals are grown this way.



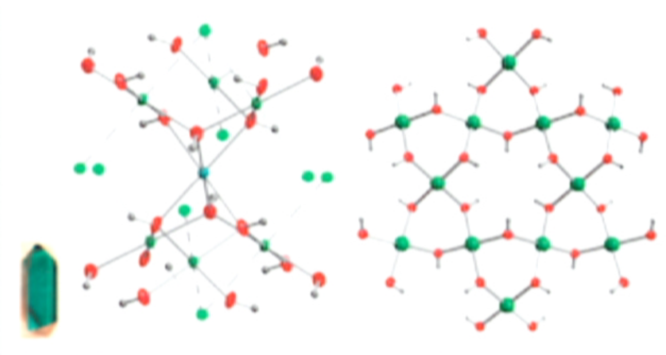
YAG crystal growth



Quartz crystal growth

Herbertsmithite

- Herbertsmithite is a mineral of formula $ZnCu_3(OH)_6Cl_2$
- The MIT group (Nocera, Lee) have recently grown crystals of this via hydrothermal methods.
- Perfect S=1/2 kagomé Cu^{2+} lattice!



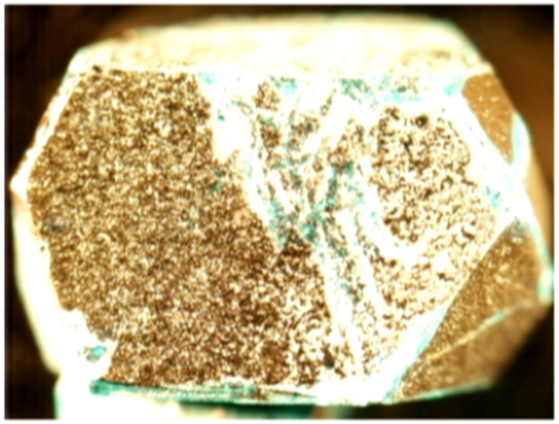
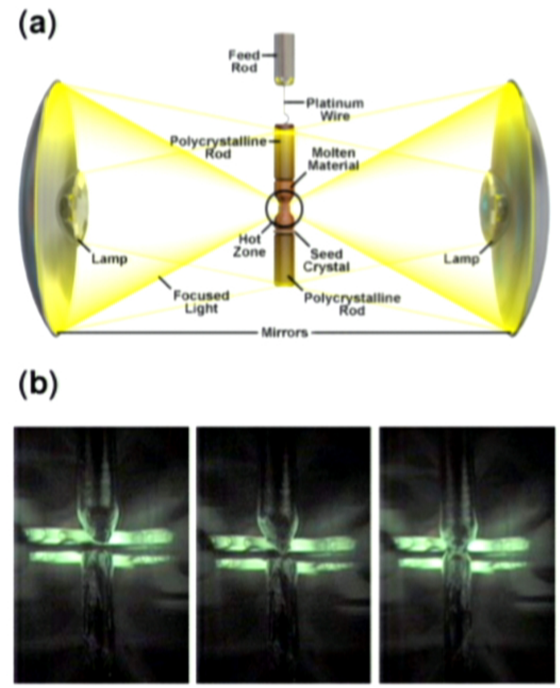
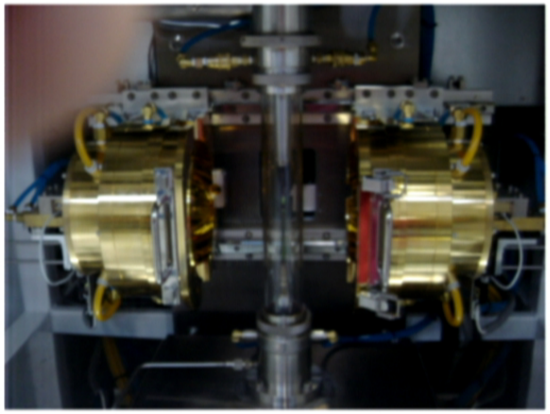


Image furnace crystal growth

- Image furnace crystal growth has left a huge impact in the landscape of condensed matter science - large, high quality single crystals of many compounds can now be grown.
- The technique uses light to grow crystals - focussed light in the hot zone heats up the polycrystalline rods to over 2000 degrees C.
- The light is so focussed that a camera can be placed a few cm away to monitor the growth in real time!



Parameters for image furnace crystal growth



Lamp size-zone size

Gas Ar, O_2, H_2/Ar, pressure
Inert, oxidize, reduce---valence

Speed

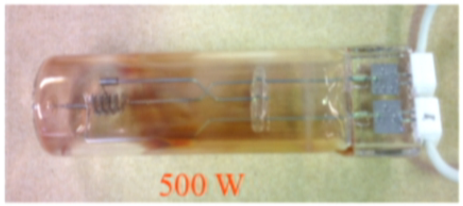
Pre-scan

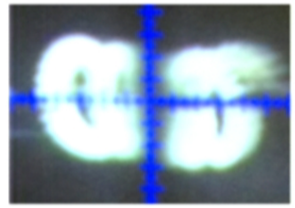
Evaporation---cold trap

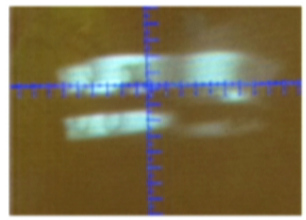
Low melting point

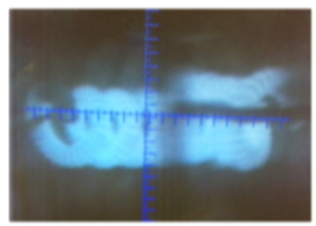
Solvent for incongruent melting

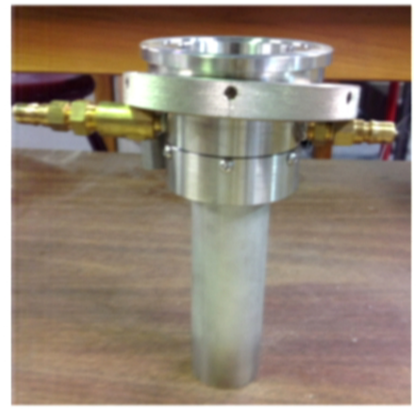
Lamp and cold trap



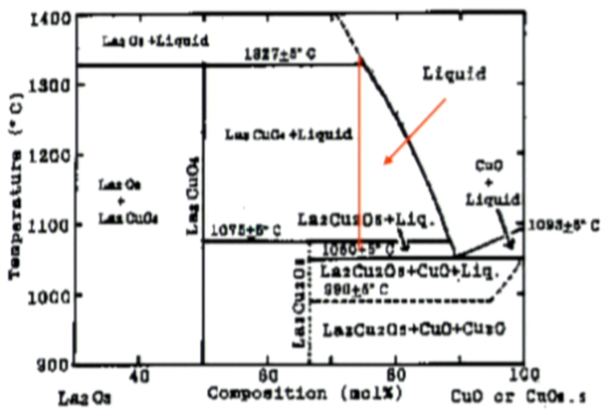








Examples of crystal growth: $La_{2-x}Sr_xCuO_4$



La_2CuO_4 coexists with a liquid phase containing 75 mol % to about 90 mol % CuO in the temperature interval 1075 °C <T< 1327 °C.

Rods: La_2O_3+$SrCO_3$+CuO (103%), 1000/1200°C/24 hr/O_2

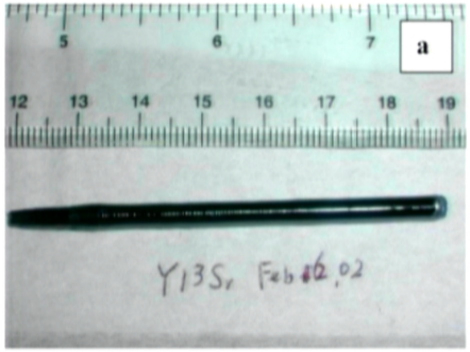
Solvent: (LaSr):CuO = 22:78
900/920°C/24 hr Air

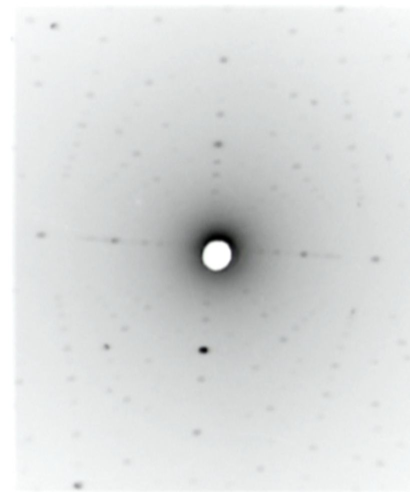
Gas: O_2

Pressure: 1 atm

Growth rate: 0.2/0.5 mm/hr

$La_{2-x}Sr_xCuO_4$





Sr_2RuO_4

Evaporation of RuO_2 Cold trap

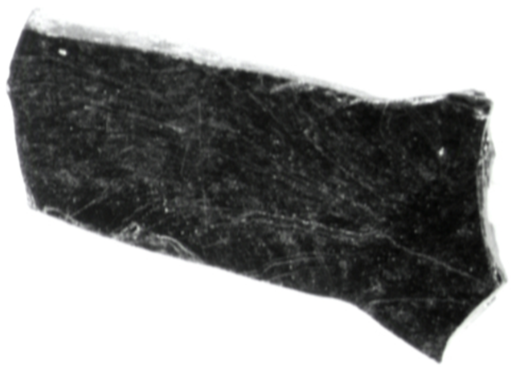
$n = 2N(Ru)/N(Sr)$

Table 1
The dependence of the quality of crystals on the nominal composition of ceramic feed rods, as well as the growth conditions

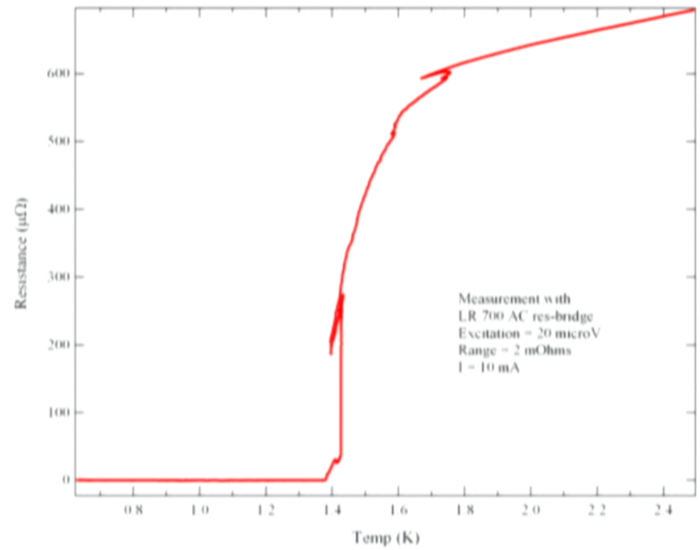
Batch no.	n	$O_2/(Ar + O_2)$	P (bar)	V_1 (mm/h)	V_2 (mm/h)	PC	T_c (K)
C66	1.10	10%	~3	60	~40	Sr214	0.454
C71	1.10	10%	~2.5	50	~30	Sr214	0.798
C75	1.10	10%	~2.5	40	~20	Sr214	0.900
C61	1.10	10%	~2.0	40	~20	Sr214	1.280
C48	1.10	10%	~2.0	21	~20	Sr214	0.740
C81	1.15	10%	~2.5	47.5	~27	Sr214	1.340
C77	1.15	10%	~2.5	40	~20	Sr214	1.372
C89	1.15	10%	~2.5	45	~25	Sr214	1.490
C117	1.15	10%	~3.0	45	>35	Sr214 + Sr113	1.441
C59	1.20	10%	~2.0	23	~23	Sr214 + Ru	
C46	1.33	10%	~2.0	16.5	~16.5	Sr214 + Ru	
C102	1.30	100%	~10.0	25	~25	Sr214 + Sr327 + a new compound	0.933

Mao Z. Q. et al, MRB (2000)

Sr_2RuO_4 crystals



As grown in NHMFL



Wiebe, Zhou, unpublished data

Image furnace growths of pyrochlores

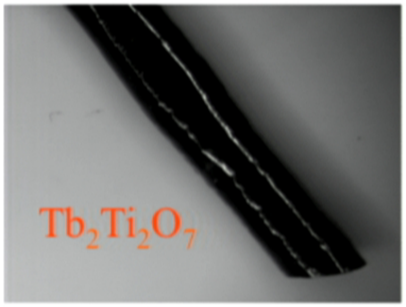
Oxygen vacancy

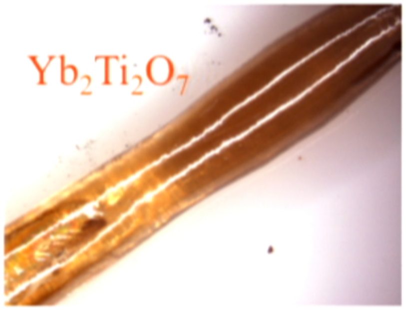
Rods: R_2O_3+TiO_2,
1200/1300°C/24 hr air

Gas: O_2

Pressure: 3 – 5 atm

Growth rate:
25/30 mm/hr pre-scan
6/7mm/hr





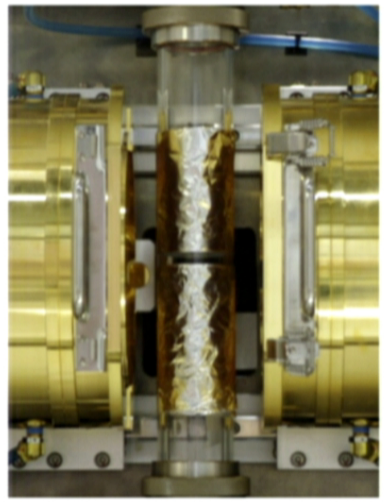
$Pb_2V_3O_9$ - 1D chain structure with alternating exchange

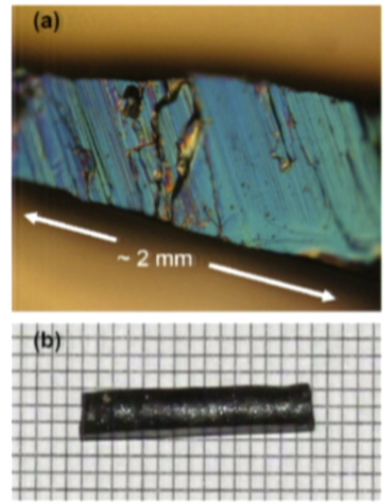
Rod: $Pb_2V_2O_7+VO_2$
950°C in vacuum

Al-foil to narrow the zone

Small diameter rod, 1"

Prescan-50mm/h------0.5mm/h





AV_2O_4 spinels

Rod	Single crystal in IF
MnV_2O_4: $MnO+V_2O_3$ in vacuumed quartz tube	Ar, 20/25mm/h
FeV_2O_4: $Fe_2O_3+Fe+V_2O_3$ in flowing Ar	Ar 20/25mm/h
MgV_2O_4: $MgO+V_2O_3$ in flowing 10%H_2/Ar	MgO comes out, extra for compensation
CoV_2O_4: $CoCO_3+V_2O_3$ in flowing Ar	V_2O_3 comes out, begin part is good crystal

Vanadium oxide
chemistry is complicated!
(many oxidation states)

Summary

We need lots of talented people!

Quantum Materials Group

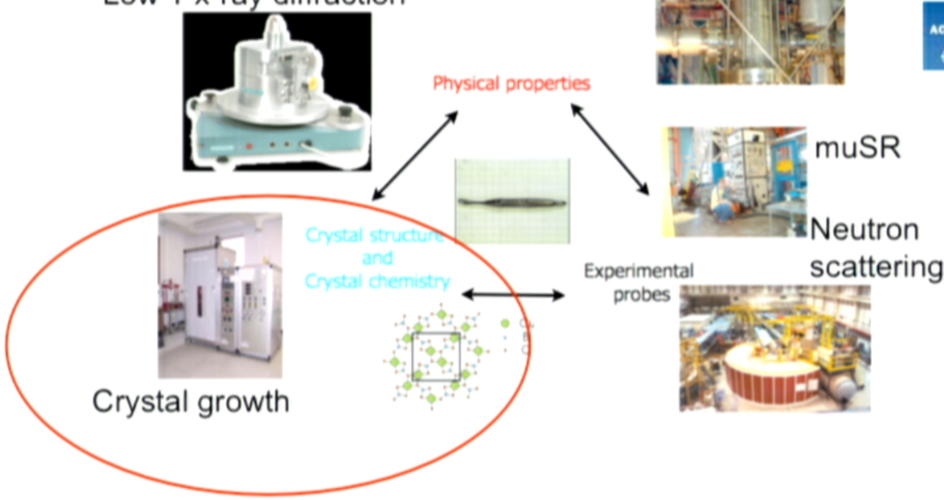
Florida State University/Manitoba

High magnetic fields

NSERC CRSNG

Canada Foundation for Innovation
Fondation canadienne pour l'innovation

ACS PRF AMERICAN CHEMICAL SOCIETY PETROLEUM RESEARCH FUND



Summary

We need lots of talented people!

Quantum Materials Group

Florida State University/Manitoba

High magnetic fields

NSERC CRSNG

Canada Foundation for Innovation
Fondation canadienne pour l'innovation

ACS PRF AMERICAN CHEMICAL SOCIETY PETROLEUM RESEARCH FUND

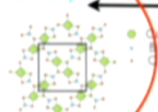
Low T x-ray diffraction

Physical properties

muSR

Neutron scattering

Crystal structure and Crystal chemistry



Experimental probes

Crystal growth

Image furnace growths of pyrochlores

Oxygen vacancy

Rods: R_2O_3+TiO_2,
1200/1300°C/24 hr air

Gas: O_2

Pressure: 3 – 5 atm

Growth rate:
25/30 mm/hr pre-scan
6/7mm/hr