Finding New Materials – a chemical perspective. Some examples.

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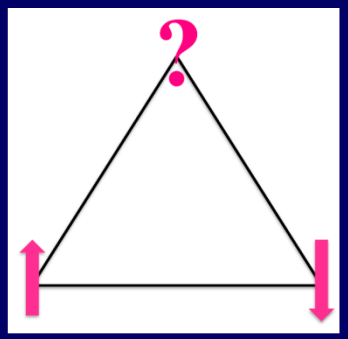
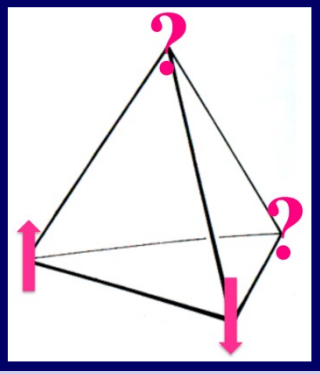
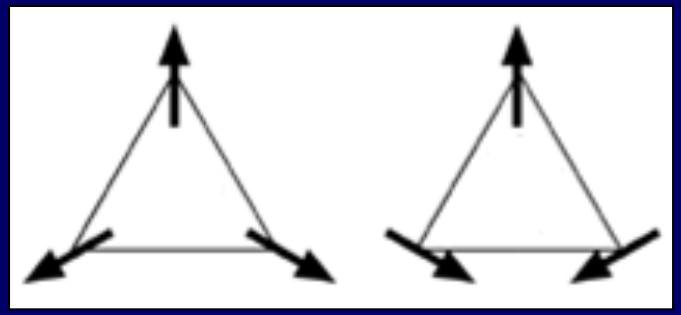
With students and postdocs at PU.
Collaborators at BNL, ANL, Johns Hopkins U, Rutgers U, and Gdansk Poland

First, geometrically frustrated magnets

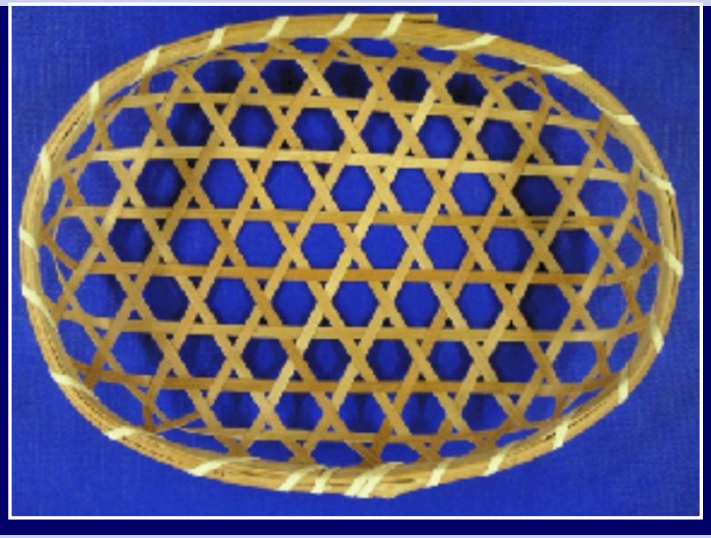




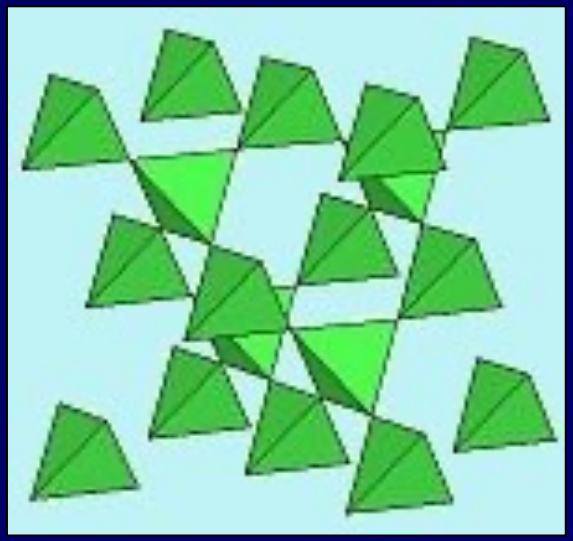


What happens at low temperatures when atoms with magnetic moments that "want" to align opposite to their near neighbors are placed on lattices based on triangles?

The low temperature spin ordering gets "frustrated"



To relate to something more familiar
Think of supercooled water



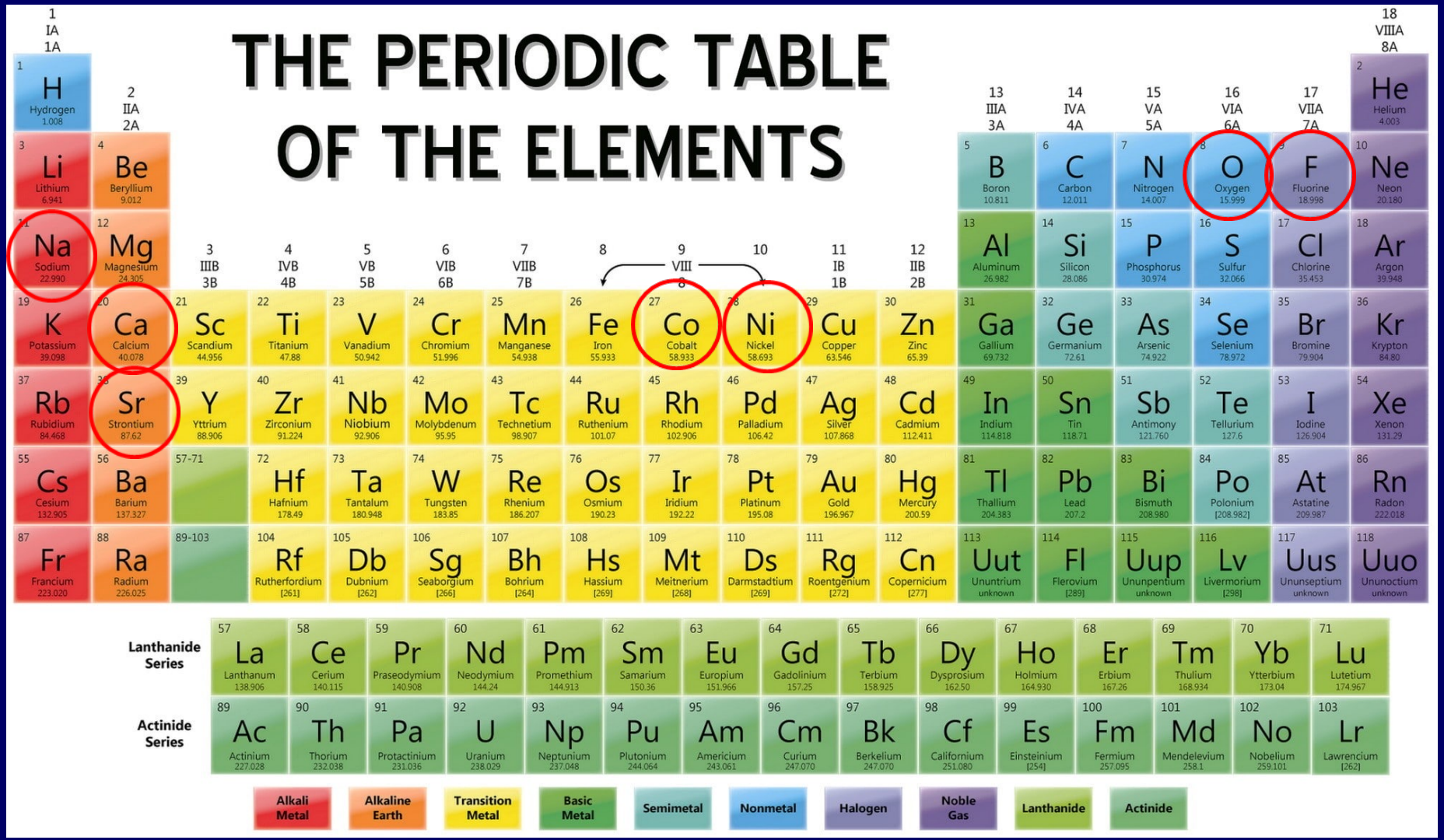
The Pyrochlore lattice. Corner sharing tetrahedra.

It is three-dimensional. The 4th point caps the Kagome.

The Kagome lattice of corner sharing triangles. It has a high number of energetically equivalent lowest energy states. It is planar.

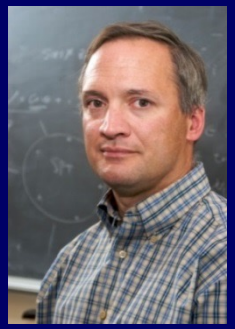
The periodic table, my happy place.

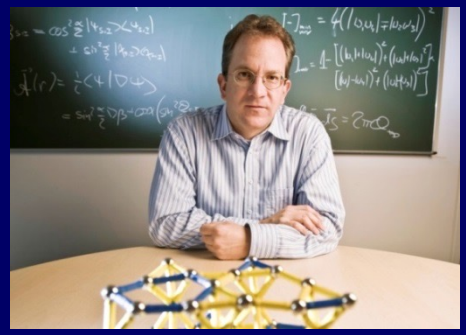
This time the elements of interest are near the top:



Transition metal fluoride pyrochlores

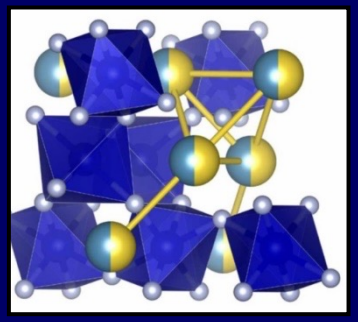
This work was motivated by several theorists –
Michel Gingras
Leon Balents and
Roderich Moessner
Who independently asked me





"can you make a pyrochlore with stronger magnetic interactions than 1 K?"
The well studied ones are based on *f* electrons where the interactions are weak

Eventually, yes. But what are the materials requirements?
Because we need stronger interactions, we need to use magnetic transition elements. Divalent *3d* transition elements are strongly magnetic but have to go on the B sites where the coordination is octahedral.
But the lower 3*d* element charge needs to be balanced.



$^{2(3+)}\ _{2}\ ^{2(4+)}\ _{2}\ ^{7(2-)} = 0$
$Dy_2\ Ti_2\ O_7$

On a normal rare earth pyrochlore
Only the A site is magnetic. *f* electrons

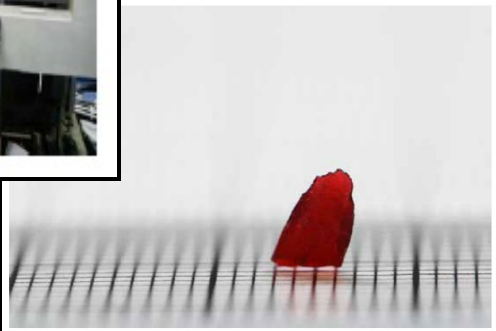
$^{2(1.5)}\ _{2}\ ^{2(2+)}\ _{2}\ ^{7(1-)} = 0$
$A_2\ B_2\ F_7$

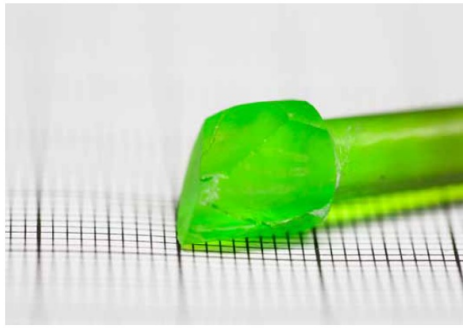
$^{1+}\ ^{(2+)}\ ^{2(2+)}\ ^{7(1-)} = 0$
$A'\ A''\ B_2\ F_7$

On a 3*d*-based pyrochlore
Only the B site is magnetic. *d* electrons

The magnetic lattice geometries are the same

Grad student Jason Krizan grew very large single crystals in a Floating Zone furnace that he cut and oriented.





$NaCaCo_2F_7$

$NaSrCo_2F_7$

$NaCaNi_2F_7$

All display nice Curie Weiss law behavior

$$\chi = \chi_0 + \frac{C}{T - \theta_{CW}}$$

χ_0 = Temperature Independent Contribution

χ = Magnetic Susceptibility

T = Temperature in K

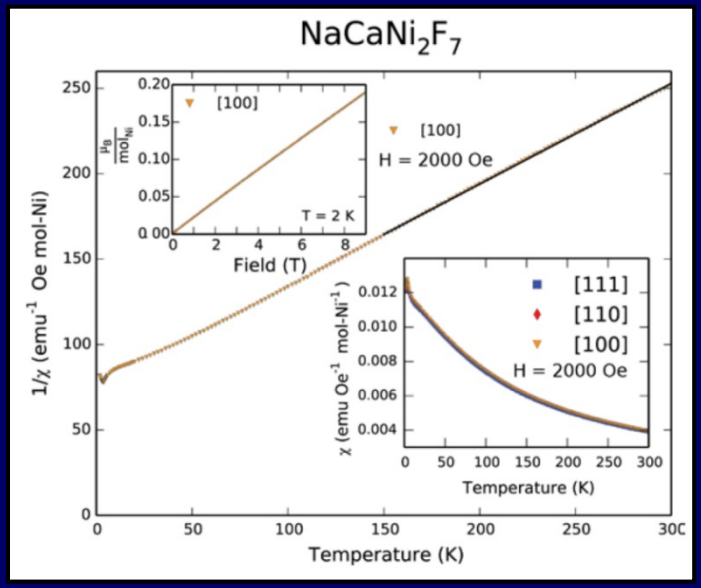
C = Curie Constant

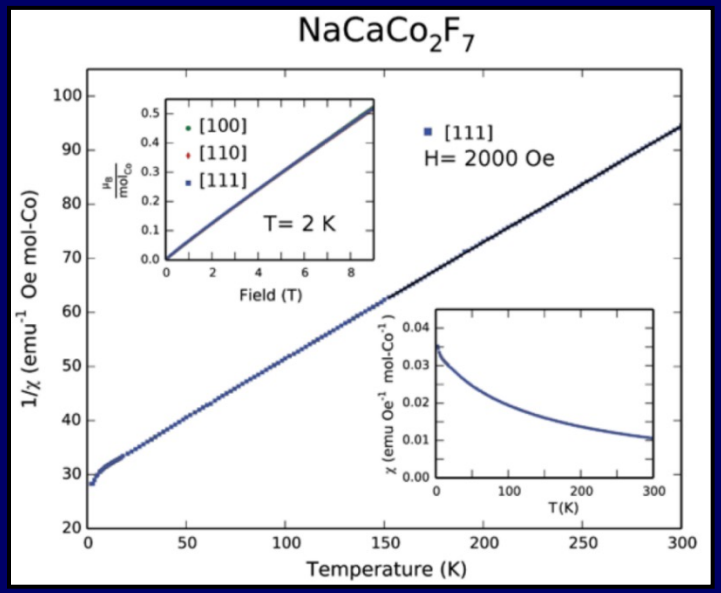
θ_{CW} =Weiss Temperature

0 → Paramagnetic

+ → Ferromagnetic

- → Antiferromagnetic

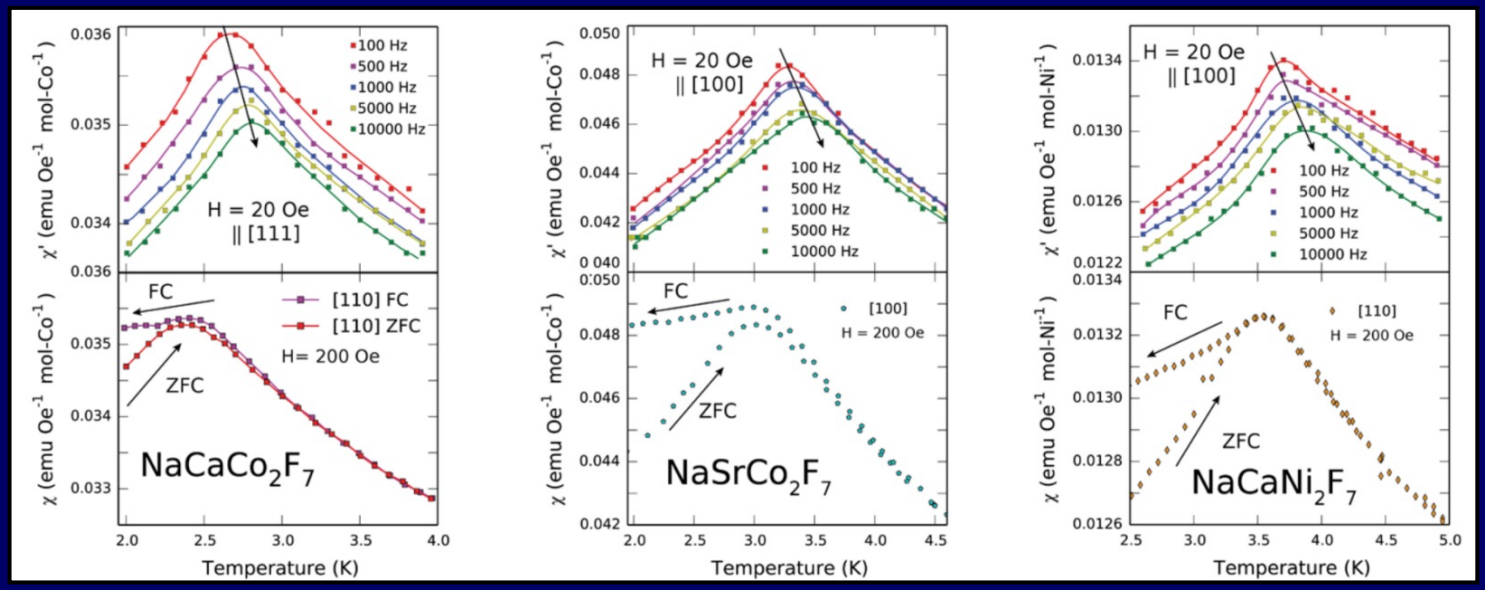




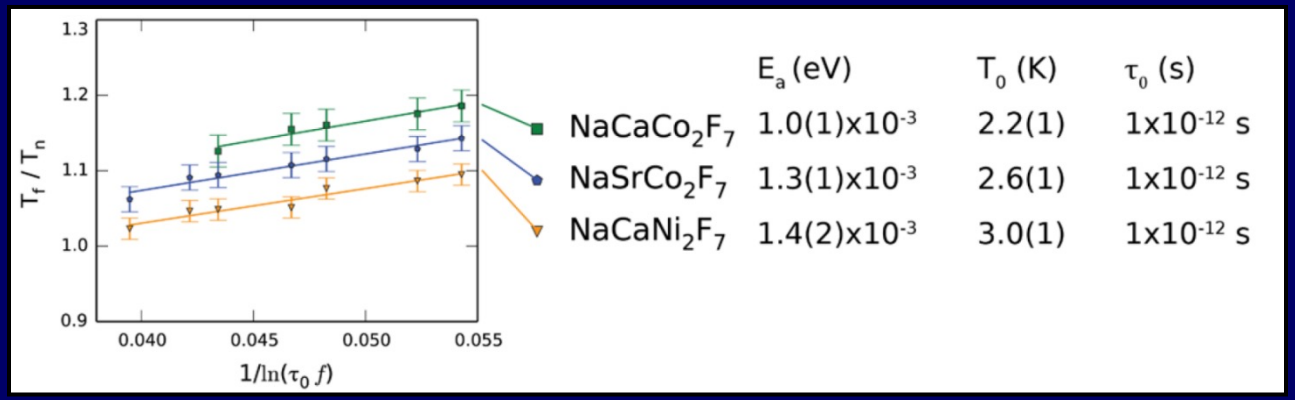
Curie-Weiss Fit:	θ (K)	p_{eff} (μ_B)
■ $NaCaCo_2F_7$	-139(1)	6.1(1)
⬟ $NaSrCo_2F_7$	-127(1)	5.9(1)
▼ $NaCaNi_2F_7$	-129(1)	3.6(1)

The magnetic interactions all larger than 100 K and the magnetic ordering transitions are 2-3 K so these are highly frustrated.

All the magnetic ordering transitions are “glassy” – ac susceptibility shows it.
We believe that it comes from the non-magnetic A site atom random mixing.
To satisfy their bond length and geometry requirements, the A site atoms move the Fluorines bonded to the Co and Ni,
introducing chemical disorder and therefore magnetic disorder.



All obey reasonable Vogel-Fulcher behavior for insulating Spin glasses



	E_a (eV)	T_0 (K)	τ_0 (s)
$NaCaCo_2F_7$	$1.0(1)\times10^{-3}$	2.2(1)	1×10^{-12} s
$NaSrCo_2F_7$	$1.3(1)\times10^{-3}$	2.6(1)	1×10^{-12} s
$NaCaNi_2F_7$	$1.4(2)\times10^{-3}$	3.0(1)	1×10^{-12} s

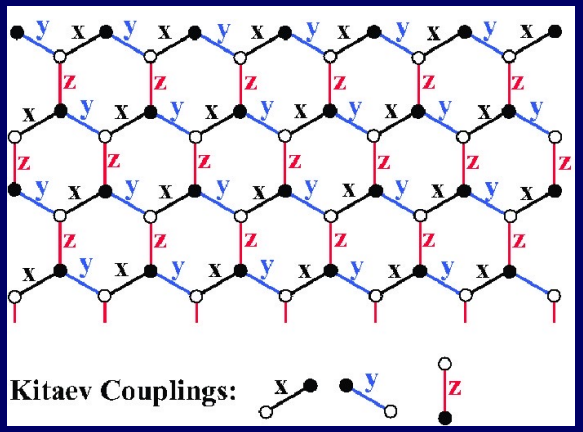
Second, Quantum Spin Liquids

Why do physicists like quantum spin liquids and honeycombs in particular?

Honeycombs are weird because of nn vs nnn interaction balance.

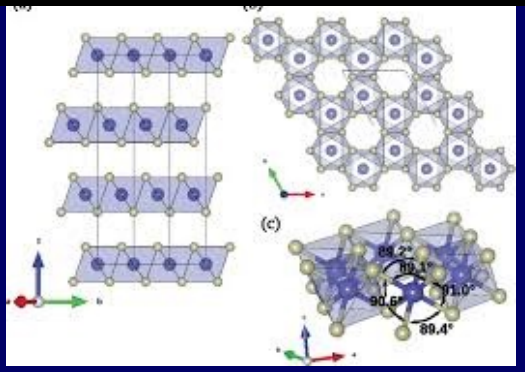
In a spin liquid magnetic moments don't "ever" thermally freeze. In a quantum spin liquid (QSL) the state they get into at low T is quantum mechanical in character.

Na_2IrO_3 (actually $Na_3(NaIr_2)O_6$ structurally) is a prime candidate for a Kitaev Spin Liquid - a QSL state that has an "exact solution" and makes predictions that **all** believe.

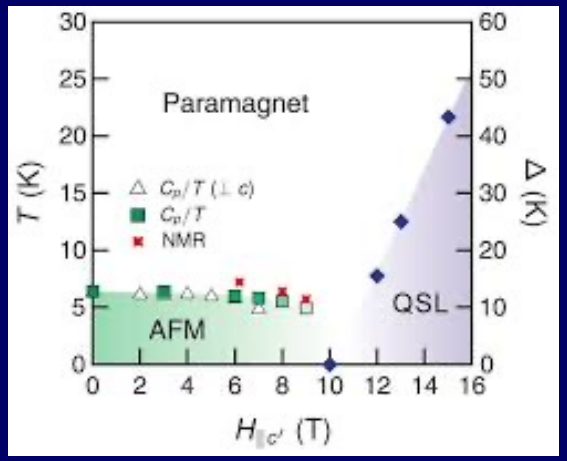


Significant spin orbit coupling is argued to be critical in this type of magnetic system, goes as m4

But Ir is insoluble in almost anything, so crystals of significant size are not possible to grow. This limits its study.



$RuCl_3$ in a magnetic field seems to work. (ORNL) Field suppresses the "normal" magnetic interactions.



Crystals are accessible. Field needed to get a potential QSL is almost too high but is OK. Limits its study.

We start again with inspiration from theorists

Zigzag Magnetic Order in the Iridium Oxide Na_2IrO_3

Jiří Chaloupka,[1,2] George Jackeli,[1,*] and Giniyat Khaliullin[1]

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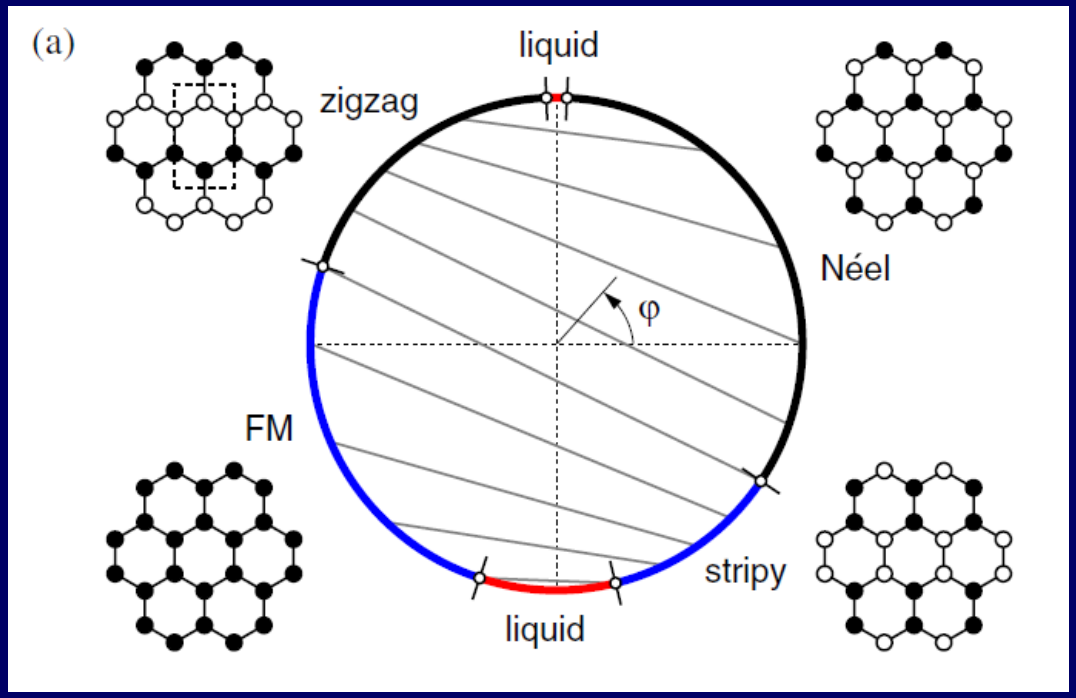


Phi (φ) describes the ratio of near neighbor to next nearest neighbor coupling

What kind of magnetic state do you expect?

which eventually motivated us to work on $BaCo_2(AsO_4)_2$, an old material with a Co^{2+} honeycomb. Co^{2+} is weird if you ask me.

A magnetic material on a honeycomb lattice.

1. Directly relevant to the Kitaev model. But does Co^{2+} have strong SOC?

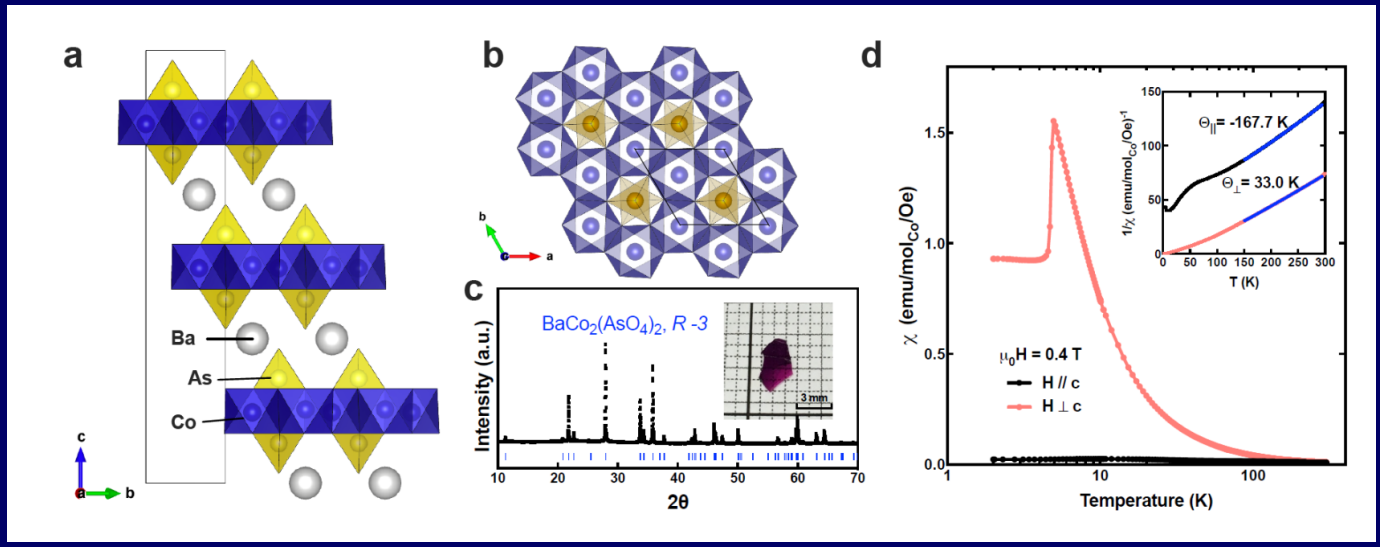
2. Sometimes you plant a seed that grows slowly

3. and watch out for arsenic

MAGNETIC ORDERING IN A PLANAR X–Y MODEL: $BaCo_2(AsO_4)_2$

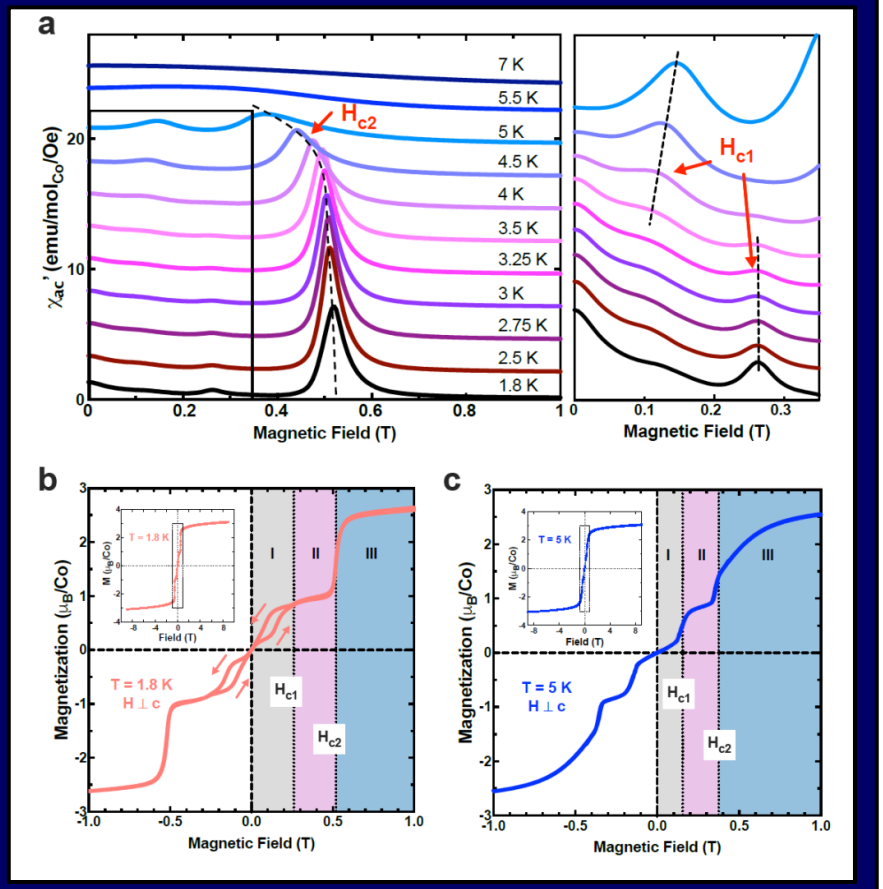
L.P. REGNAULT, P. BURLET and J. ROSSAT-MIGNOD
DRF/DN, Centre d'Etudes Nucléaires, 85X, 38041 Grenoble Cedex, France

Physica 86–88B (1977) 660–662 © North-Holland

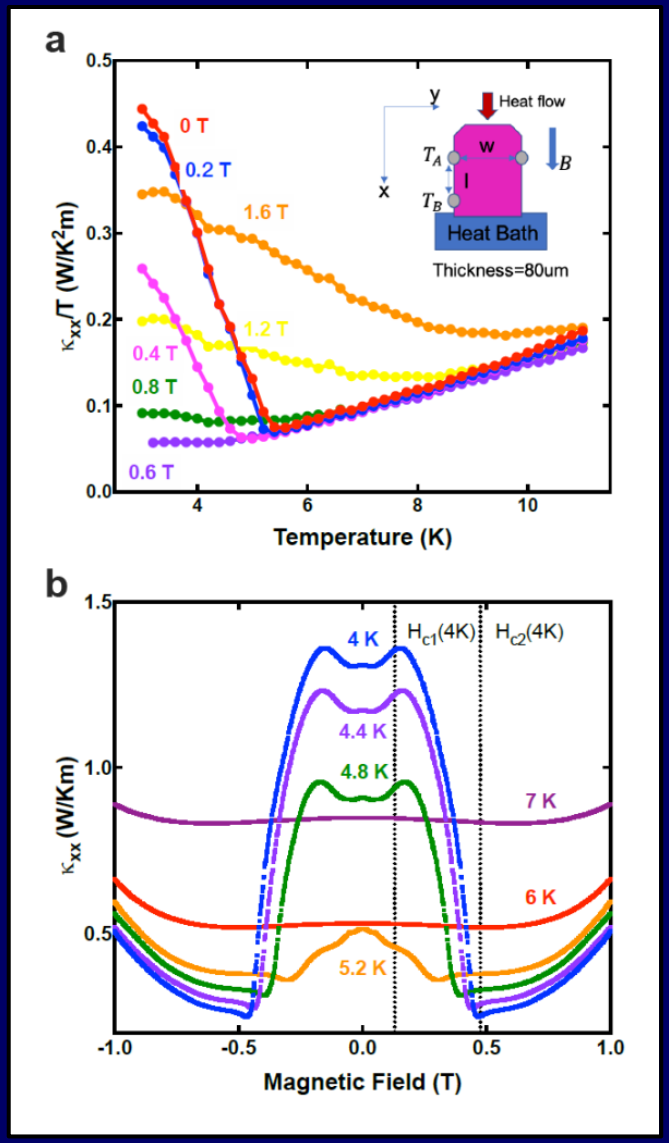


Postdoc Ruidan Zhong grew crystals and we got new data

Some of its properties



There are dramatic magnetization steps in a “weak” magnetic field

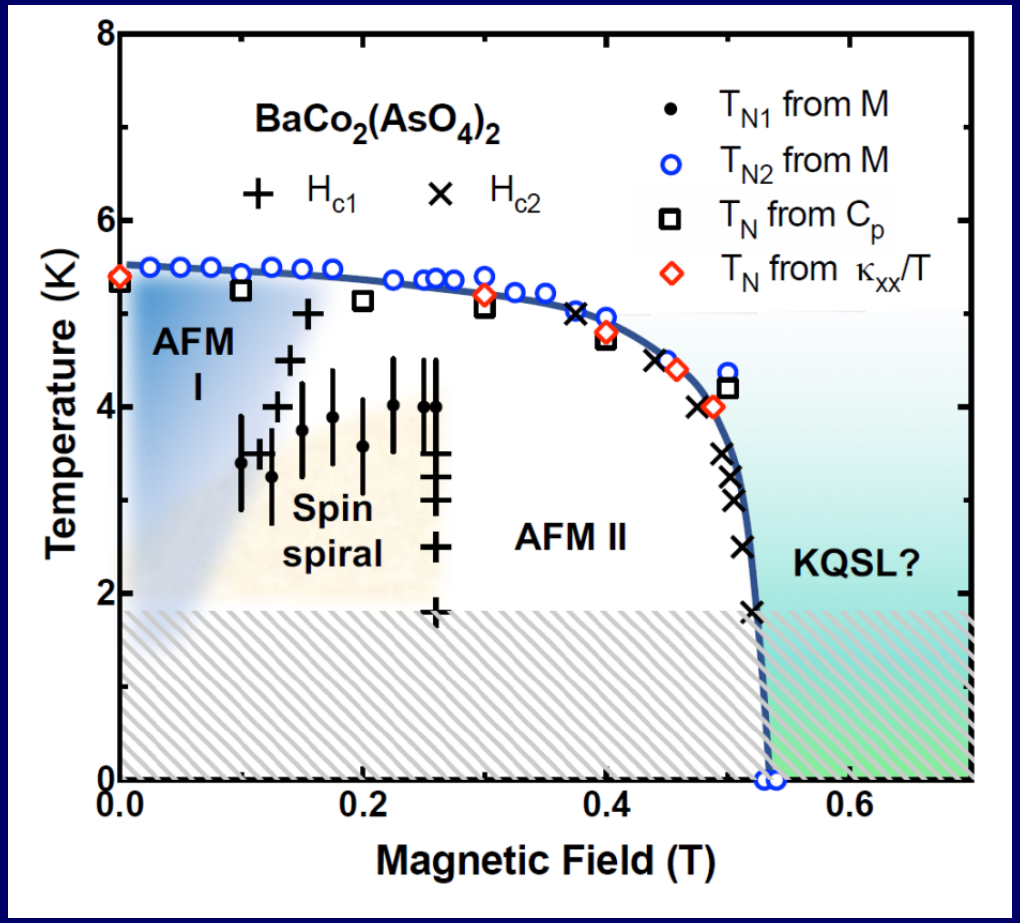


Lots of analogies to $RuCl_3$

Take the thermal conductivity for example.

Heat is carried by lattice vibrations of course, and in this electrical insulator also by magnetic excitations.

Our magnetic phase diagram for $BaCo_2(AsO_4)_2$



Is it a low spin Co^{2+} honeycomb with strong spin orbit coupling?

An AFM at low temperatures and low applied magnetic fields that enters a non-magnetic state in a field of 0.4 T.

Good size crystals grow, unlike the iridium oxides, but like the $RuCl_3$ does.

But better than that one because the candidate QSL state appears at 0.5 Tesla rather than 8 Tesla, making it possible to probe by neutron scattering.

So Why isnt this **it**?
Are there too many trees in the forest to see this one?

third. Gold!

This time we start with a chemical question:
Why is gold interesting to some solid state chemists?

1. Gold is a “noble metal”, which means that normally it is uncharged.
It stays an element: Au^0

2. From its position in the periodic table it is a single electron donor in intermetallics, i.e. Au^{+1}

Co	Ni	Cu	Zn
Rh	Pd	Ag	Cd
Ir	Pt	Au	Hg

($Y_3Au_3Sb_4$ is a semiconductor)

3. Well, so far OK. but from a 2005 paper by experimentalist Martin Jansen:

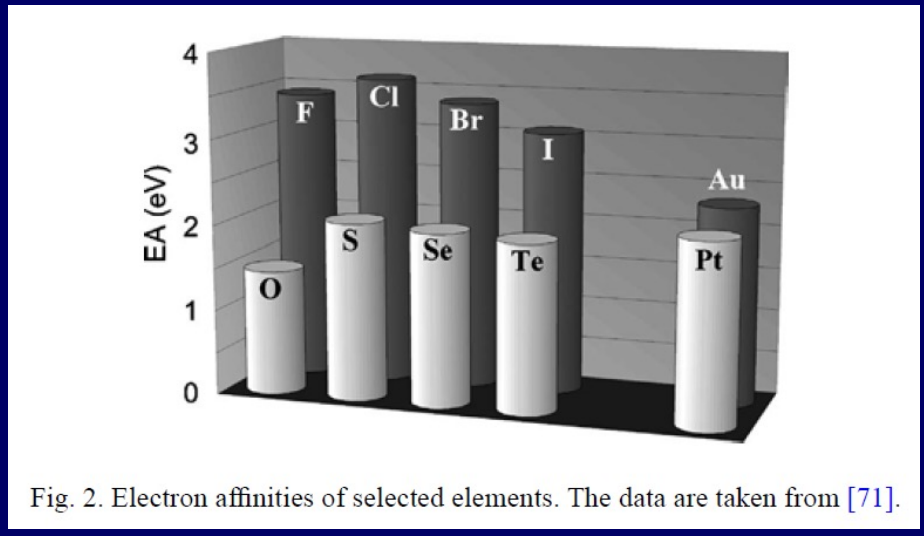
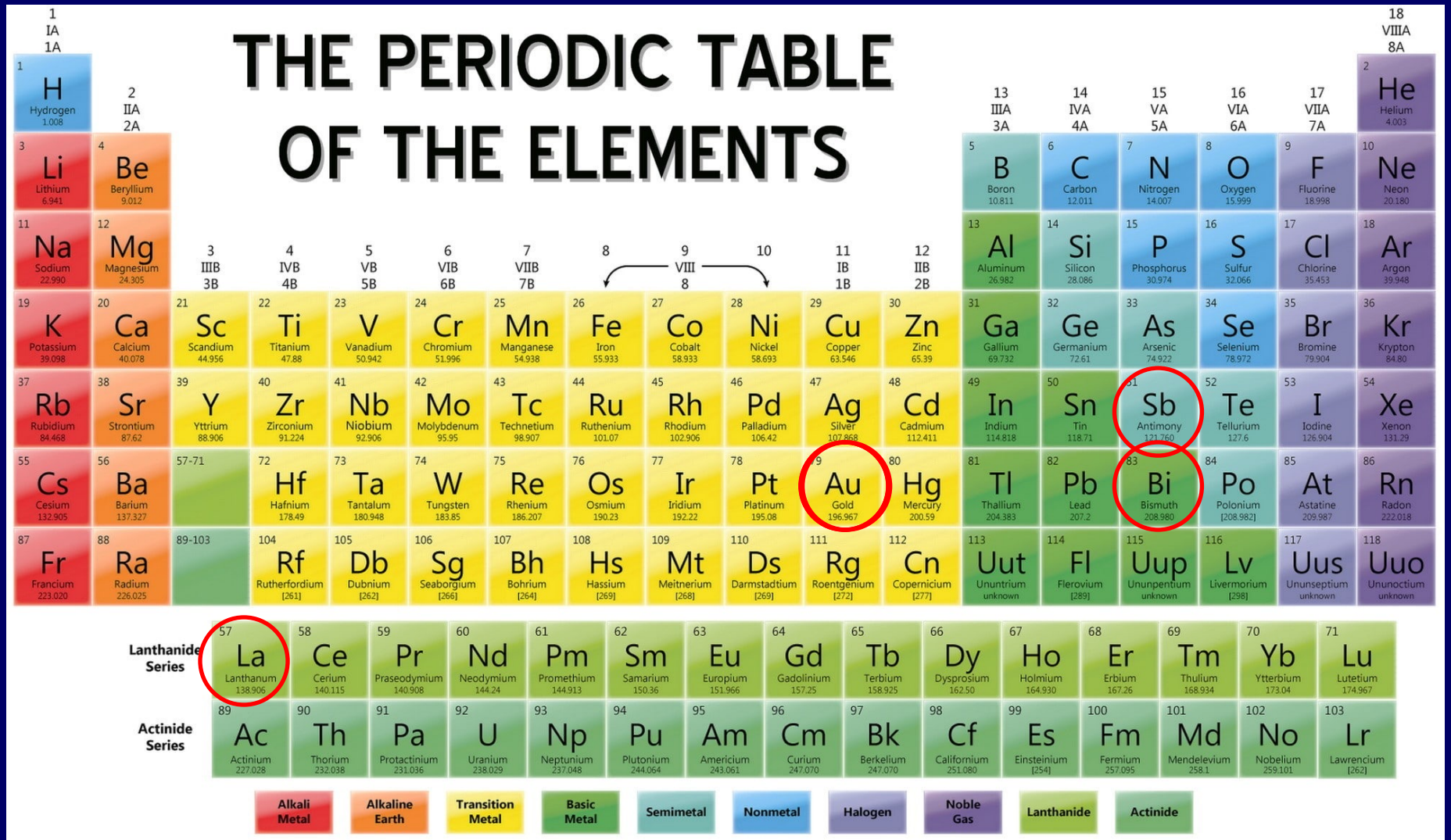


Fig. 2. Electron affinities of selected elements. The data are taken from [71].

So Au likes to accept an electron as much as S, Se, or Te do?
i.e. Au^{-1} is stable! So what do you get? Au^{1+}, Au^0 or Au^{-1}?

The periodic table, again. This time near the bottom:



Its interesting, so we started looking for new Au compounds

We used Au

plus

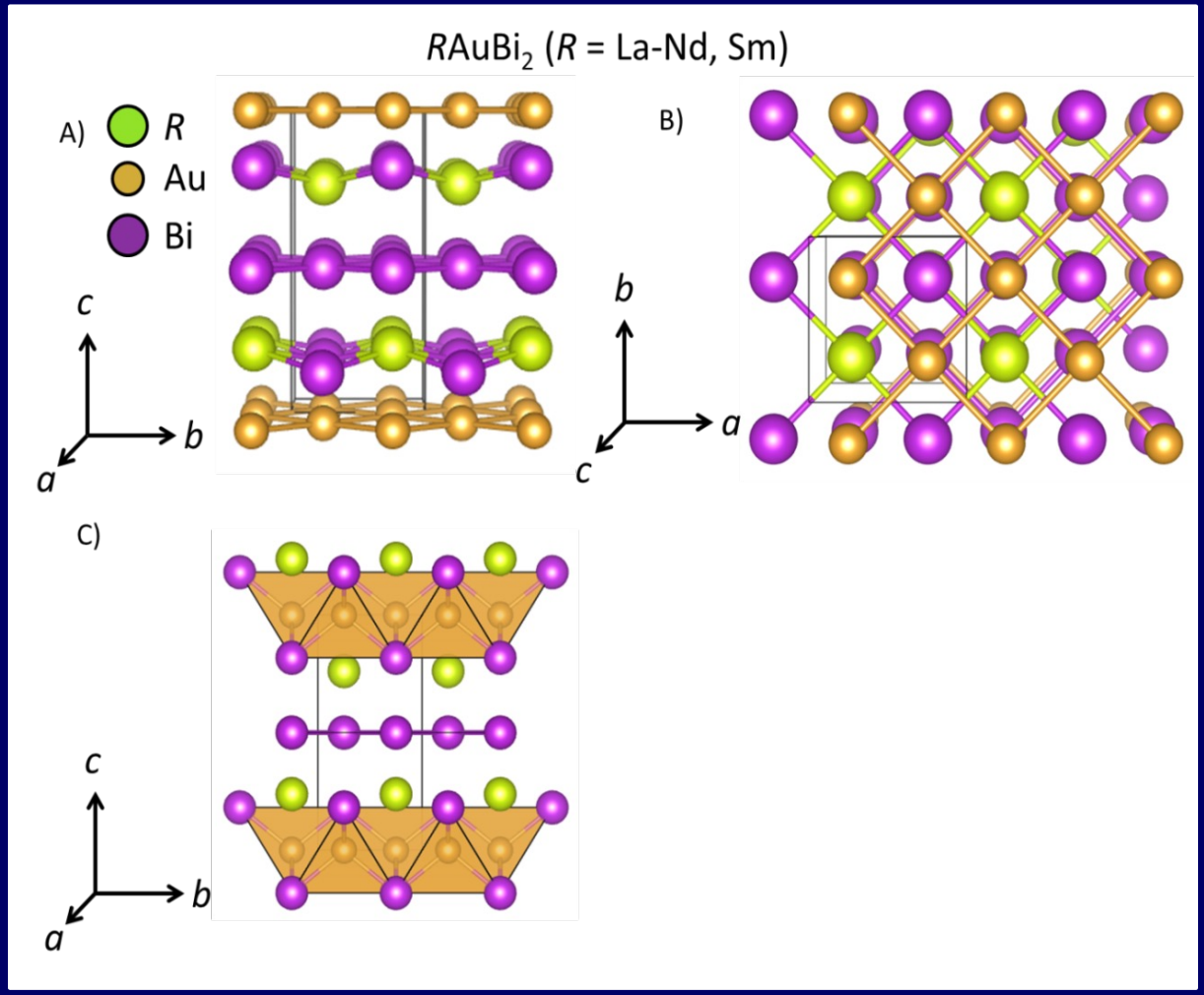
an electropositive element

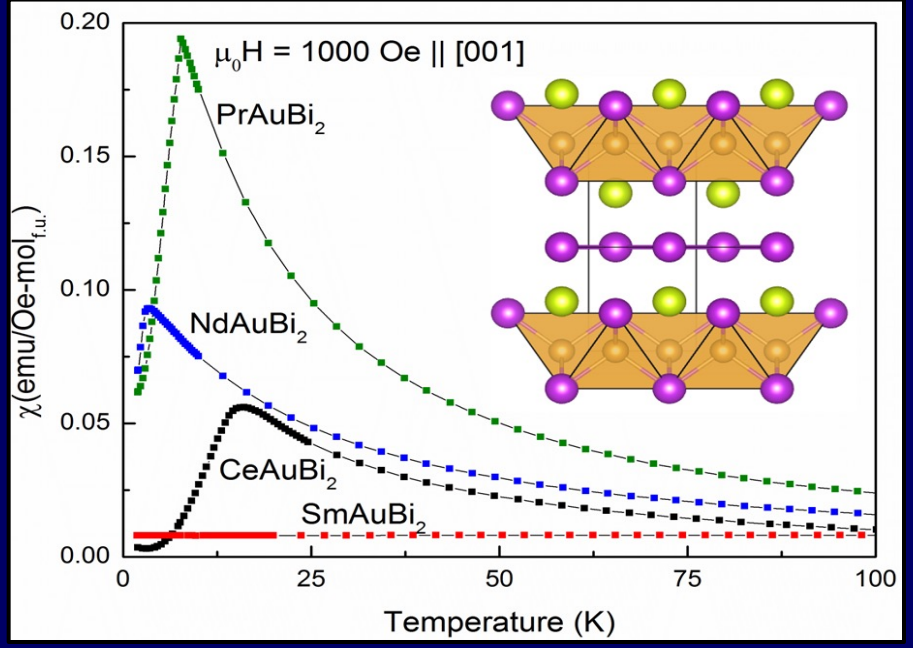
plus

an electronegative element

To “confuse” the Au.

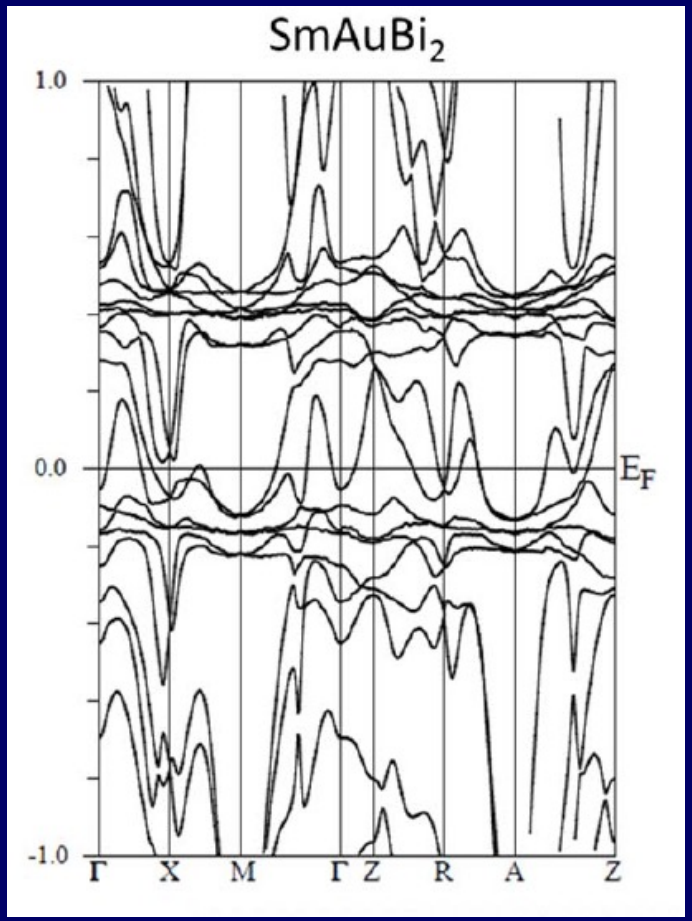
First, we found $RAuBi_2$





All show magnetic behavior due to the rare earths present.

(Wien 2K, an electronic structure calculating program, is easily used, even by chemists.)



The Bi layer dominates the states at the Fermi energy

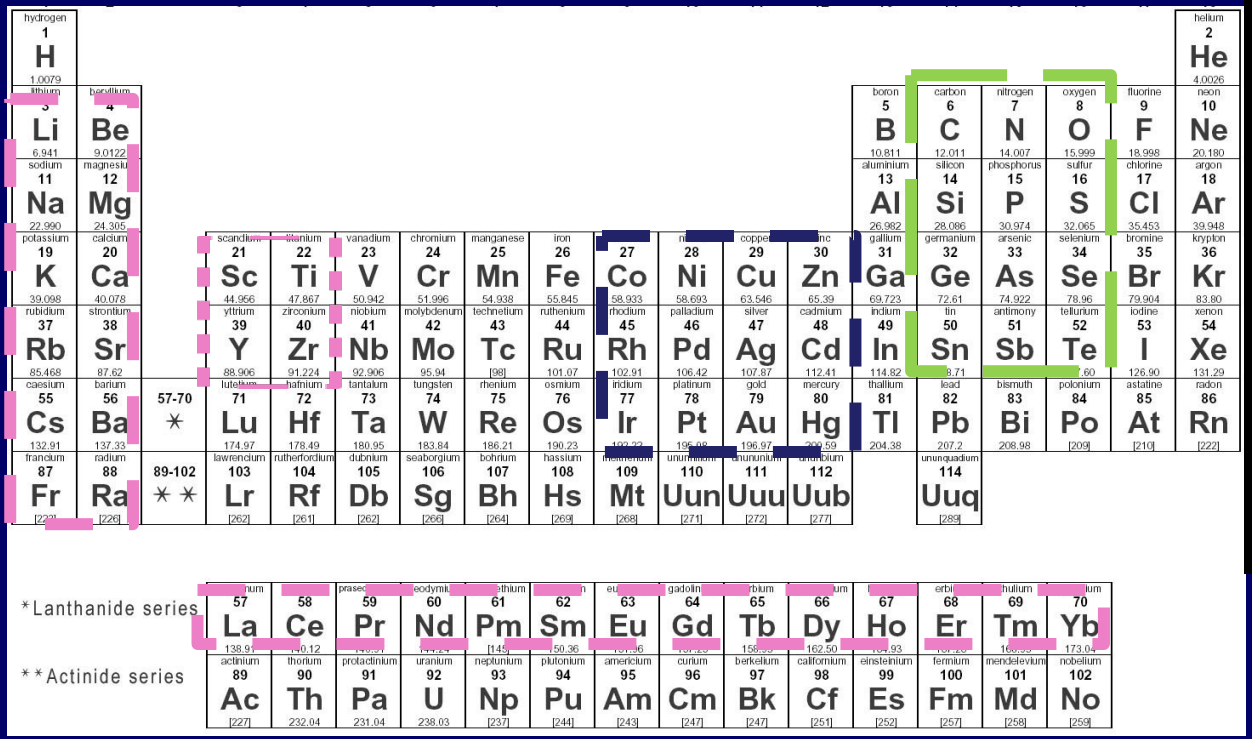
The materials can be thought of as R^{3+} -$(AuBi)^{2-}$ -Bi^{1-} -

Leaving holes in the Bi layer.
Square planes of Bi, are interesting in topological materials

But chemically it is Au^{+1} so its not the chemical crazyness we were after.

Consider 1:1:1 *AYZ* ternary compounds many semiconductors are found in this family

(even “complex” materials can follow simple chemical rules)

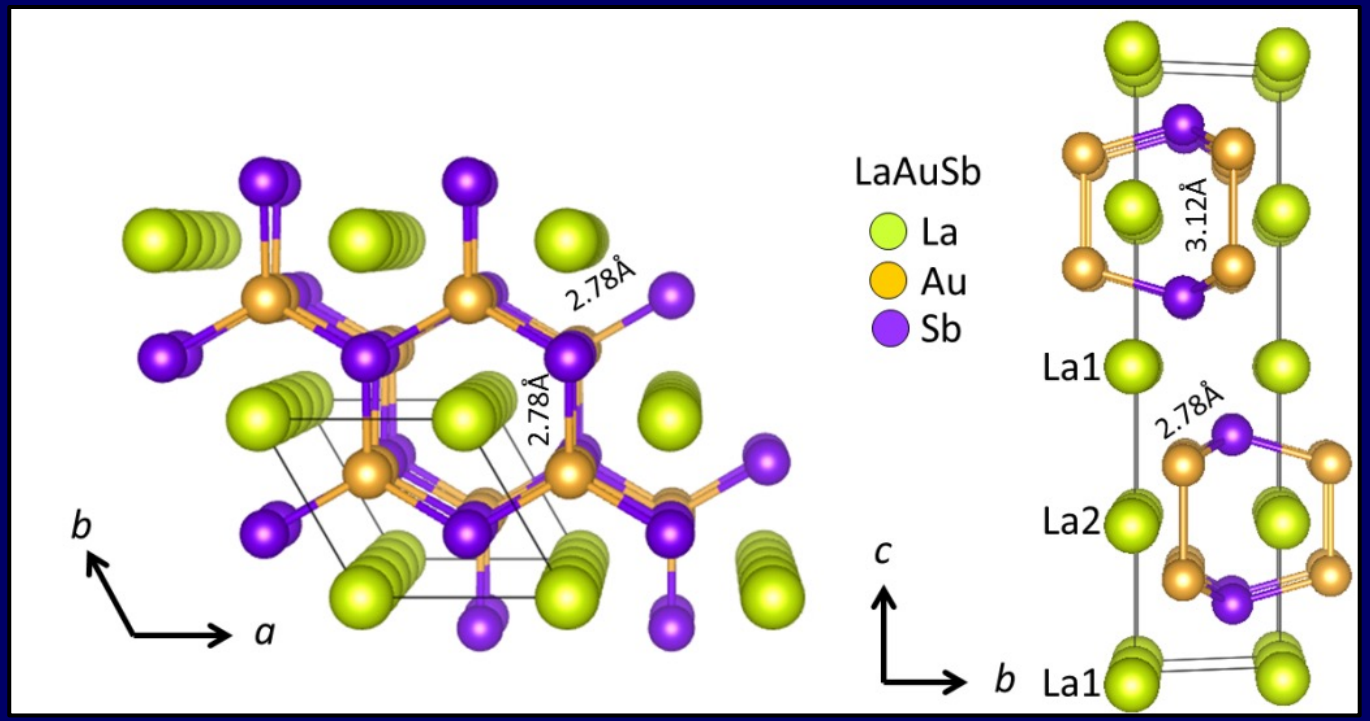


Stability and semiconductivity happen due to the “18 electron rule”

Its not “rocket science”
No DFT is needed.
Just count electrons.

e.g.
GdPtBi
ZrNiSn

When we made 1:1:1 with Ln, Au, and Sb something interesting happened.

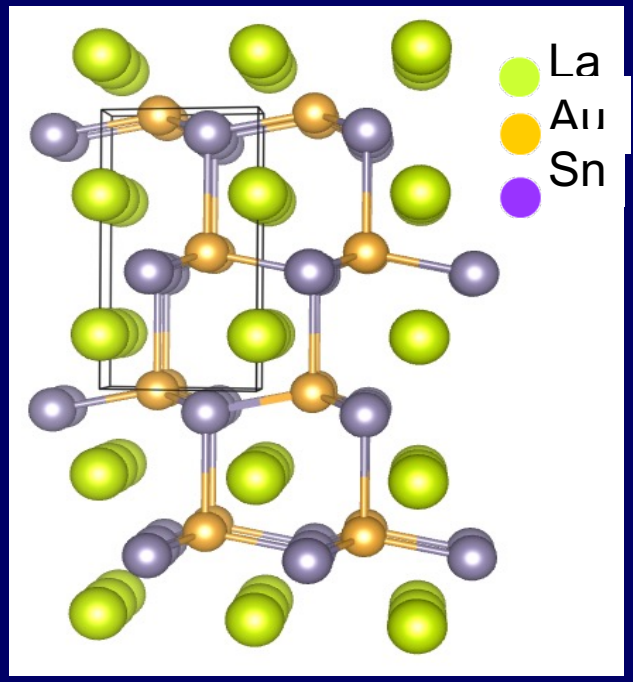


Its crystal structure has very buckled layers with the Au's pulled together– why?

Is this an Au-Au bond in a solid?
A bond between inert atoms?

Counting the electrons

LaAuSn – a normal compound with 18 electrons

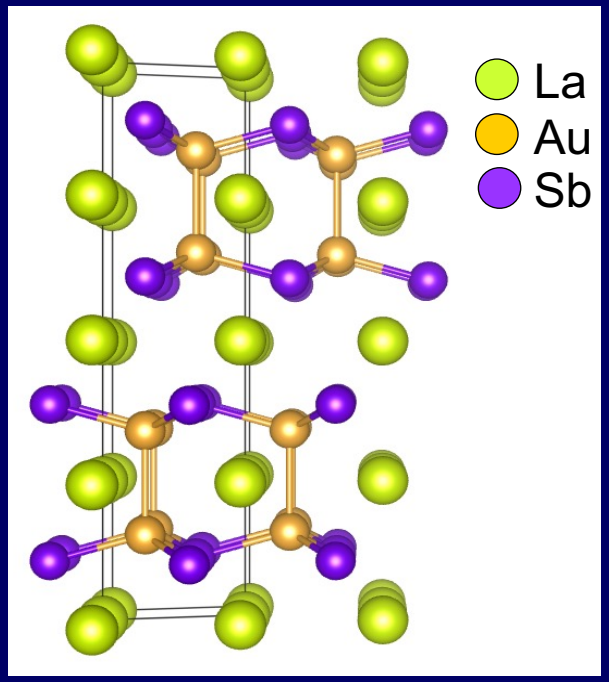


3e- + 11 e- + 4e- = 18e-

La^{3+} Au^{1+} Sn^{4-} → $La^{3+}[AuSn]^{3-}$

LaAuSb - too many electrons (19, not 18) What happens?

+ 1 e-

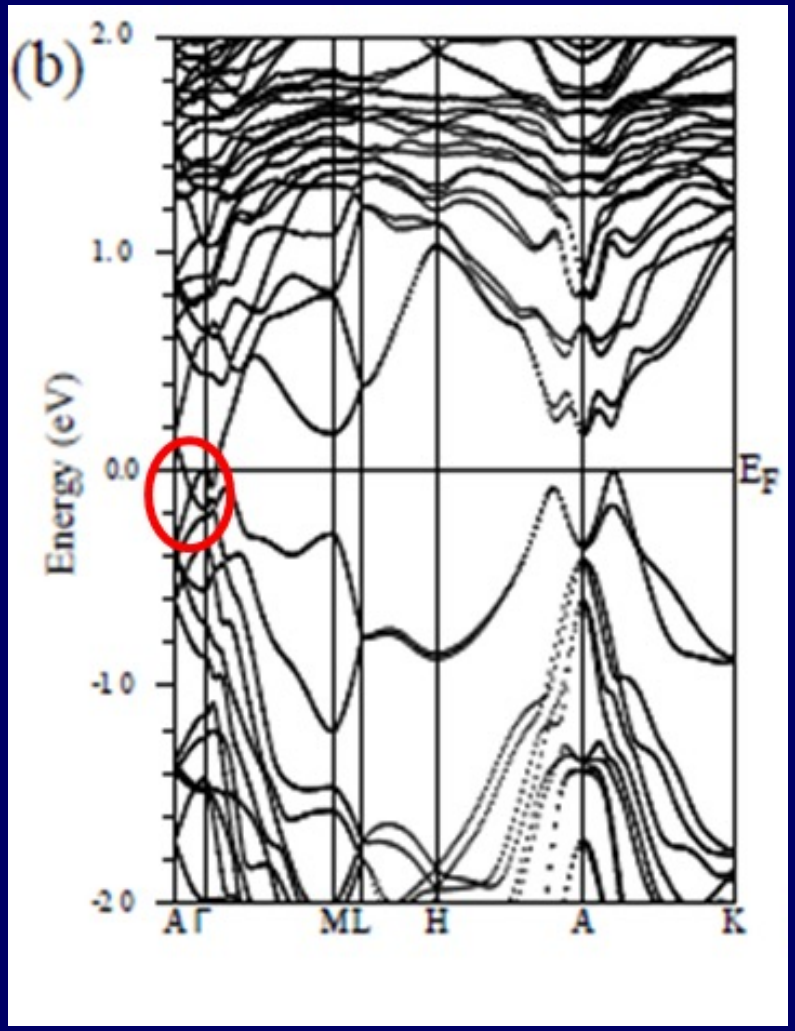


3e- + 11 e- + 5e- = 19e-

$2La^{3+}$ $(Au^{0}\text{-}Au^{0})$ $2Sb^{3-}$ → $La_2Au_2Sb_2$

Double the formula and "eat" the extra electrons by forming an Au-Au bond between inert atoms. Our first JACS paper!

The result calculates to have almost a complete band gap. Essentially a 19 electron semiconductor. but not quite – is it a Dirac Semimetal?



- Bulk Dirac cone just below calculated E_F
- Possibly unusual electronic properties but no fancy measurements have been done

Liz Seibel

Weiwei Xie

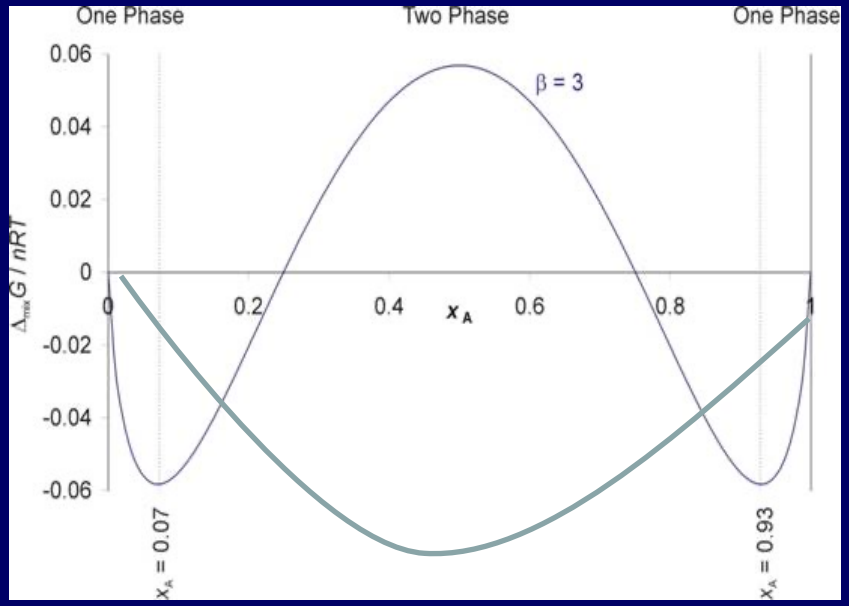
Finally, High Entropy Alloy (HEA) superconductors

Fabian von Rohr

Tomasz Klimczuk

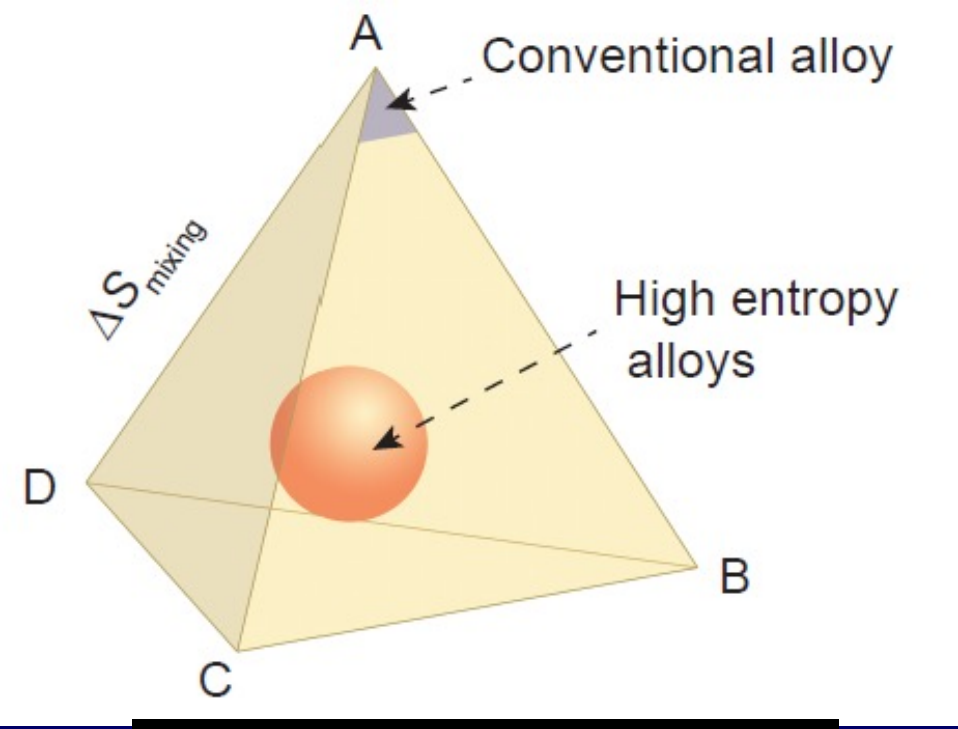
$\Delta G = \Delta H - T\Delta S$
the golden rule of materials science

Usually one only thinks about (or calculates) ΔH not ΔS when considering equilibrium between solid phases (most solids have similar entropies)



But the entropy of mixing is large in solid solutions with major fractions of mixed elements

This makes some surprising mixtures of elements stable in solid solution alloys



Example – a 4 element mixture

HEAs are not like most conventional alloys - where the properties of a dominant element are modified by small additions.

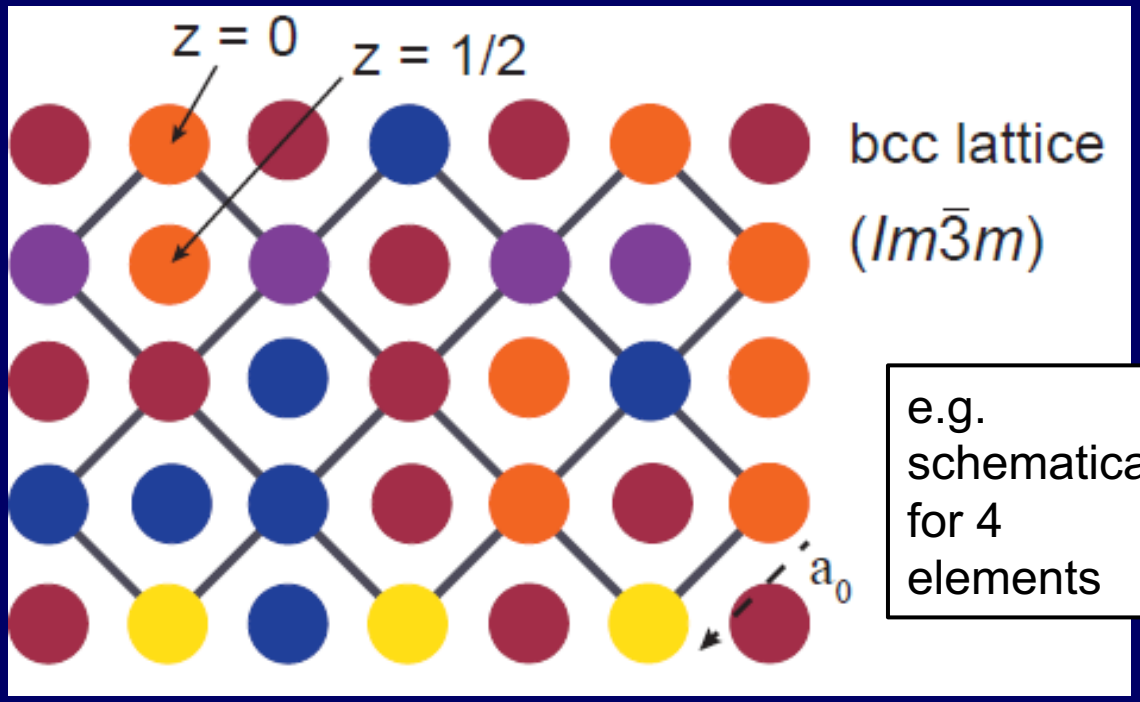
The properties of HEAs emerge as a property of the mixture of elements, which are all present in significant proportion.

Metallurgists are interested in them due to their excellent mechanical properties.
Materials Scientists due to their microstructures and magnetism

I wondered, are there any HEA superconductors?

Yes. In Ta-Nb-Hf-Zr-Ti reported a few years ago.
Its existence was reported but not much information about it.

This HEA superconductor is BCC



e.g. schematically for 4 elements

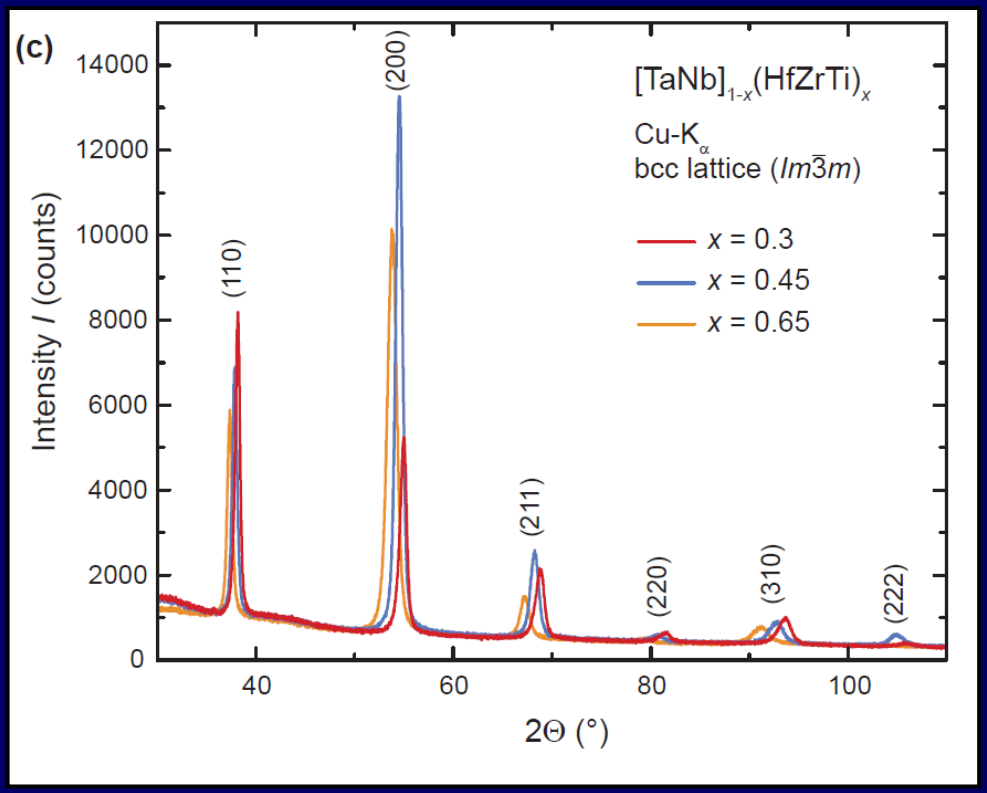
Nb and Ta are BCC
Hf, Zr, are FCC
Ti is HCP
But the HEA is BCC

We tested the effects of electron count, alloy complexity and the elements present

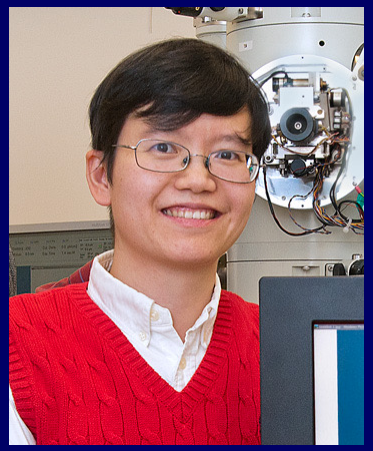
The alloy of interest is (TaNb)1-x(HfZrTi)x

For example x = 0.33 is ~ Ta33Nb33Hf11Zr11Ti11

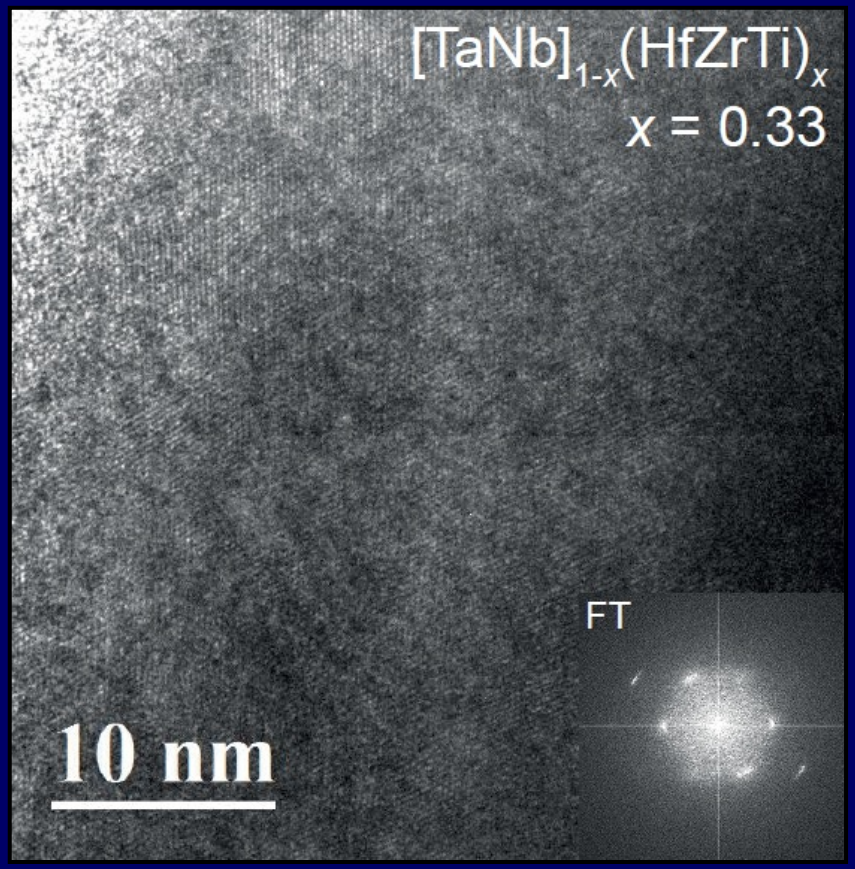
x = 0.67 is ~ Ta16Nb16Hf22Zr22Ti22

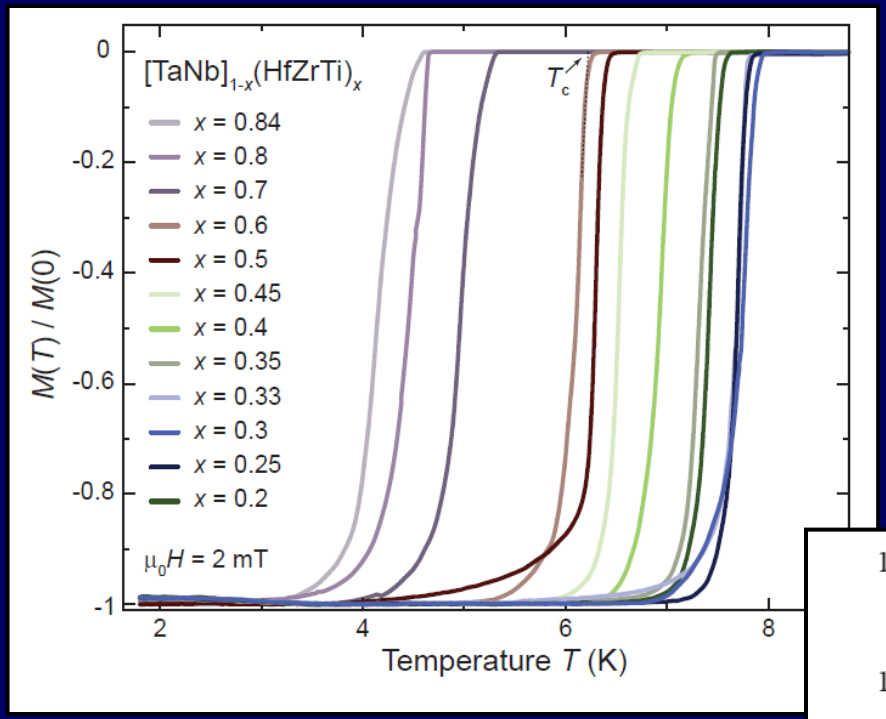


First, the average structure is BCC



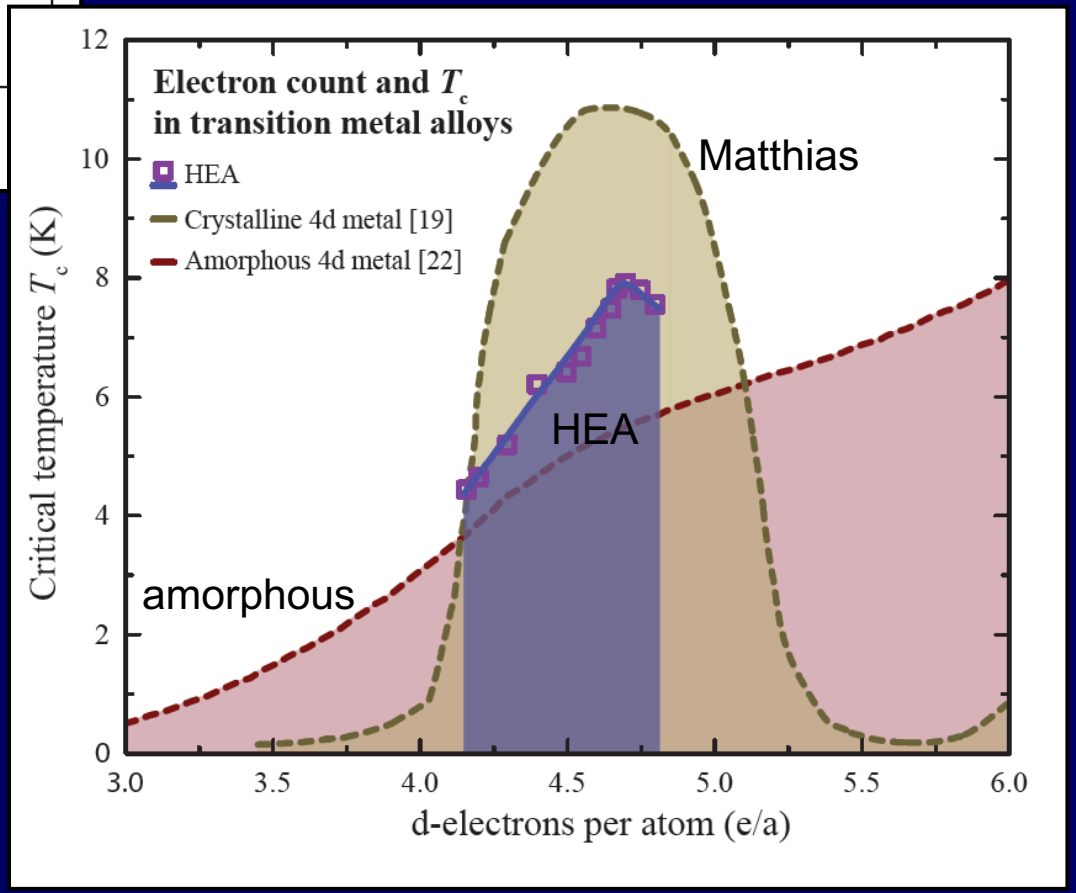
The local level structure is important. Can it really be a random mix? Looking down the [111] direction of the HEA in the HRTEM.
It's a random distribution of elements in a BCC lattice.
No nanometer scale clusters.
(Jing Tao at BNL now IOP)





Changing x changes the electron count.
Nice, sharp Tc, full superconductors in all cases until the stability of the crystal structure breaks down.

The electron count variation in Tc is intermediate between amorphous alloys and binary crystalline metal alloys.
The range of stability is shown



But are we done yet with the first HEA superconductor?

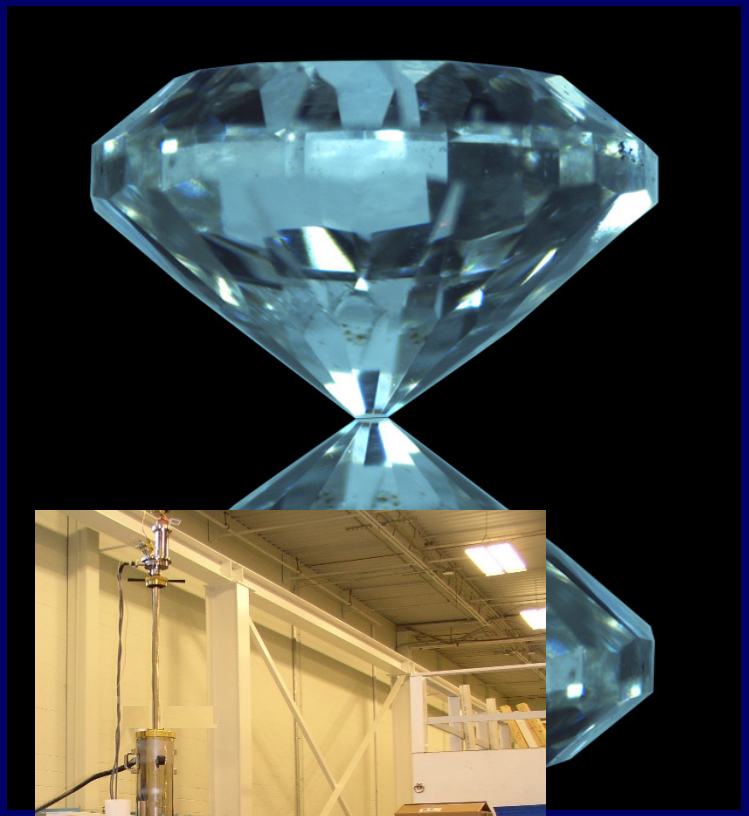
No!

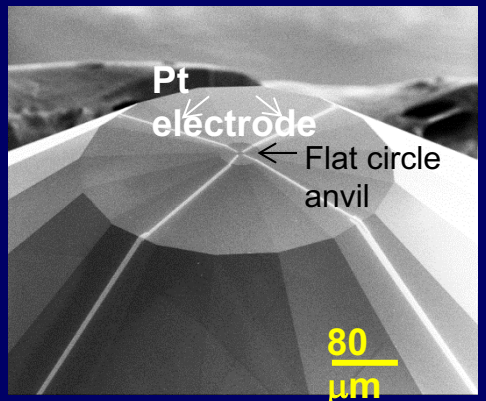
We cant grind the samples!

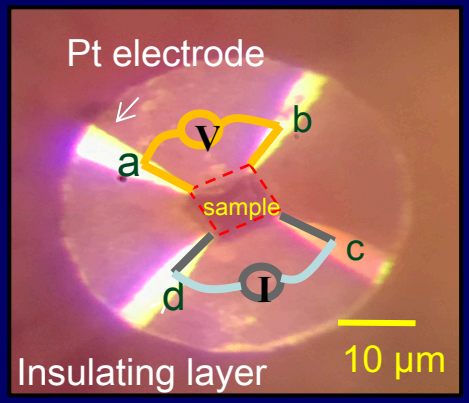
We have to flatten the samples in a roller and then snip or file off pieces to get an X-ray pattern.

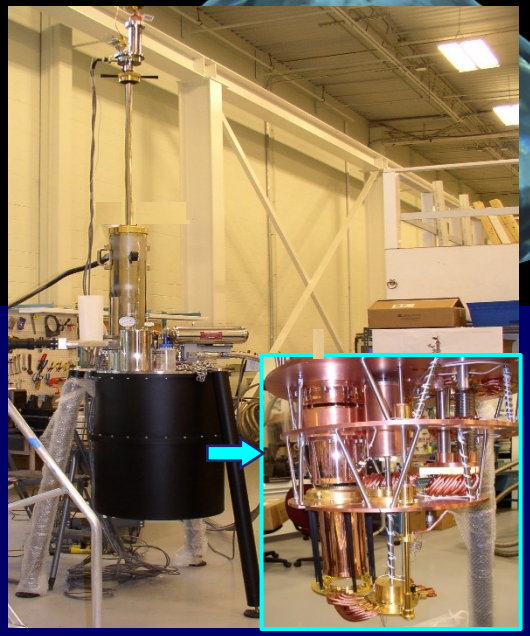
That suggests that the material is very hard.
How hard is it?
Will it mechanically survive to high pressures without failing?

Taking the high entropy alloy superconductor to very high pressures







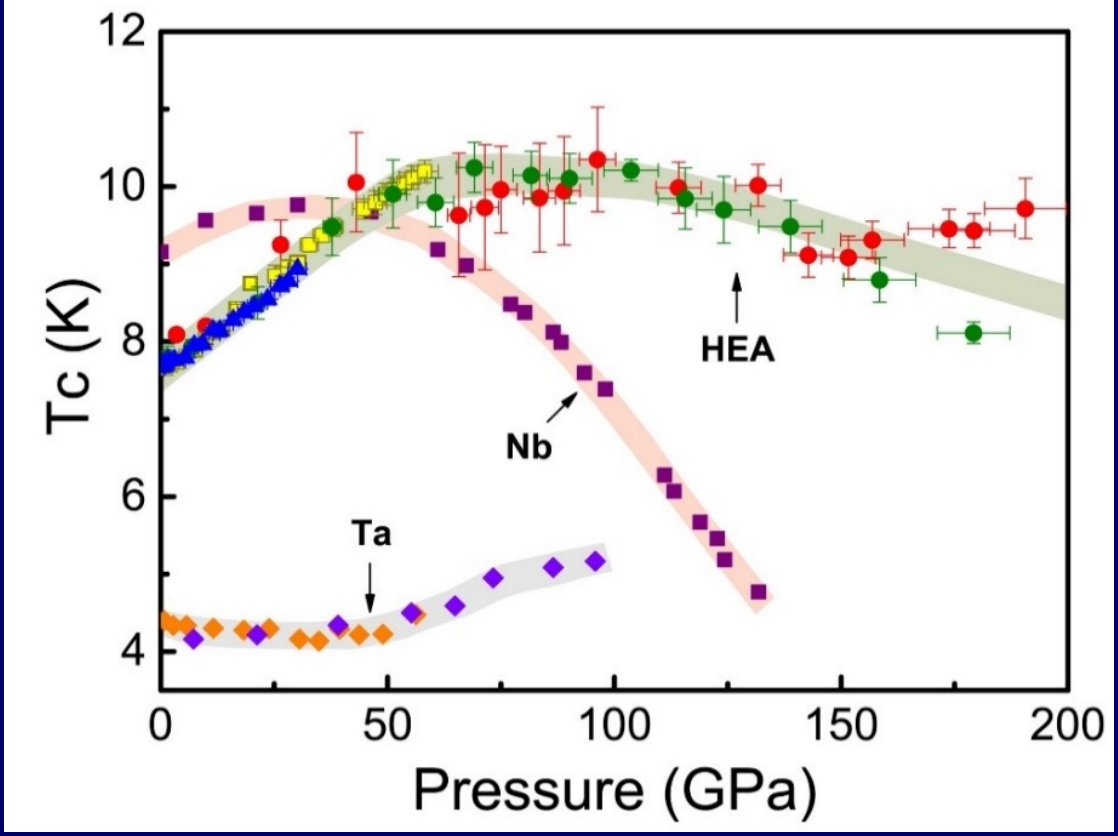


ZX Zhao
head of
superconductivity
At IOP and an old friend

Liling Sun IOP Beijing

Jing Guo IOP Beijing

What did they find?

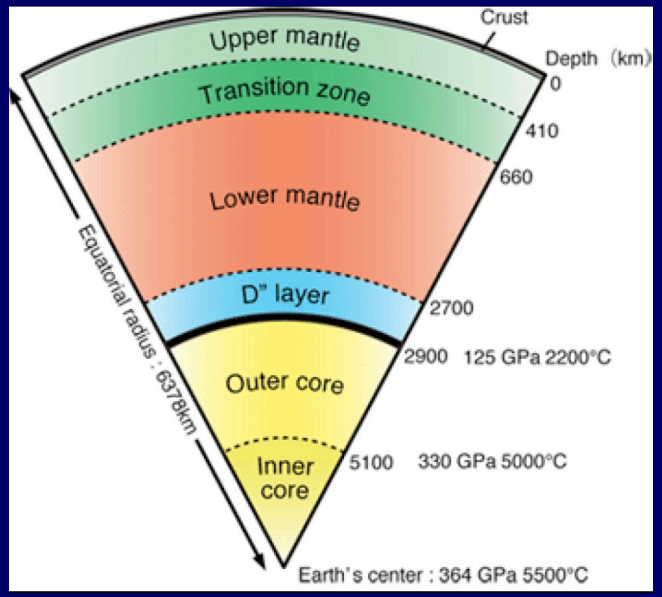


Tc vs. pressure.

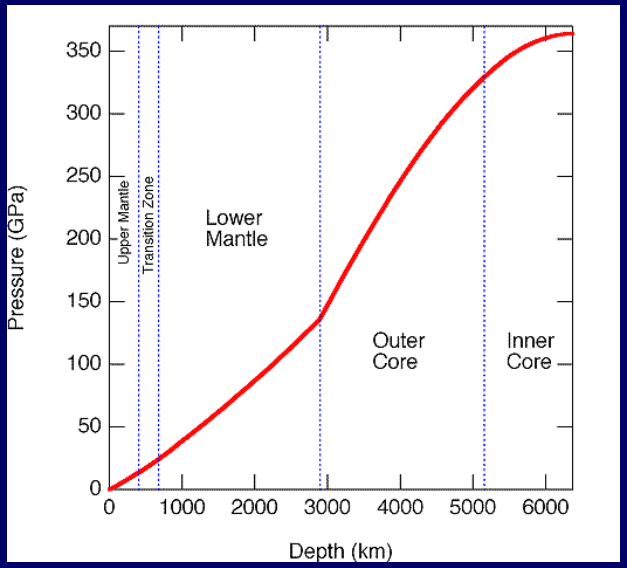
Different colors are different experiments
(they break the diamonds)

The material is continuously superconducting from 1 atmosphere to 200 GPa.

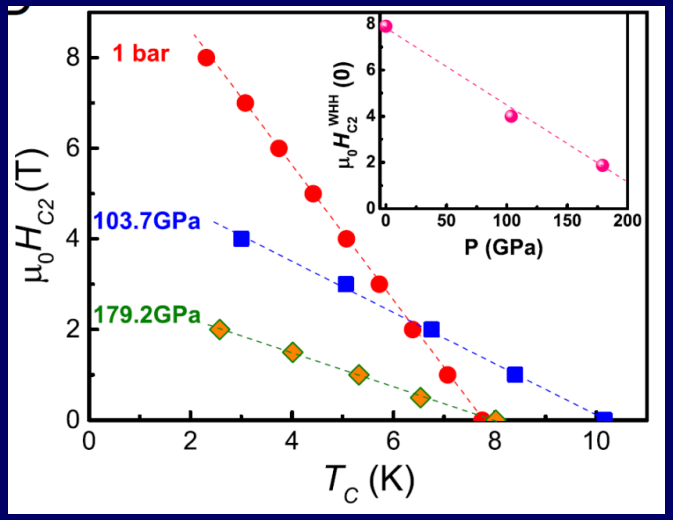
Really? Just how high is 200 Gpa in pressure?



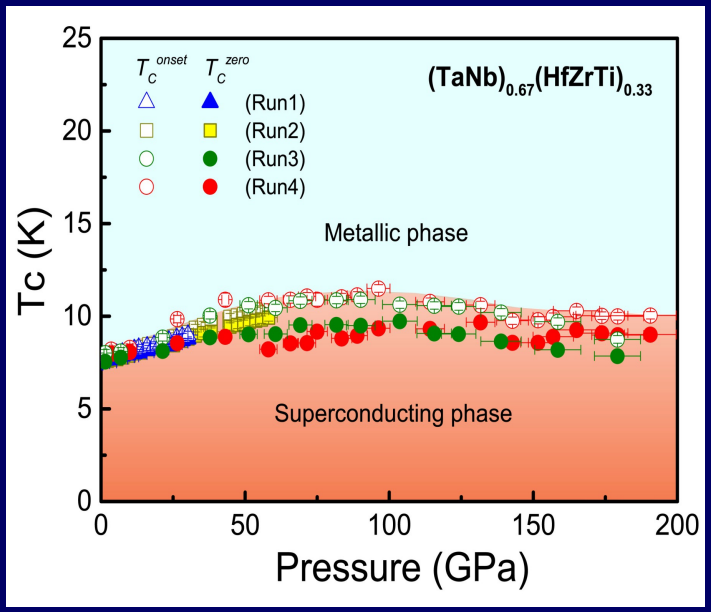
Very high



Core of the earth high



The physicists can measure HC2 (the applied field needed to kill superconductivity) at those extreme pressures.
The material is still superconducting.



Conclusion:

There are more opportunities in new materials research than you can at first imagine.

In my opinion there are a lot of papers nowadays where people don't understand the role of theorists and "predictions".
It's the ideas that count for me.

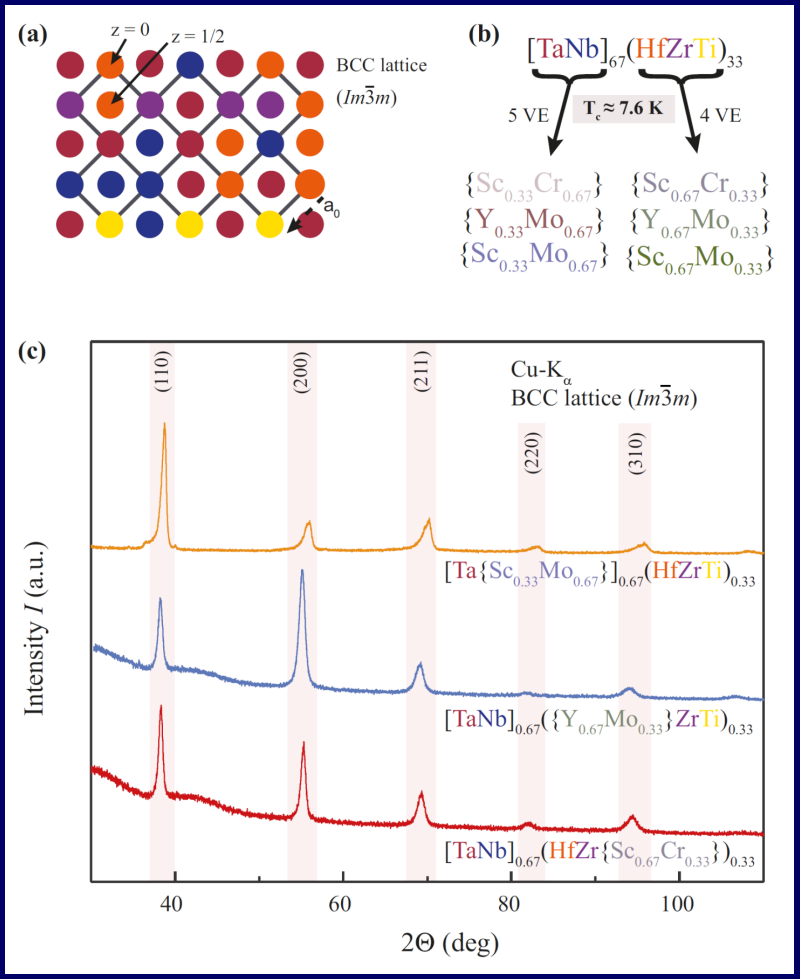
You have to be willing to try some things that don't work and not be afraid to appear stupid for trying.

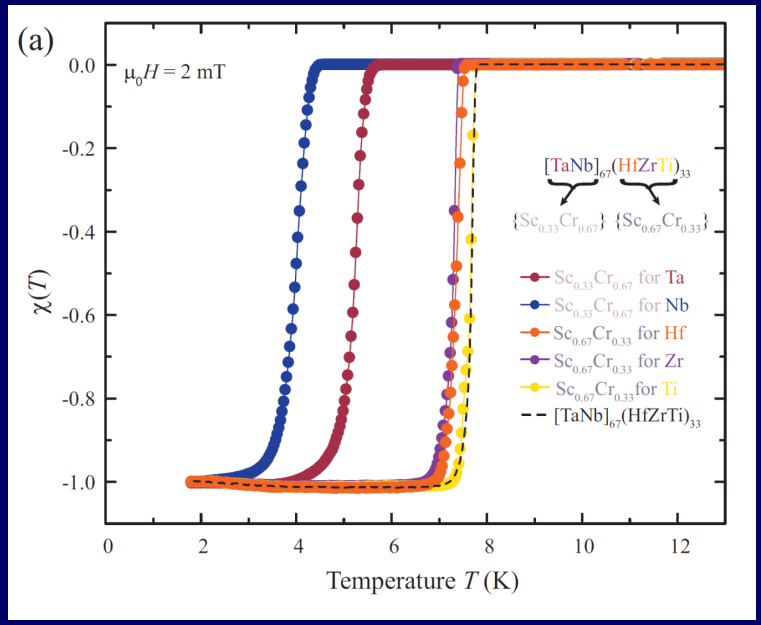
If one unexpected thing works, then you have done something special.

To close, In the words of my late uncle Conrad:

"Believe all religions. One of them may be right."

More on the constituents - Lets maintain the electron count and change the elements. Is our superconductor "the best that it can be?"





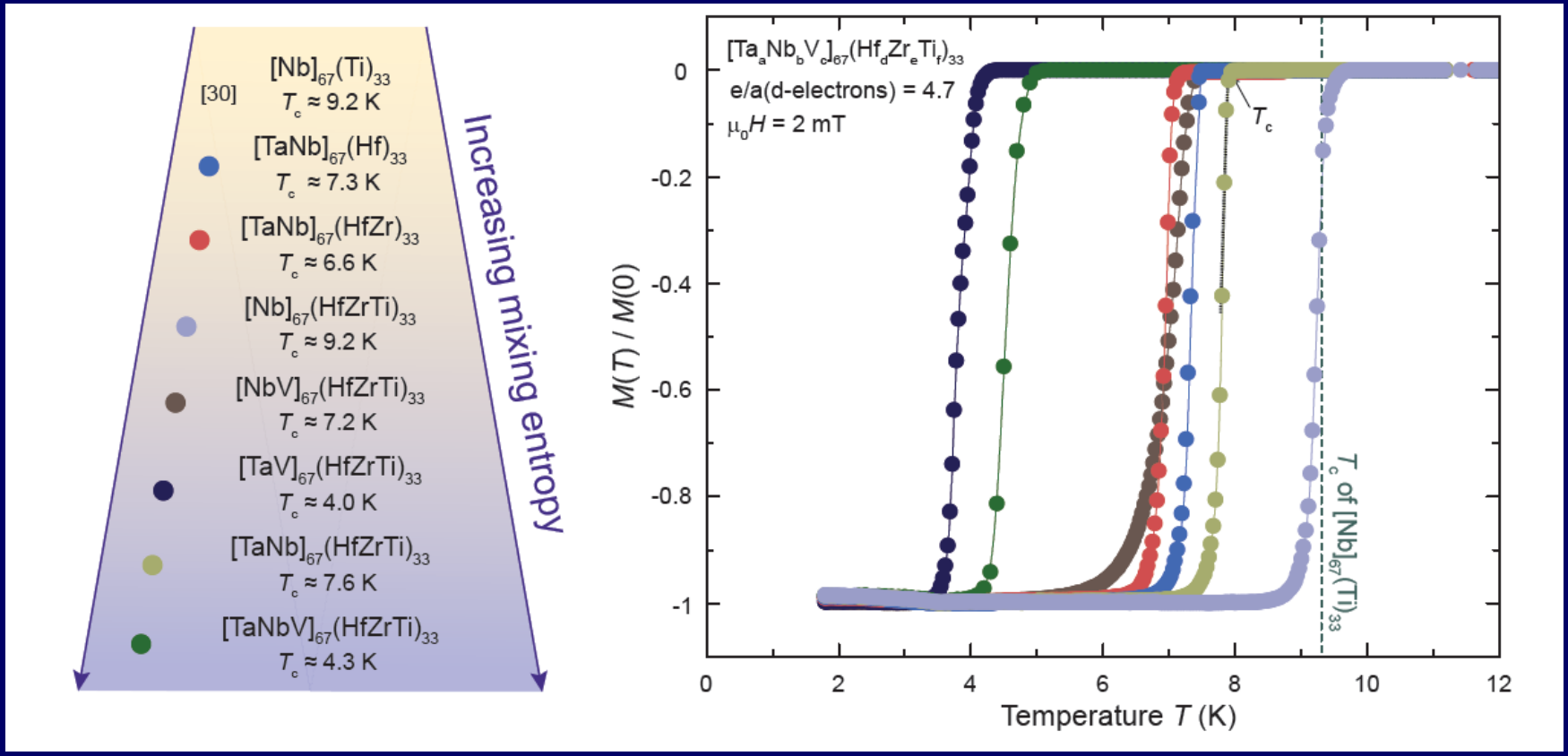
Substitution \ Original element	Ta	Nb	Hf	Zr	Ti
$Sc_{0.33}Cr_{0.67}$	5.6	4.4	—	—	—
$Sc_{0.67}Cr_{0.33}$	—	—	7.5	7.4	7.6
$Y_{0.33}Mo_{0.67}$	4.7	3.5	—	—	—
$Y_{0.67}Mo_{0.33}$	—	—	7.6	6.7	7.5
$Sc_{0.33}Mo_{0.67}$	4.4	2.9	—	—	—
$Sc_{0.67}Mo_{0.33}$	—	—	7.5	6.6	7.5

Nb and Ta are important. Hf, Sr, Ti are less so.

In a high entropy alloy superconductor

– do the elements present actually matter

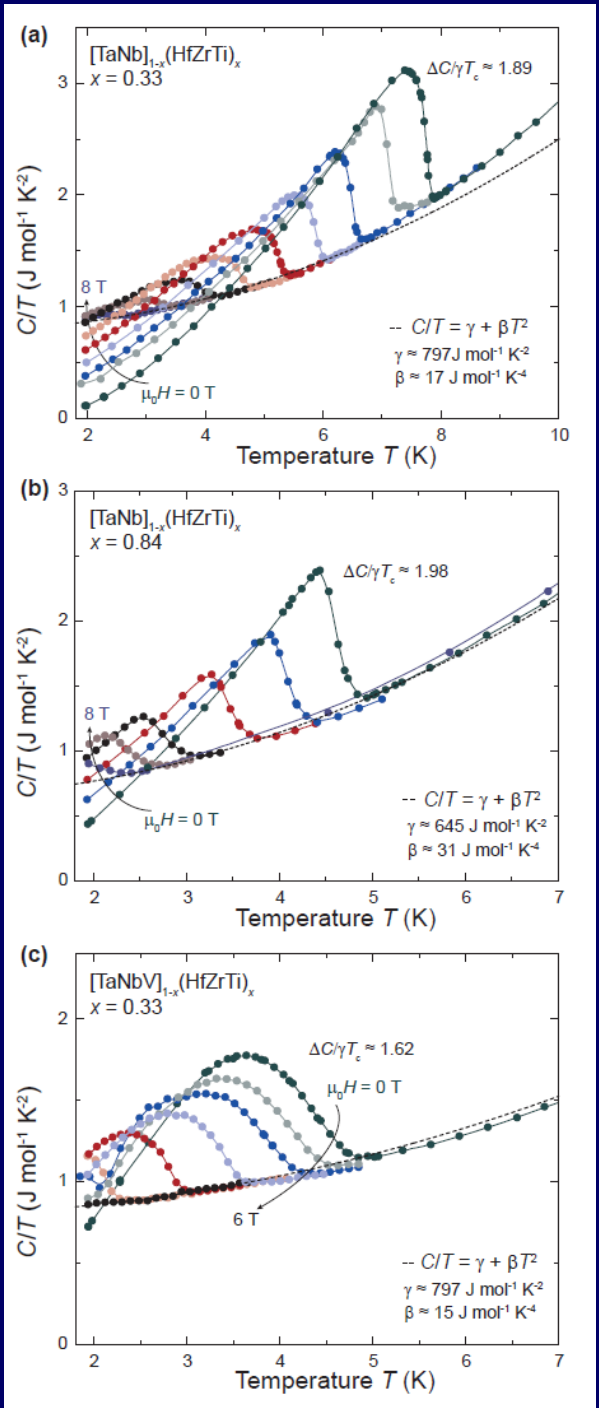
Or is it only the electron count?



Nb is always good for Tc. V is always bad for Tc

Hf, Zr, Ti mixtures don't hurt Tc.

So the elements do matter. But why?



We looked at the specific heats.

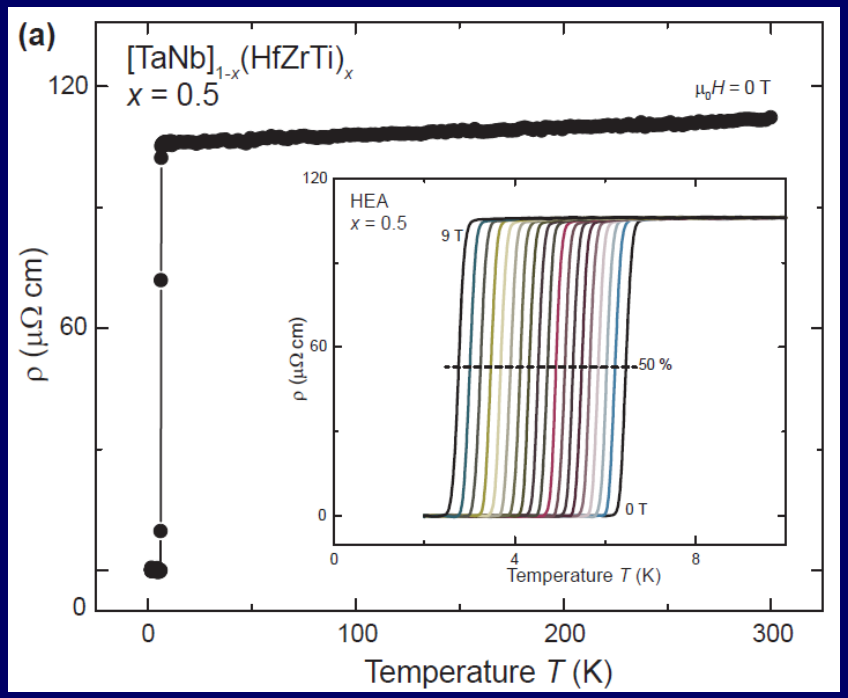
The gamma values are comparable for the high and low Tc materials.
But for the V-containing HEA the electron phonon coupling is weaker.

We don't really know why.
How can 33% Nb matter over 33% V?

(If you're thinking percolation then how can that change Tc or E-ph coupling?

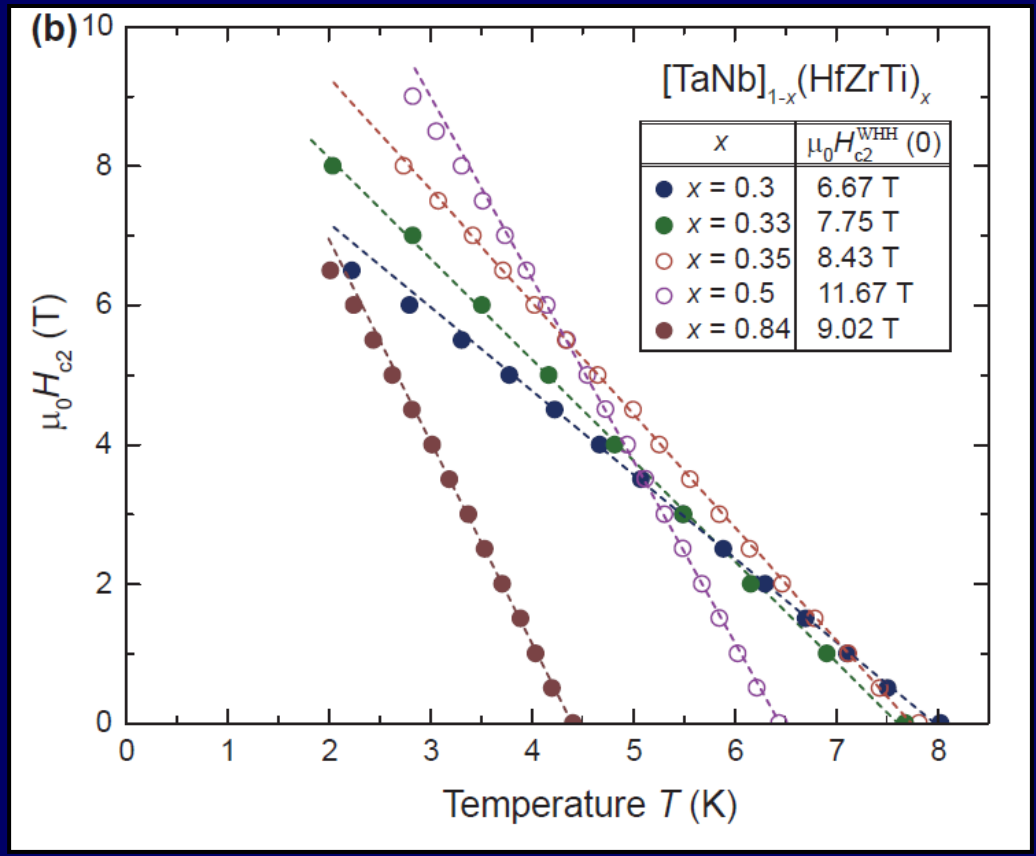
There are lots of interesting things to try in superconducting HEAs.

Here are some more…



More: $H_{C2}(T)$ for different x.

Nice behavior

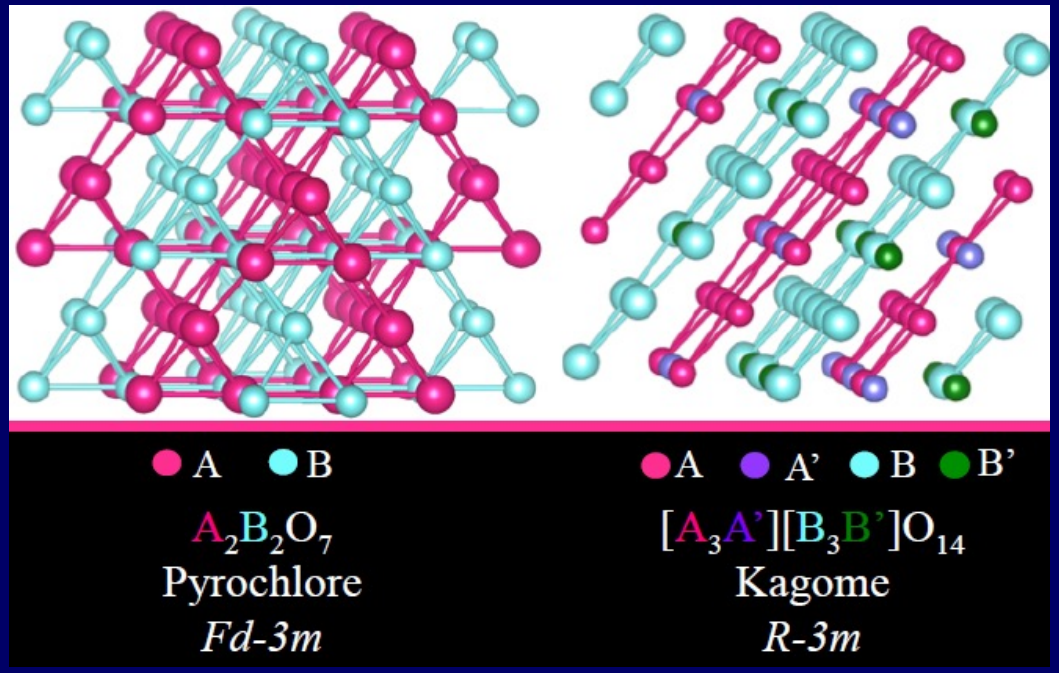


The highest Tc material does not have the highest $H_{C2}(0)$.
That one is Ta25Nb25Hf16Zr16Ti16.
The alloy with the highest mixing entropy we studied.

New rare earth Kagome compounds

The most-well-known geometrically frustrated magnets are the rare earth pyrochlores.
But no rare earth kagome's were known.
(Kagome planes are the next-most-famous magnetically frustrating geometry)

Can we compare Pyrochlores and Kagomes?
How can we make a rare earth Kagome that has a pyrochlore equivalent?

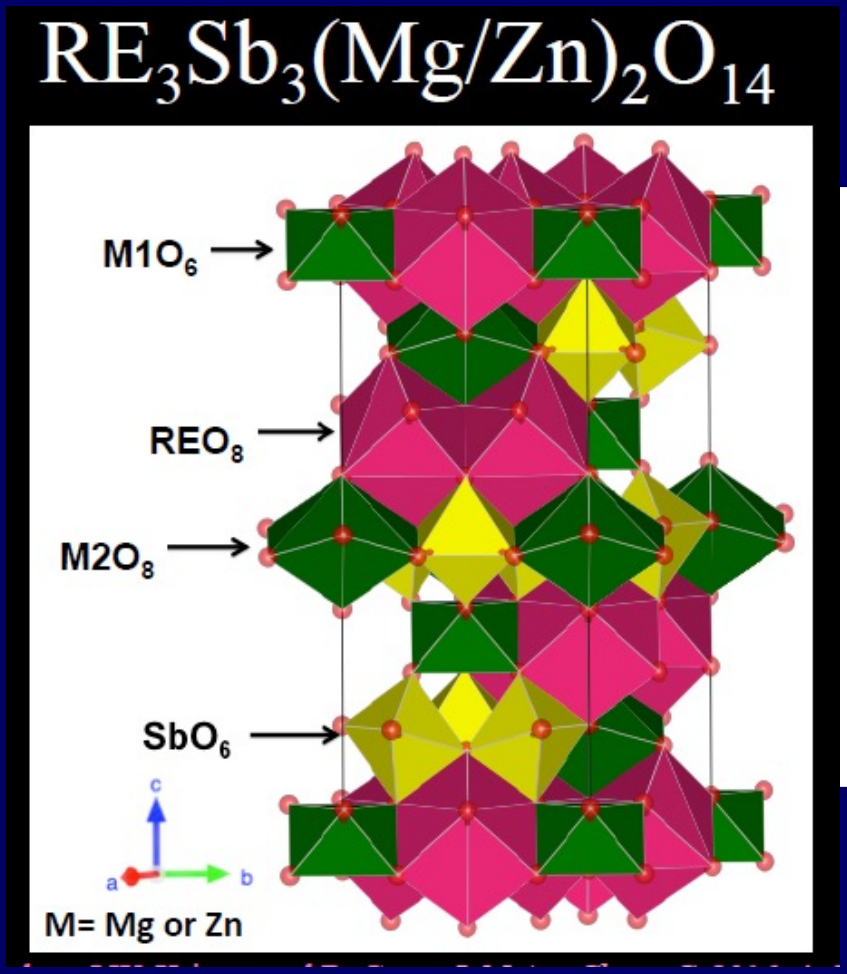


Marisa Sanders

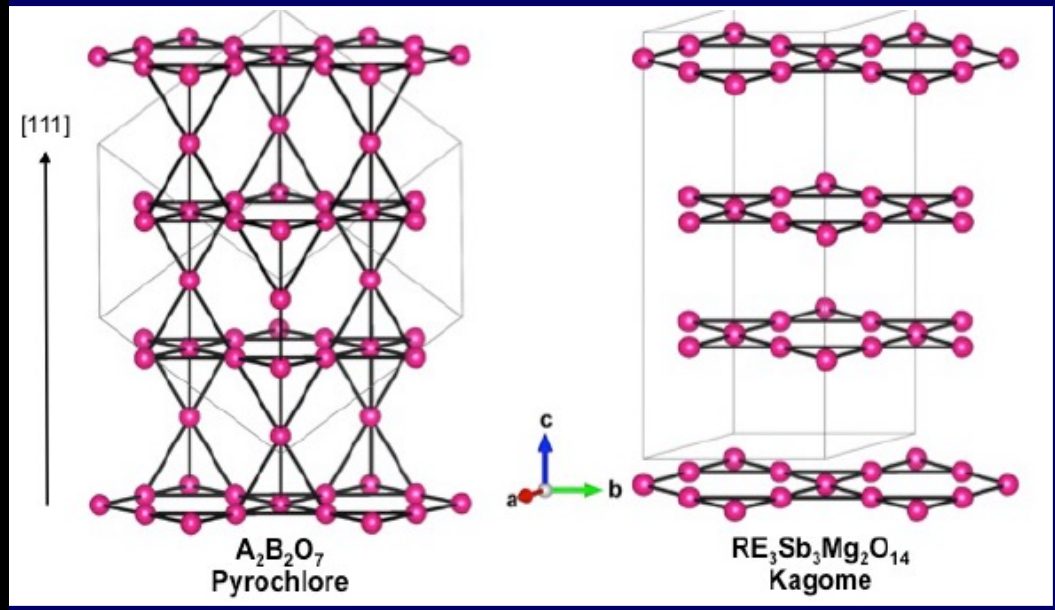
Yes. By separating one kagome plane from the others in a pyrochlore by chemical substitution using non-magnetic elements.

A atoms are the only magnetic ones. Here they are rare earths.

Different ways to look at the structure:



The usual way
MO_n coordination polyhedra



An unusual way –
extract the magnetic (A) RE atoms only

The trick, as usual, is to see the forest through the trees

For the large rare earths Marisa could make both the Kagome and the Pyrochlore structures, i.e. the both 2D and 3D magnetic lattices. So a direct comparison is possible.

$$\chi = \chi_0 + \frac{C}{T - \theta_{CW}}$$

χ_0 = Temperature Independent Contribution

χ = Magnetic Susceptibility

T = Temperature in K

C = Curie Constant

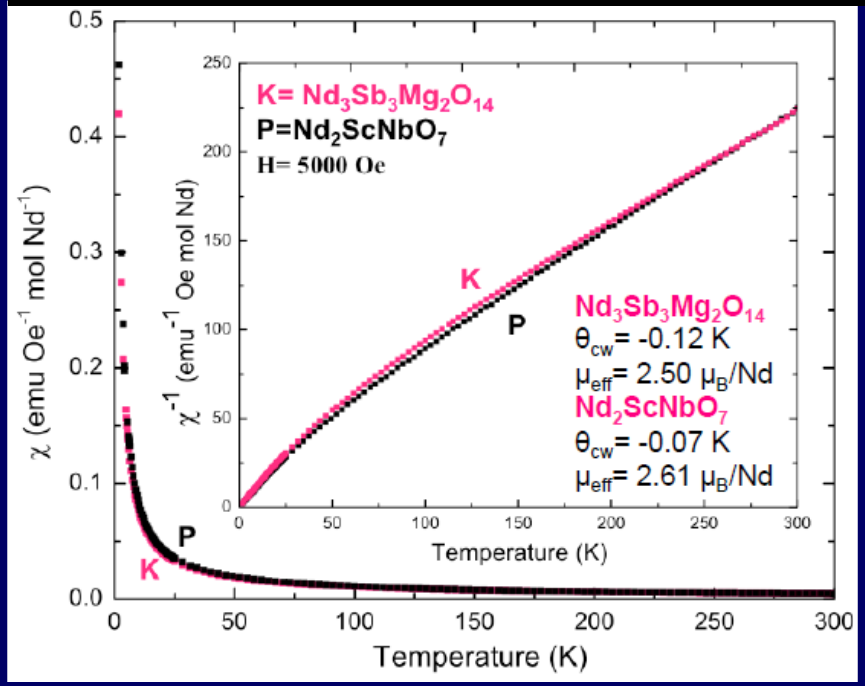
θ_{CW} = Weiss Temperature

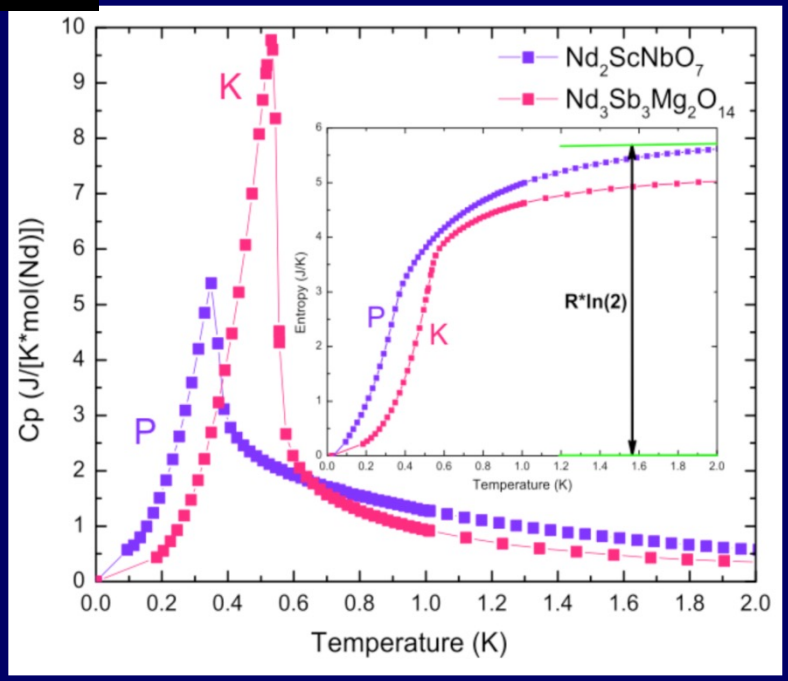
0 → Paramagnetic

+ → Ferromagnetic

- → Antiferromagnetic

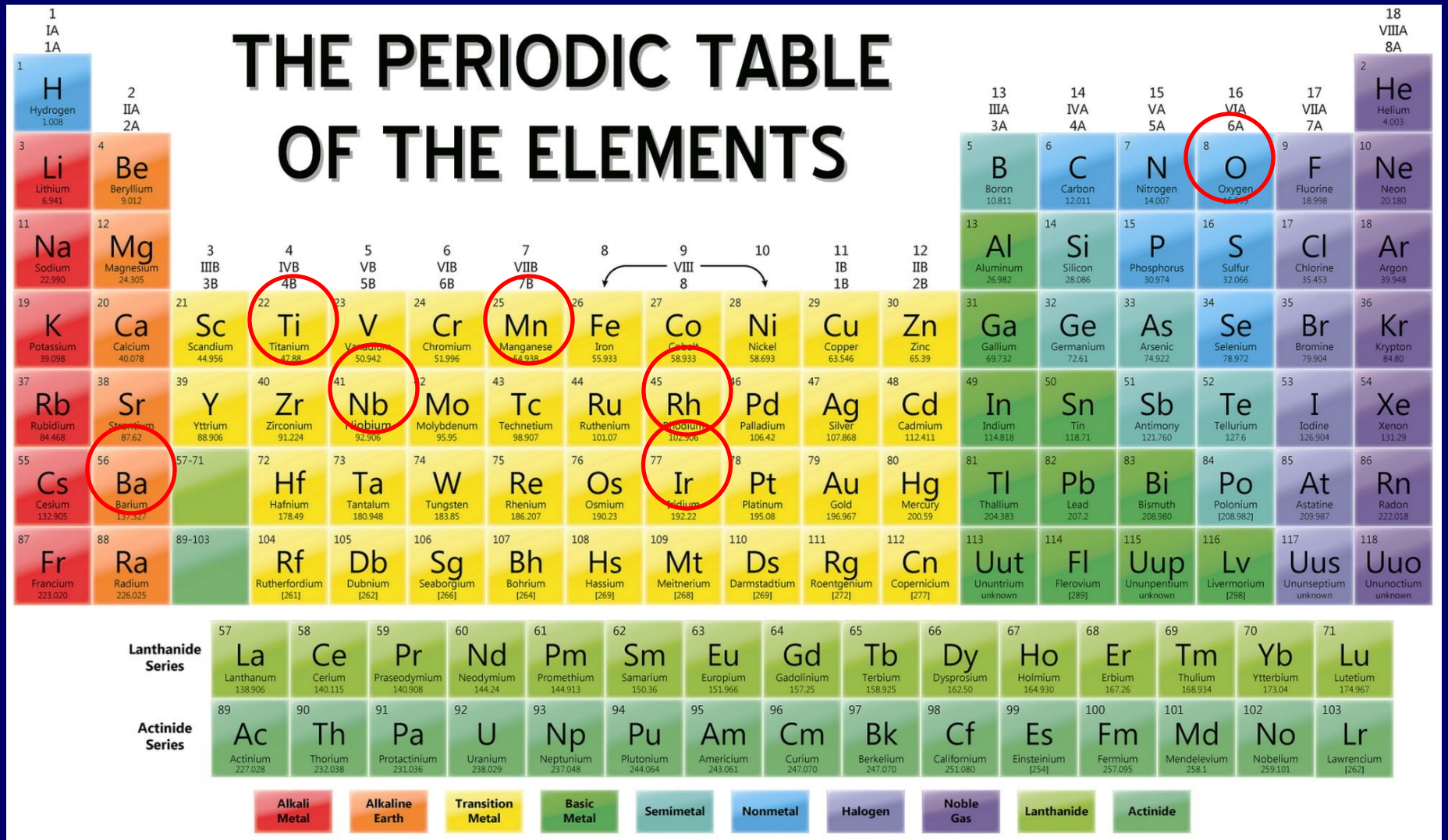
Comparison of the magnetic properties of the $Nd_2(ScNb)O_7$ pyrochlore and the $Nd_3Sb_2Mg_2O_{14}$ kagome.





First comparison of its kind – no gross difference in behavior

The periodic table again again.

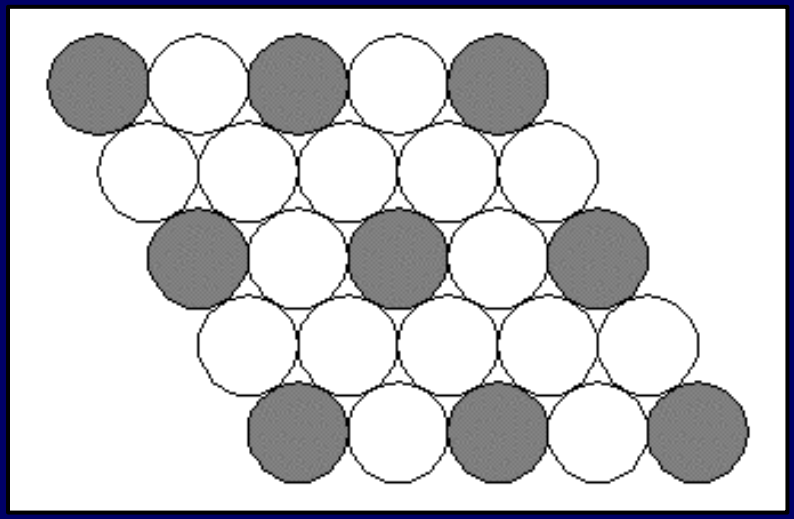


Final topic – 4. hexagonal perovskites

Hexagonal perovskites
Are materials based on ABO_3 formulas
with hexagonal symmetry
or minor distortions of it.
Rather than the usual cubic perovskites

In my opinion, at their heart is the structural stability of a close packed oxygen array where an A^{n+} ion is about the same size as an O^{2-} ion. Ba^{2+} is the winner.

There are a large number of variations.
A good chemical excuse for me to work on whether there are localized electrons or delocalized electrons on M_nX_m clusters.

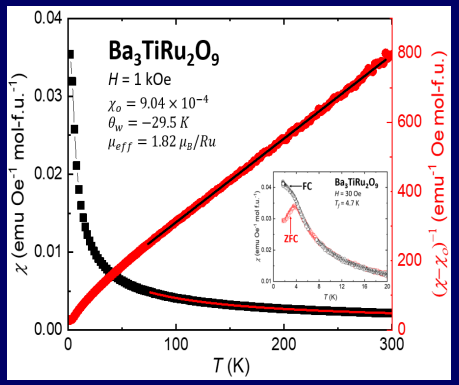


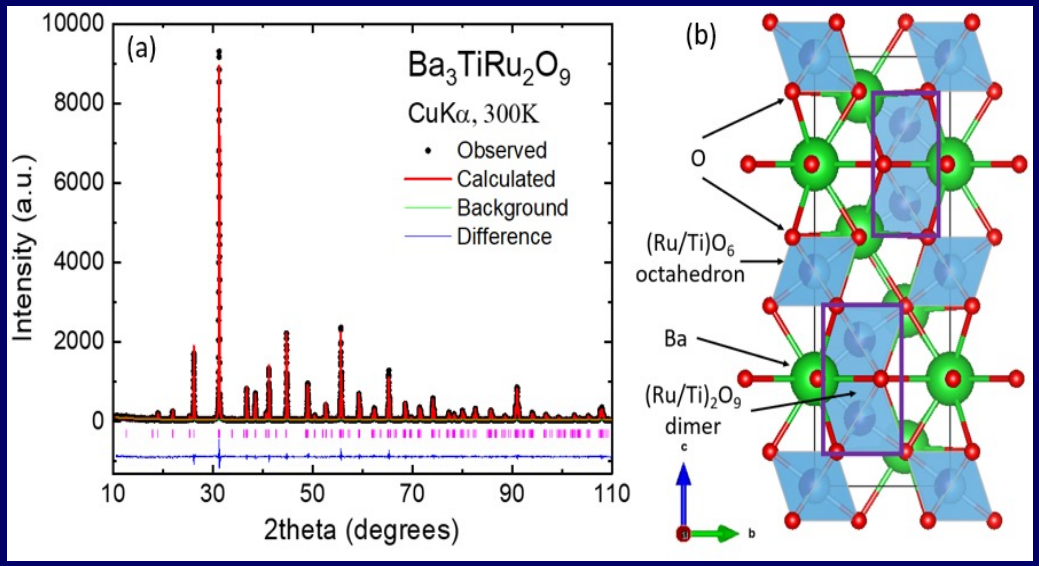
Ba^{2+} (gray) in a close packed plane of O^{2-} (white)

The first of our work on hex perovskite oxides -a dimer compound $Ba_3TiRu_2O_9$. Good news is that the dimers contain Ru^{4+} ($4d^4$ spin 1)
Bad news is that it has structural disorder and so it is a spin glass.

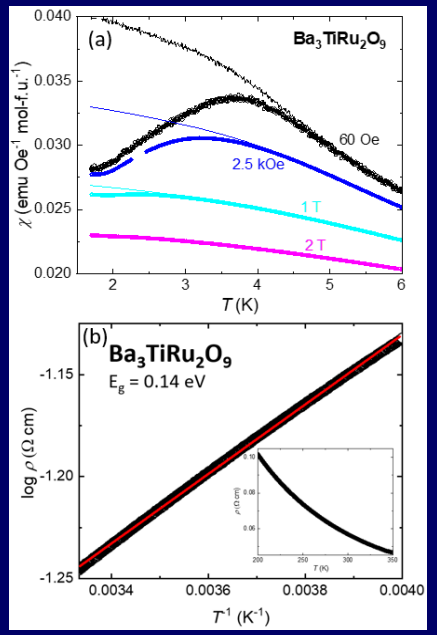
Many dimer systems have been studied by physicists.
Nice but not so interesting for me because they don't directly address the issue of localized vs itinerant electrons on clusters.

Loi Nguyen



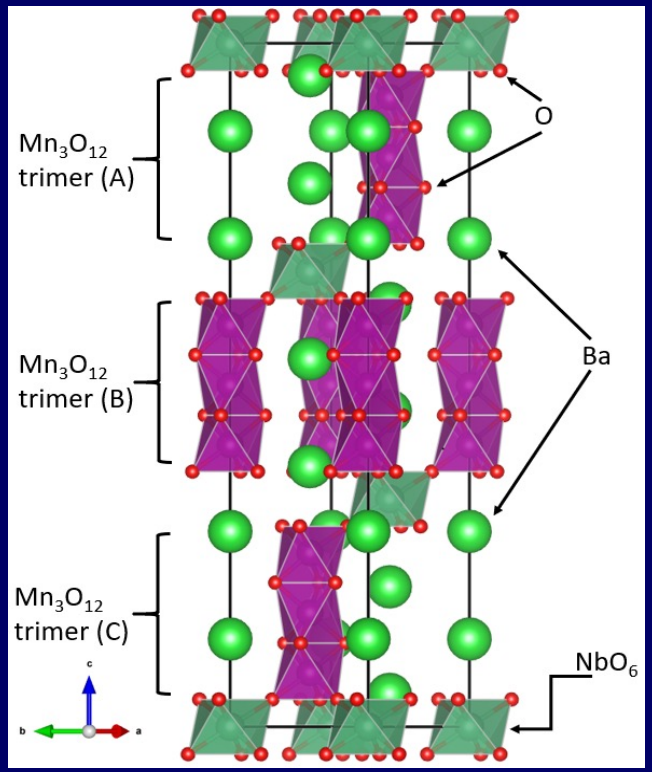


The first of our many insulators In this family

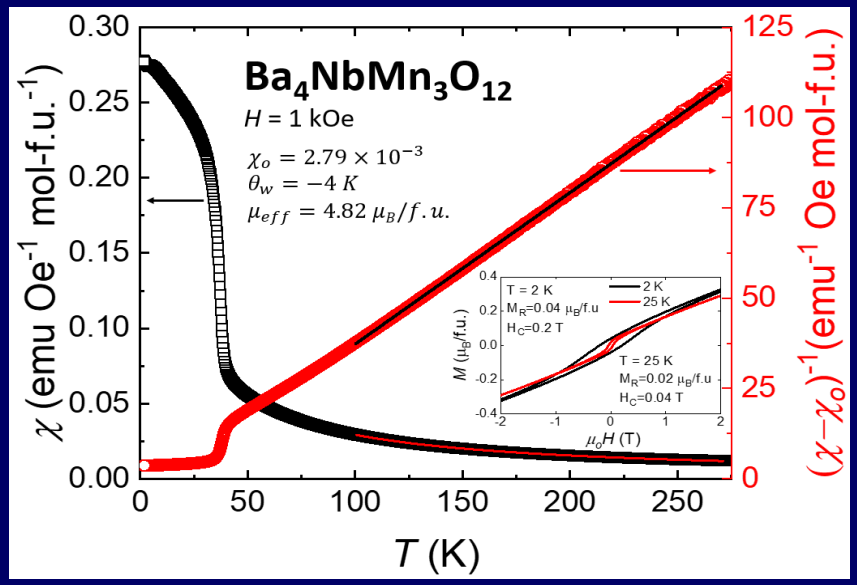


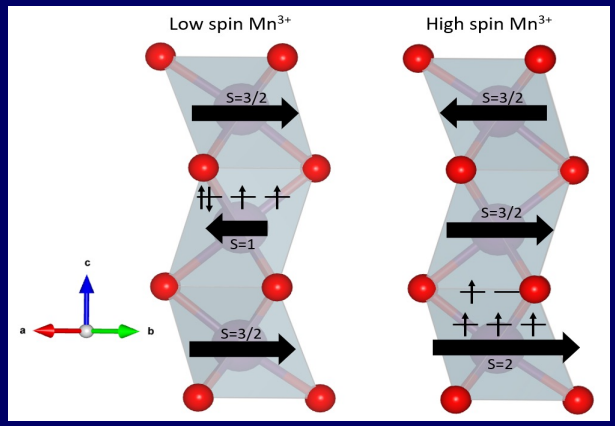
Now the first of several trimer compounds.
First one is based on a 3*d* element (Mn).

I like trimers because "wheres the spin?"



Ba^{2+} and Nb^{5+} are not magnetic
So all magnetism is from Mn. a 3*d* ion.
Two Mn^{4+} $3d^3$
One Mn^{3+} $3d^4$





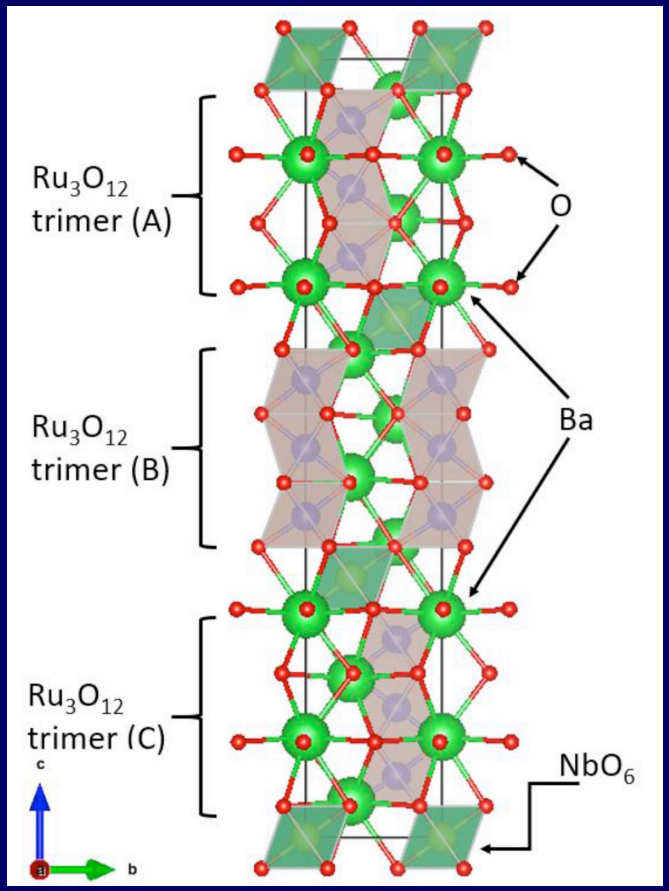
As we progress from 3*d* to 4*d* to 5*d* magnetic elements
Does a local moment picture break down?

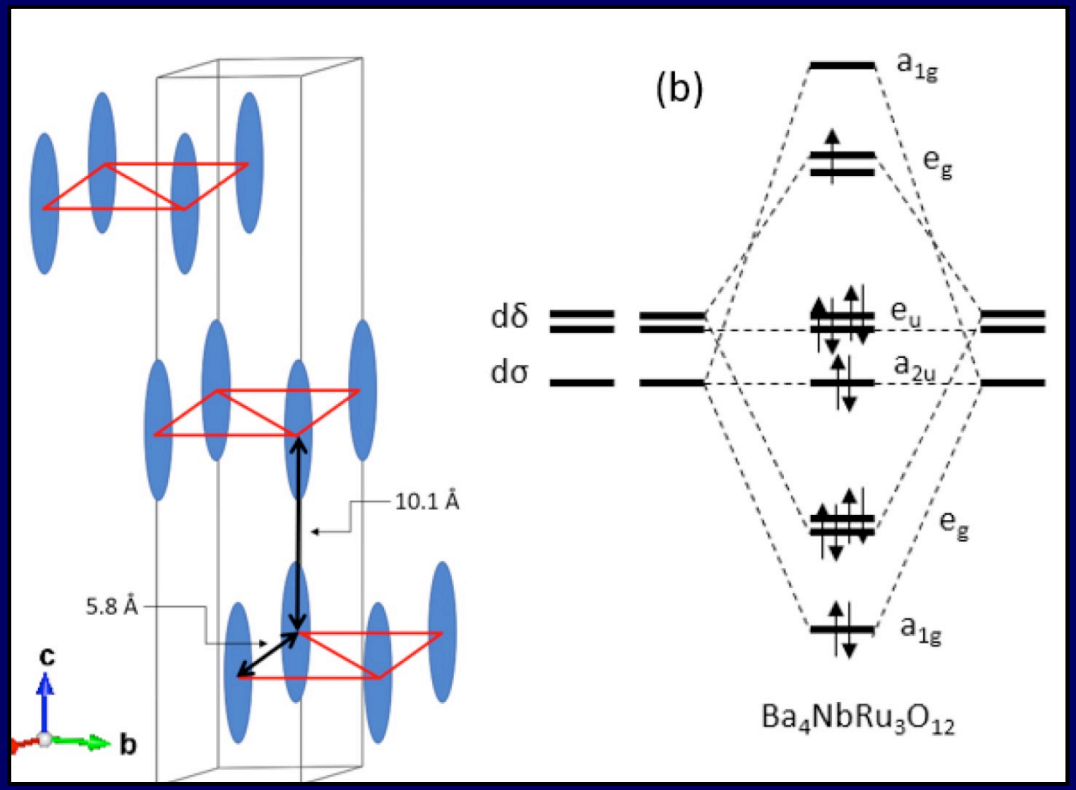
In this case a local picture works. Russian theorists Komleva Khomskii and Streltsov did it.

Now a second trimer compound $Ba_4NbRu_3O_{12}$. Based on a 4*d* element that is often magnetic in oxides. (Ru)

A Geometrically Frustrated Trimer-Based Mott Insulator

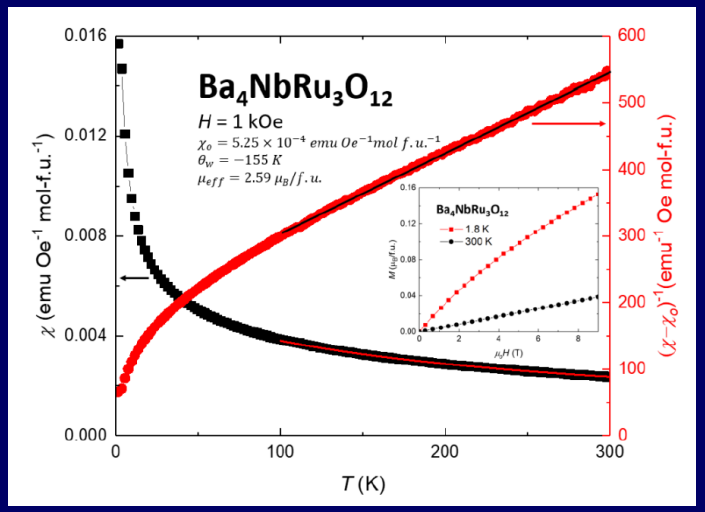
Loi T. Nguyen[1], T. Halloran[2], Weiwei Xie[3], Tai Kong[1], C.L. Broholm[2] and R.J. Cava[1]

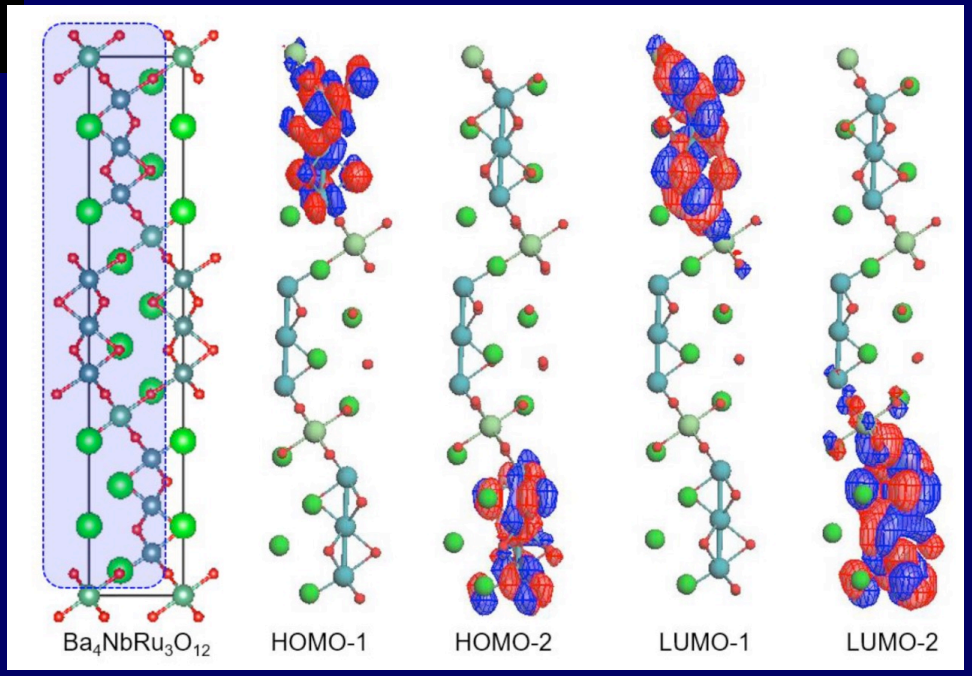




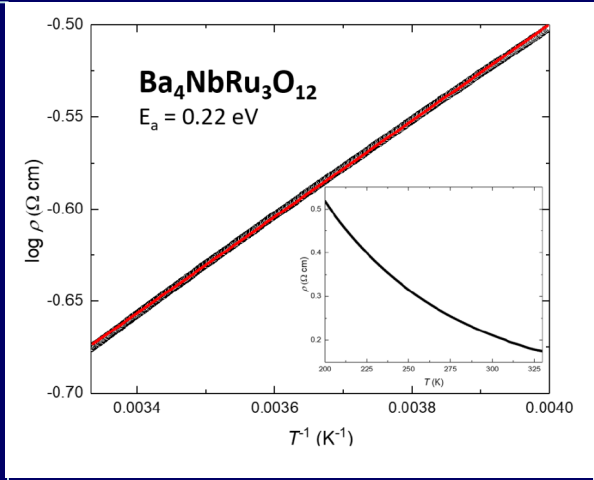
Two Ru 4+ and one Ru3+
= 13 electrons per trimer = spin ½ per trimer
a nice spin.
Cigar-shaped spin ½ molecules on a triangular lattice.

Now things are looking interesting.





Magnetic moment is too low for a simple localized picture. Too high for a simple molecular picture. Classic frustrated Magnetism chi vs T



And its an electrical insulator

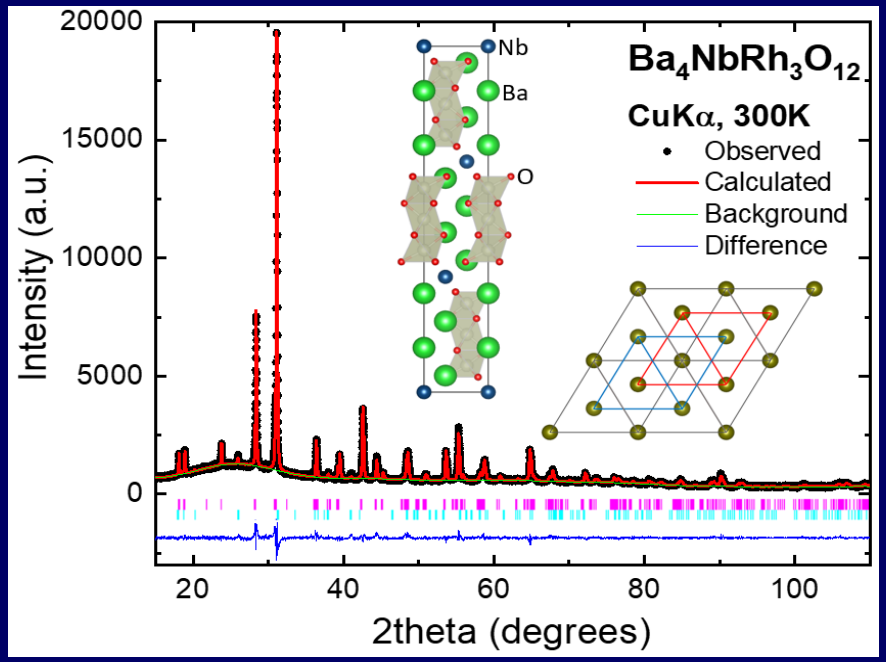
In a molecular picture, where are the electrons?
- on the Trimers, in hybridized Ru-O molecular orbitals.
In DFT with SOC and no U the material is a metal, but it is actually an insulator.
= the definition of a Mott insulator?

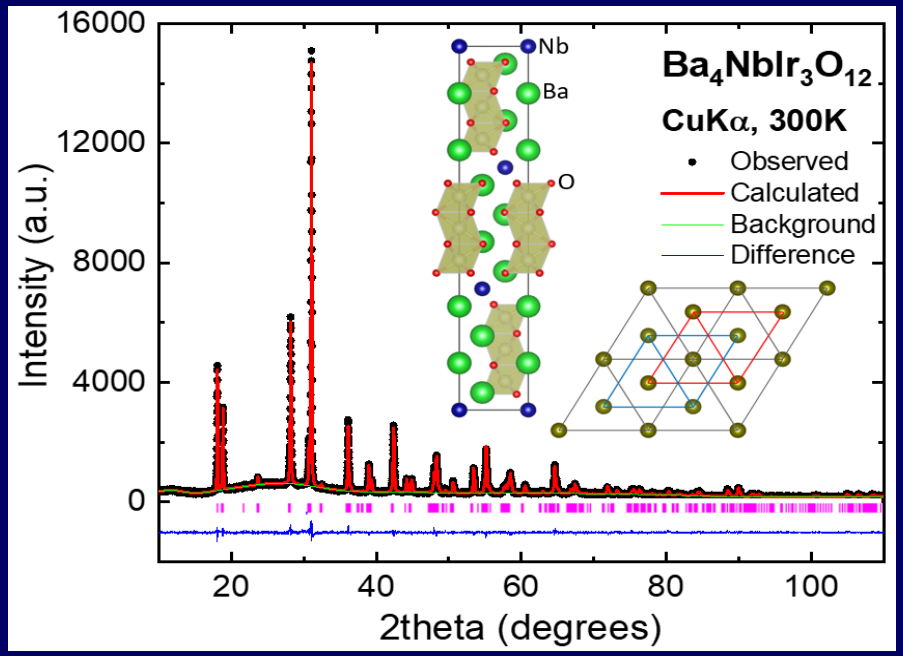
Two more: with Ir_3O_{12} and Rh_3O_{12} trimers in the new materials $Ba_4NbRh_3O_{12}$ and $Ba_4NbIr_3O_{12}$.

Compares magnetism in Hex perovskites for 4*d* and 5*d* elements from the same column of the periodic table = same number of valence electrons.

Note its Co - Rh - Ir down the column.

The Co one makes an annoying disordered cubic perovskite.

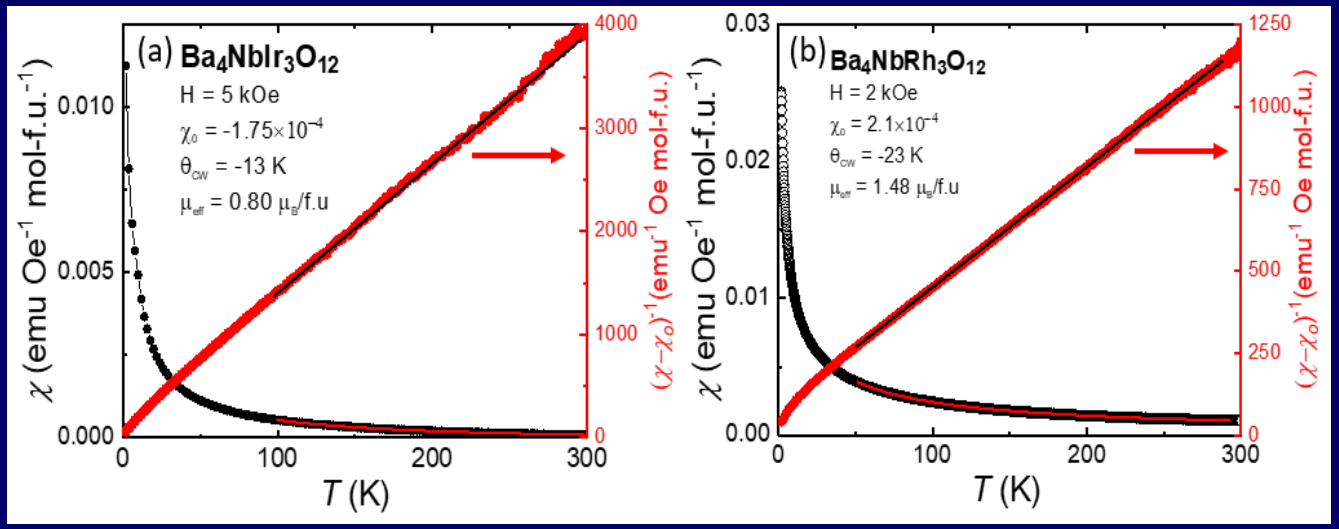




- Had the idea but then we actually made them and figured out their crystal structures.

They are 4*d* and 5*d*-based trimer compounds with no detectable structural disorder

Now lets look at their magnetism



To 1st order they seem very similar magnetically

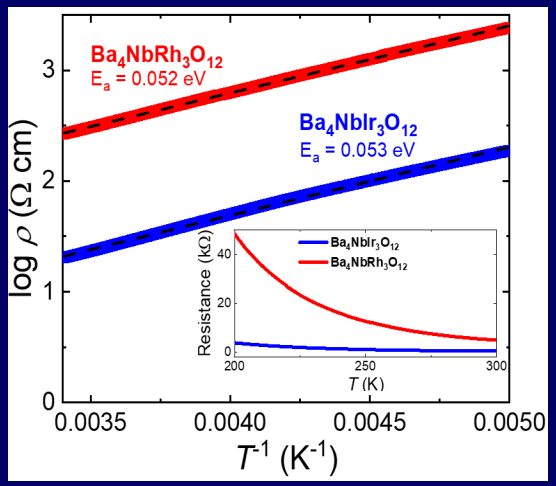
Very small moments - both effective moments are less than spin ½ per trimer. and the Θ_{CW} are in the -15 to -25 K range

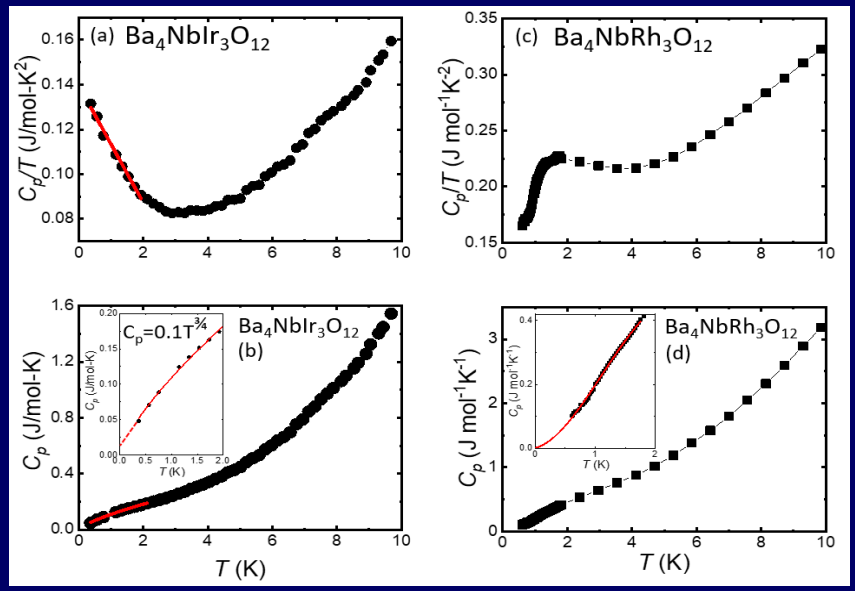
And there is no sign of magnetic ordering above 2 K

We have two 4+ ions and one 3+ ion
In these 4*d*-based (Rh) and 5*d*-based (Ir) trimer materials.

Rh $^{3+}$ and Ir^{3+} are d^6 and possibly boring.
Rh^{4+} and Ir^{4+} are d^5 and are not.
But where are the moments?
Localized on the atoms or in the trimer Molecule orbitals?

Like the other hexagonal perovskites we looked at, these are electrically insulating





And something is going on in the heat capacity at low T

I suppose there must be some hexagonal perovskites that aren't insulating.
But what are they?

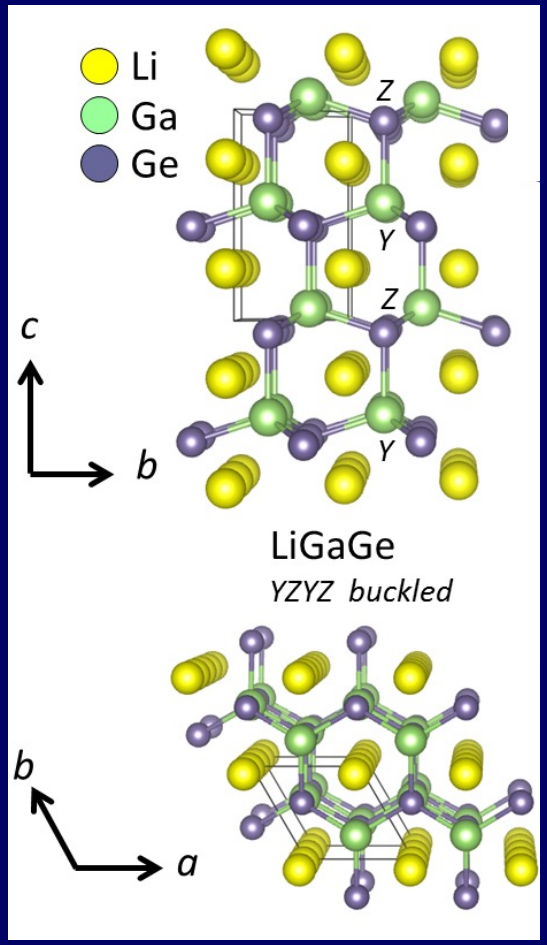
$Ba_4NbIr_3O_{12}$ is doing something strange. No magnetic phase transition, Cp/T continues to rise down to 0.35 K and does not extrapolate to 0 at T = 0.

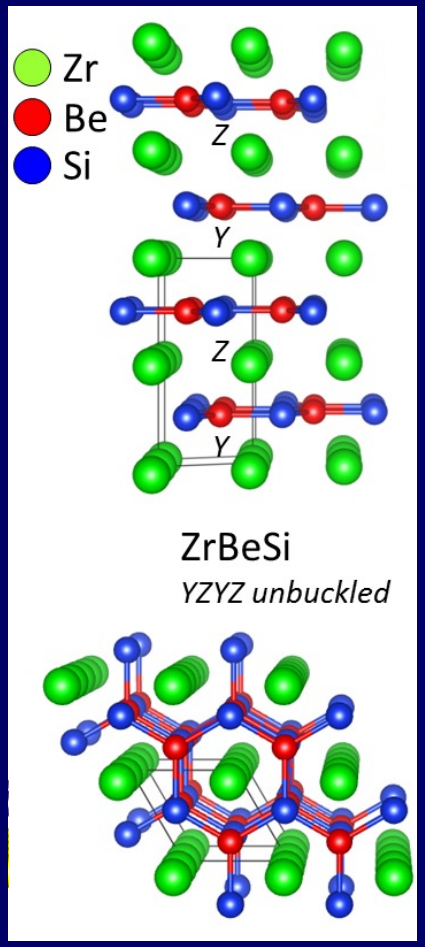
$Ba_4NbRh_3O_{12}$ is losing entropy at around 2 K. and Cp/T extrapolates to 0 at T = 0. It behaves like its supposed to I guess.
But the Rh is magnetic?
Very rare but not the first case.

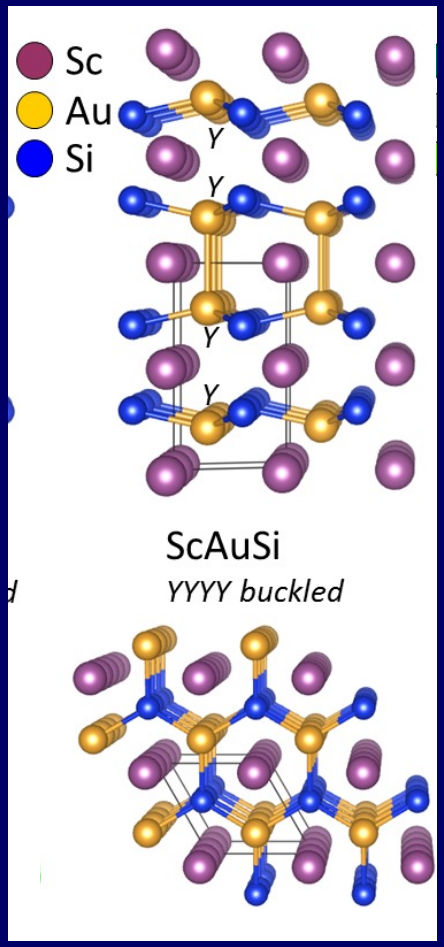
Can the Ir one be a quantum spin liquid?

People are working on it.

Stable variations of the Hexagonal 1:1:1 crystal structures







Honeycomb rings in flat or buckled layers, differences in stacking

Conclusions

Fields are the most dynamic when theory, experiment, and new materials discovery develop in parallel.

Our primary role is to introduce new materials whose electronic and magnetic properties may be interesting to experts.

Please ask me for crystals to do experiments on,

or for us to try to make a material to illustrate a theoretical concept that you have.

Thank you.