

Finding New Materials – a chemical perspective. Some examples.

R.J. Cava, Chemistry and Materials, Princeton U

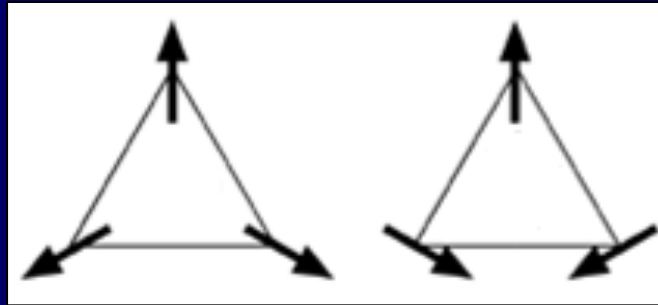
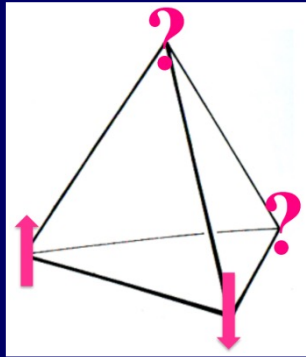
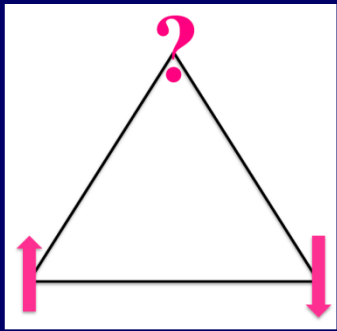


With students and postdocs at PU.

Collaborators at BNL, ANL, Johns Hopkins U, Rutgers U, and Gdansk Poland

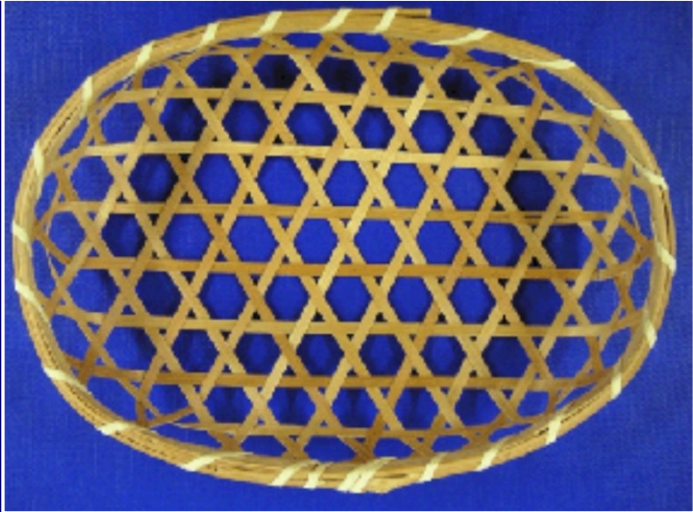


First, geometrically frustrated magnets



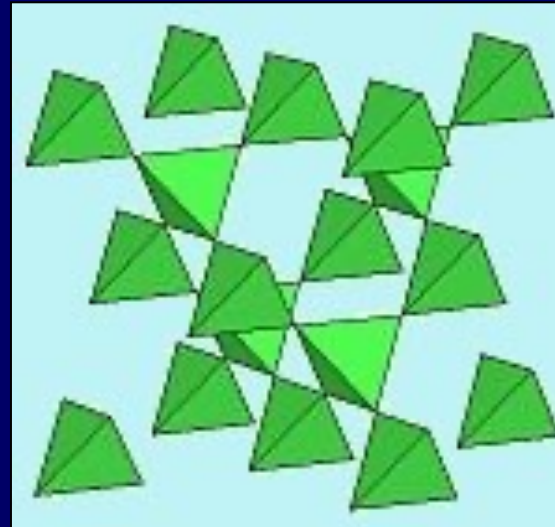
The low temperature spin ordering gets “frustrated”

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?



To relate to something more familiar
Think of supercooled water

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



The Pyrochlore lattice. Corner sharing tetrahedra.

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

The periodic table, my happy place.

This time the elements of interest are near the top:

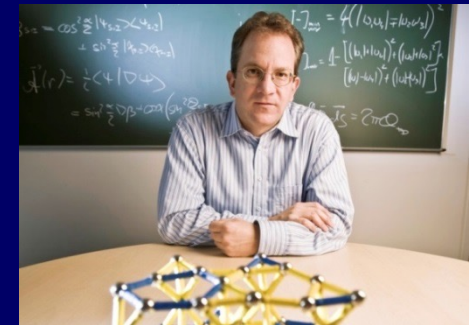
THE PERIODIC TABLE OF THE ELEMENTS

The periodic table is color-coded by groups. Elements of interest are circled in red: Sodium (Na), Calcium (Ca), Strontium (Sr), Oxygen (O), Fluorine (F), Cobalt (Co), and Nickel (Ni). The table includes the Lanthanide and Actinide series at the bottom.

1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A		
1 H Hydrogen 1.008												5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180		
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19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80		
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29		
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87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [293]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown		
Lanthanide Series		57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967			
Actinide Series		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]			
Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide										

Transition metal fluoride pyrochlores

This work was motivated by several theorists –
 Michel Gingras
 Leon Balents and
 Roderich Moessner



Who independently asked me

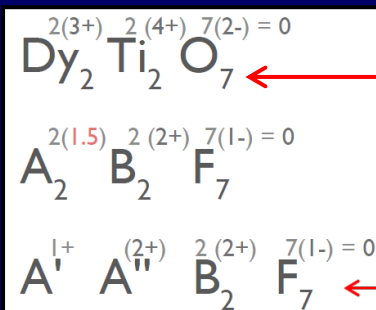
“can you make a pyrochlore with stronger magnetic interactions than 1 K?”

The well studied ones are based on *f* electrons where the interactions are weak

Eventually, yes. **But what are the materials requirements?**

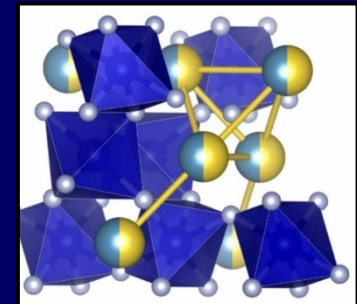
Because we need stronger interactions, we need to use magnetic transition elements. **Divalent** 3*d* transition elements are strongly magnetic but have to go on the B sites where the coordination is octahedral.

But the lower 3*d* element charge needs to be balanced.



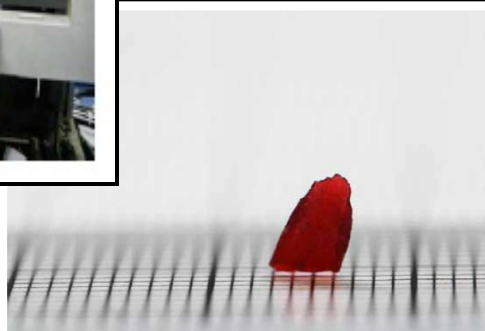
On a normal rare earth pyrochlore
 Only the A site is magnetic. *f* electrons

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.



$\text{NaCaCo}_2\text{F}_7$



$\text{NaSrCo}_2\text{F}_7$



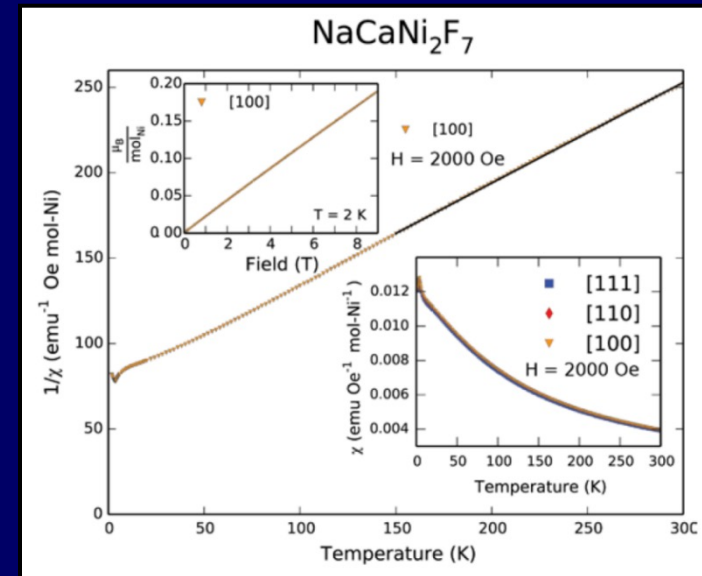
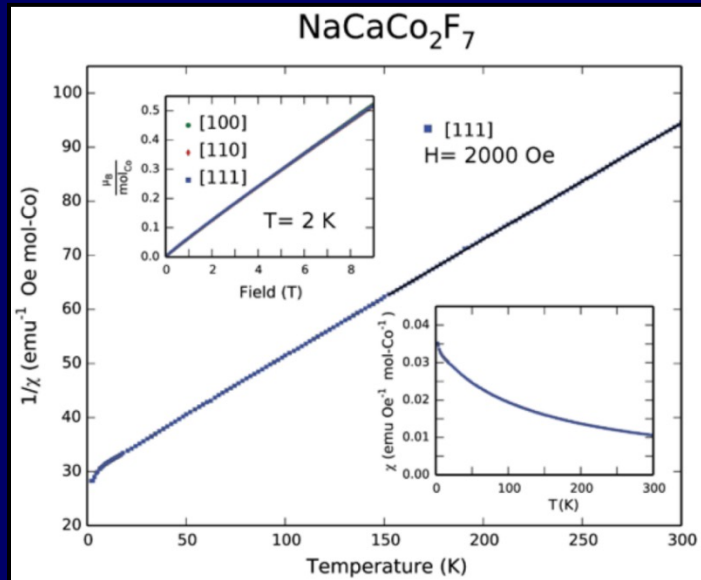
$\text{NaCaNi}_2\text{F}_7$



All display nice Curie Weiss law behavior

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

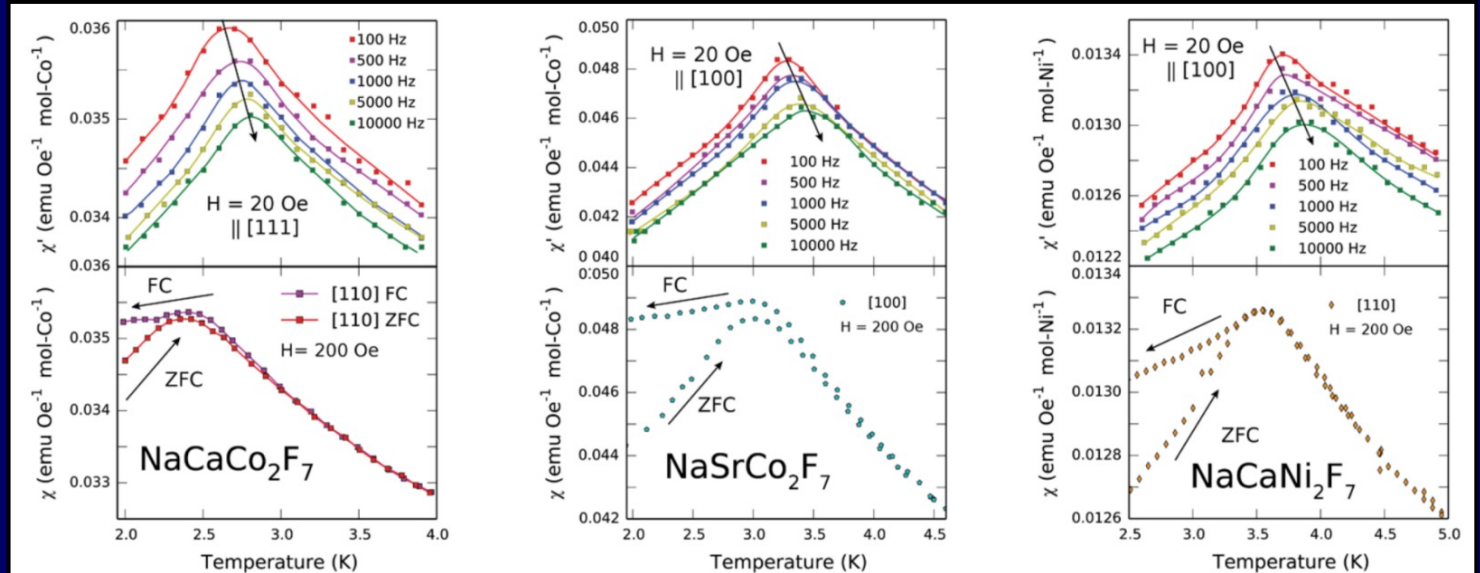
- χ_0 = Temperature Independent Contribution θ_{CW} = Weiss Temperature
 χ = Magnetic Susceptibility 0 \rightarrow Paramagnetic
 T = Temperature in K + \rightarrow Ferromagnetic
 C = Curie Constant - \rightarrow Antiferromagnetic



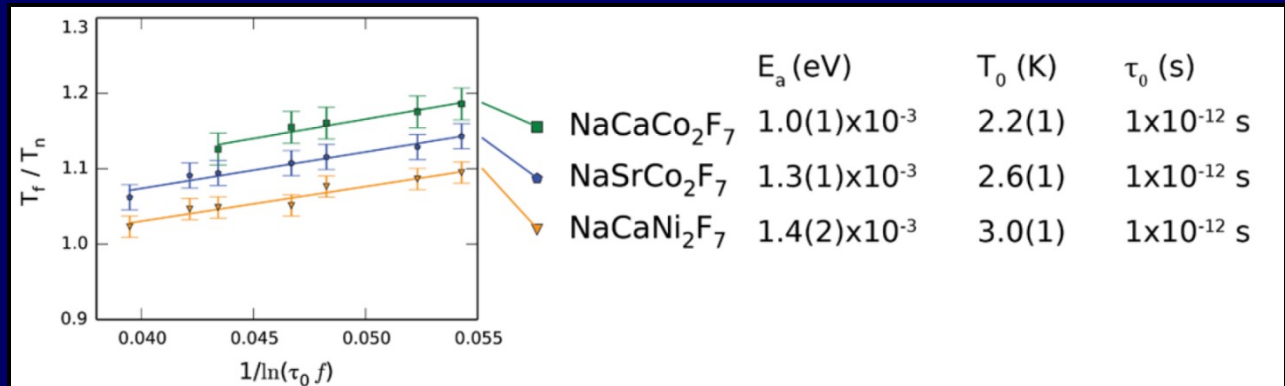
Curie-Weiss Fit:	θ (K)	ρ_{eff} (μ_B)
■ NaCaCo ₂ F ₇	-139(1)	6.1(1)
◆ NaSrCo ₂ F ₇	-127(1)	5.9(1)
▼ NaCaNi ₂ F ₇	-129(1)	3.6(1)

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



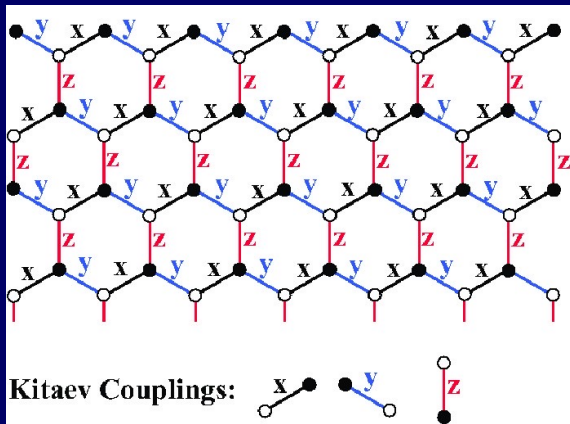
Second, Quantum Spin Liquids

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

Honeycombs are weird because of nn vs nnn interaction balance.

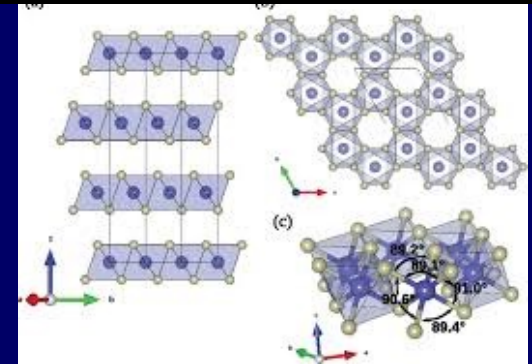
In a spin liquid magnetic moments don't "ever" thermally freeze. In a quantum spin liquid (QSL) the state they get into at low T is quantum mechanical in character.

Na_2IrO_3 (actually $\text{Na}_3(\text{NaIr}_2)\text{O}_6$ structurally) is a prime candidate for a Kitaev Spin Liquid - a QSL state that has an "exact solution" and makes predictions that all believe.

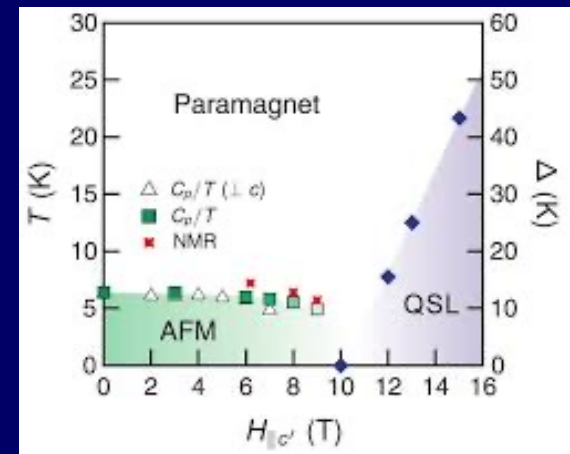


Significant spin orbit coupling is argued to be critical in this type of magnetic system, goes as m^4

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

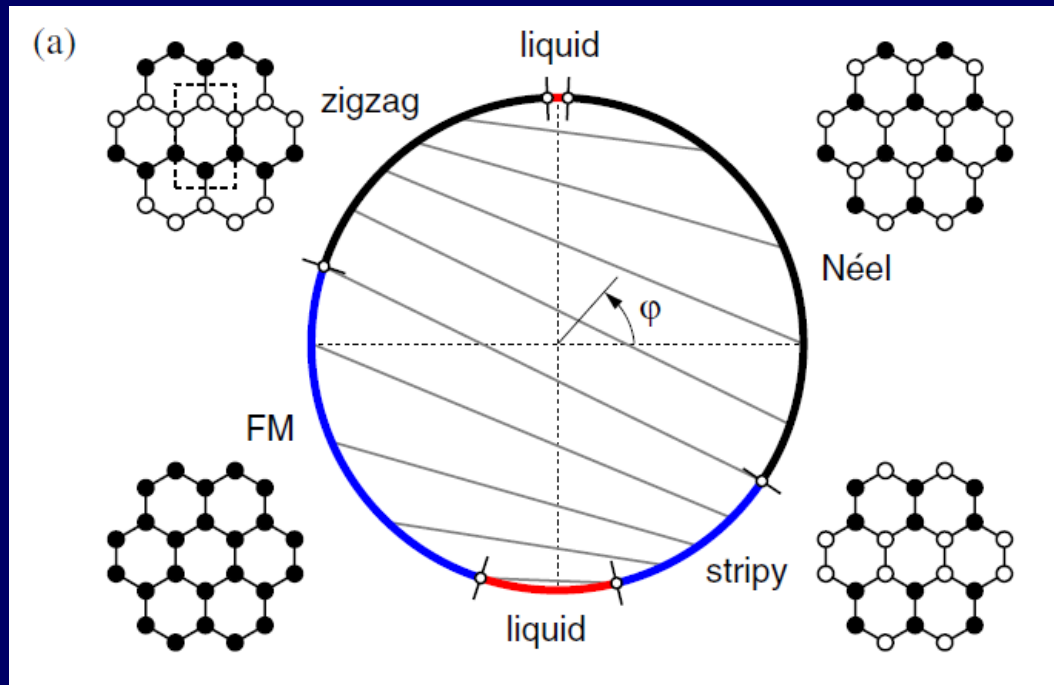
Zigzag Magnetic Order in the Iridium Oxide Na_2IrO_3

Jiří Chaloupka,^{1,2} George Jackeli,^{1,*} and Giniyat Khaliullin¹

¹Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

²Central European Institute of Technology, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic

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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 $\text{BaCo}_2(\text{AsO}_4)_2$, 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

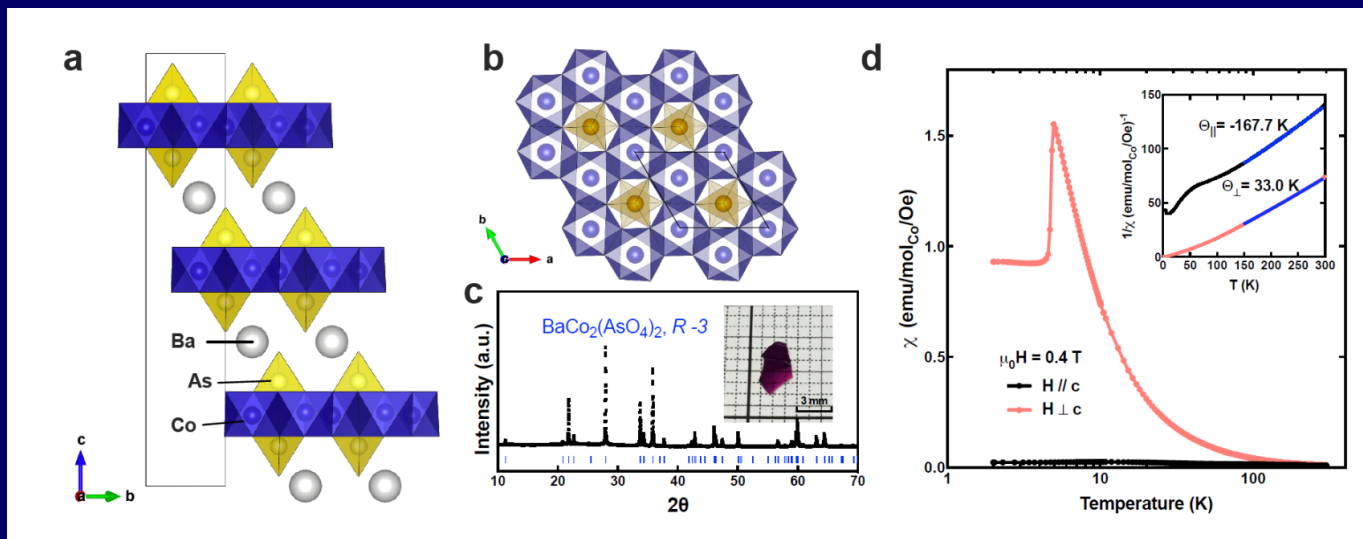


Postdoc Ruidan Zhong grew crystals and we got new data

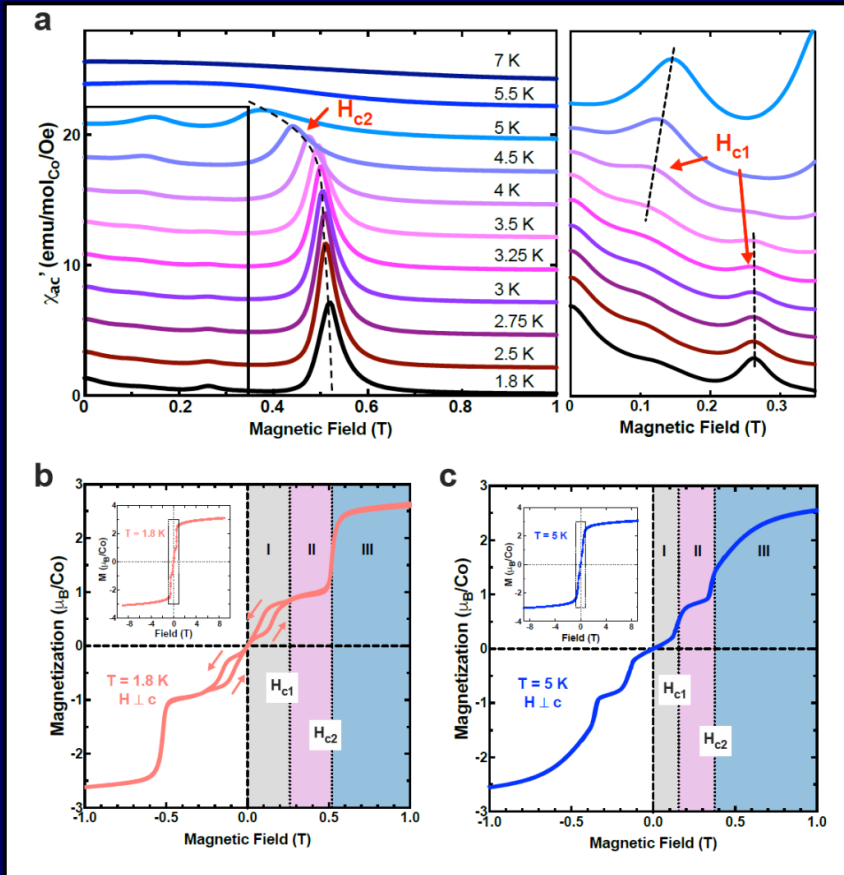
MAGNETIC ORDERING IN A PLANAR X-Y MODEL: $\text{BaCo}_2(\text{AsO}_4)_2$

L.P. REGNAULT, P. BURLET and J. ROSSAT-MIGNOD
DRF/1DN, Centre d'Etudes Nucléaires, 85X, 38041 Grenoble Cedex, France

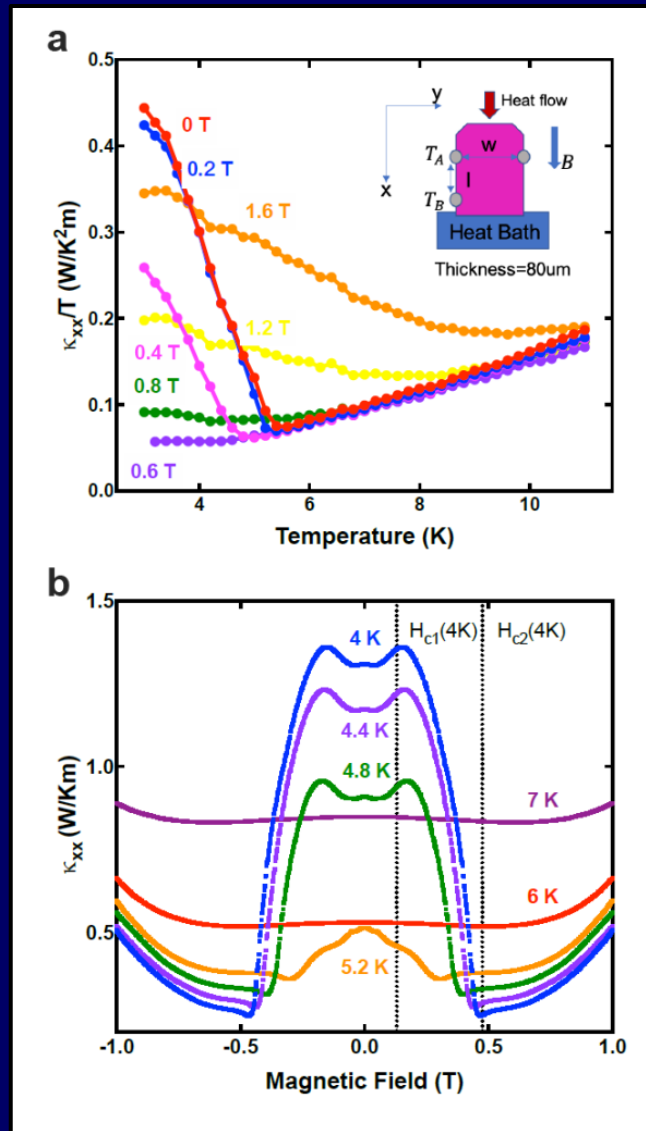
Physica 86–88B (1977) 660–662 © North-Holland



Some of its properties



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

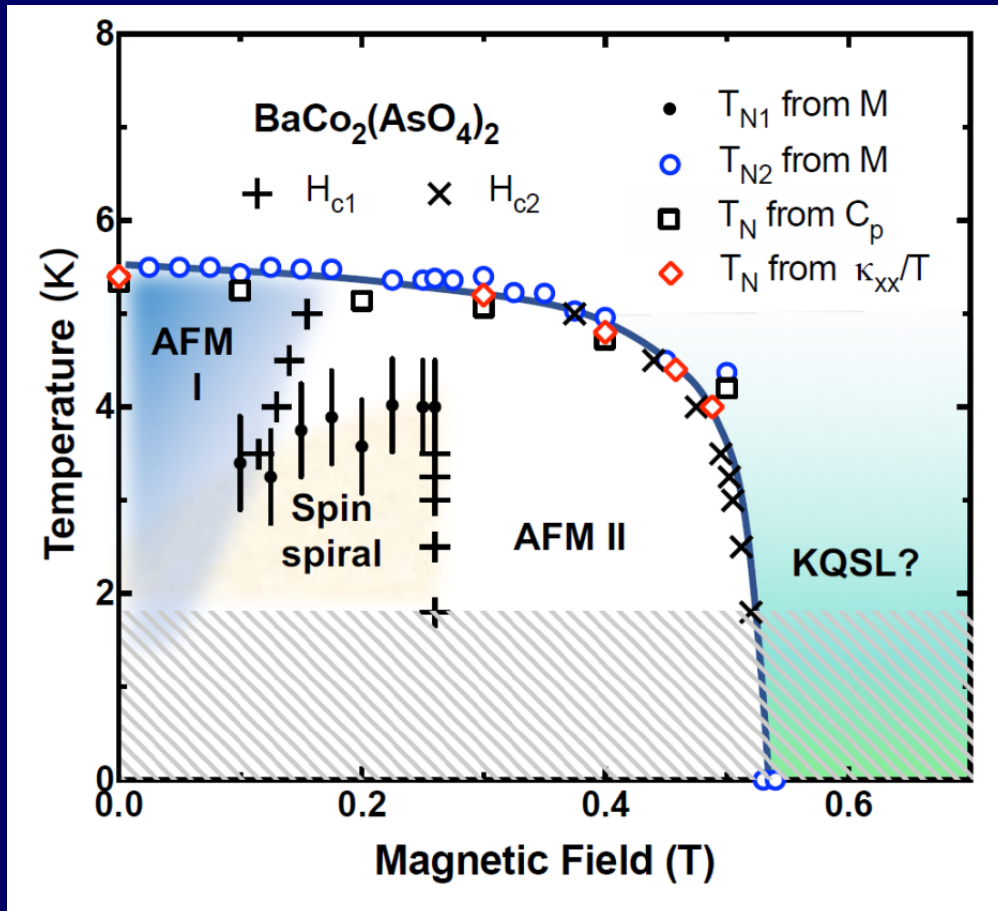


Lots of analogies to RuCl_3

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 $\text{BaCo}_2(\text{AsO}_4)_2$



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

($\text{Y}_3\text{Au}_3\text{Sb}_4$ is a semiconductor)

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

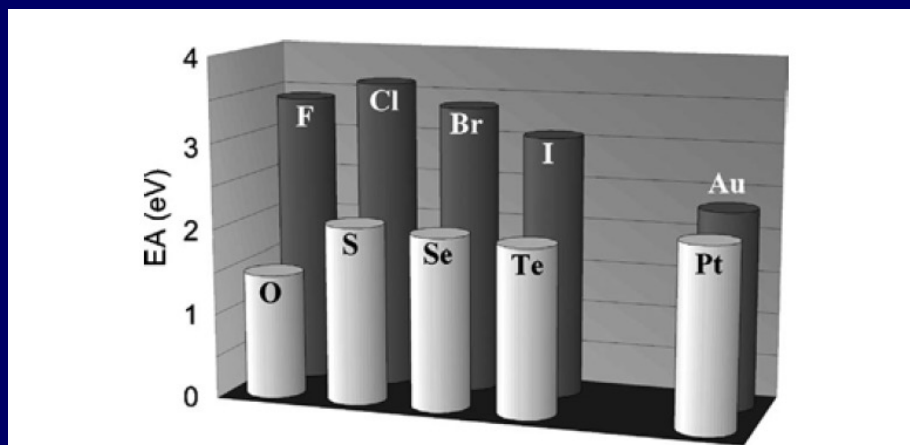


Fig. 2. Electron affinities of selected elements. The data are taken from [71].

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:

THE PERIODIC TABLE OF THE ELEMENTS

The periodic table is color-coded by groups: Alkali Metal (red), Alkaline Earth (orange), Transition Metal (yellow), Basic Metal (green), Semimetal (light blue), Nonmetal (blue), Halogen (purple), Noble Gas (dark purple), Lanthanide (light green), and Actinide (dark green). Elements Au, Bi, and Sb are circled in red. The Lanthanide and Actinide series are shown at the bottom, with La and Ac also circled in red.

1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A	
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11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80	
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29	
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		Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide							

Its interesting, so we started looking for new Au compounds

We used Au

plus

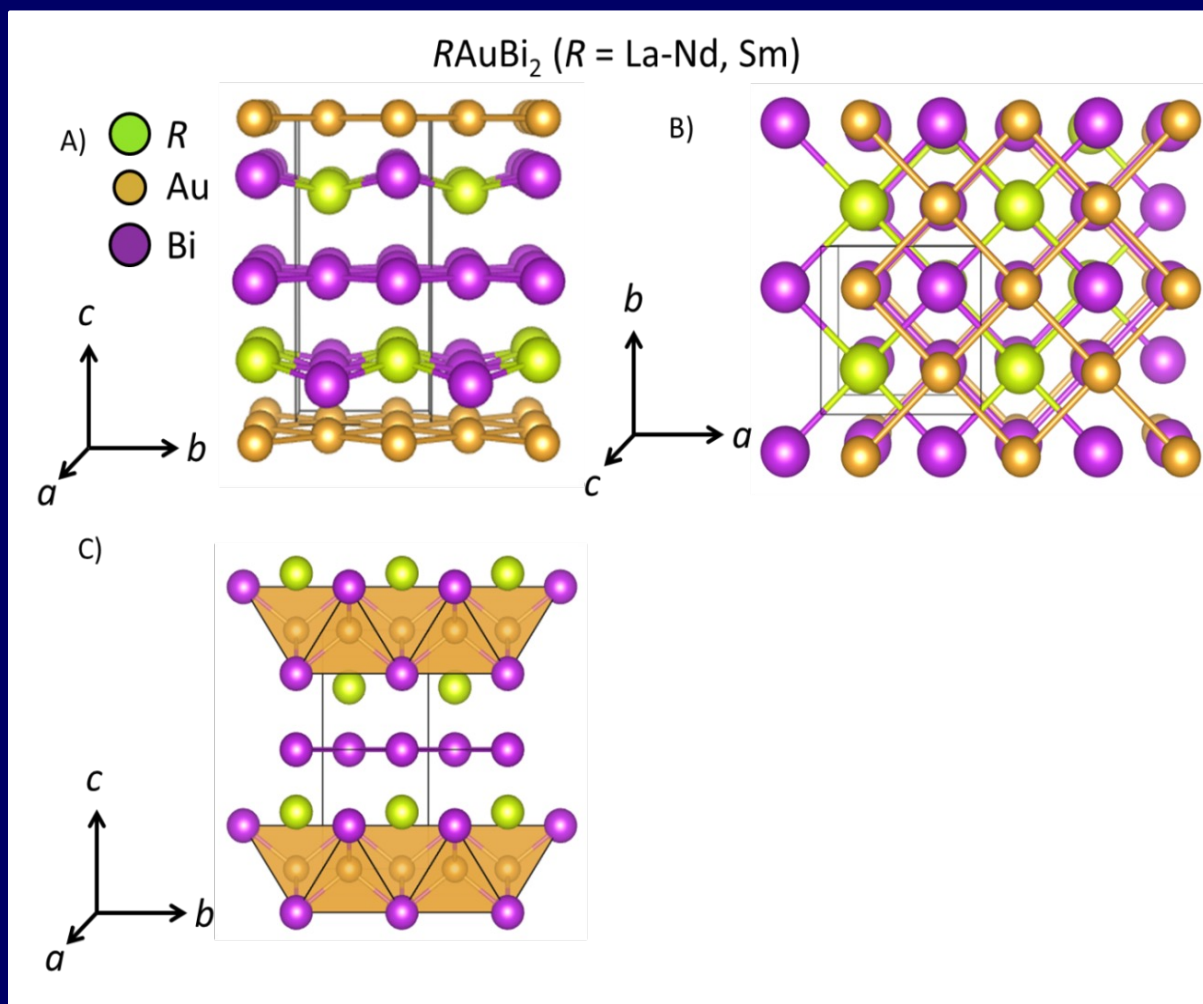
an electropositive
element

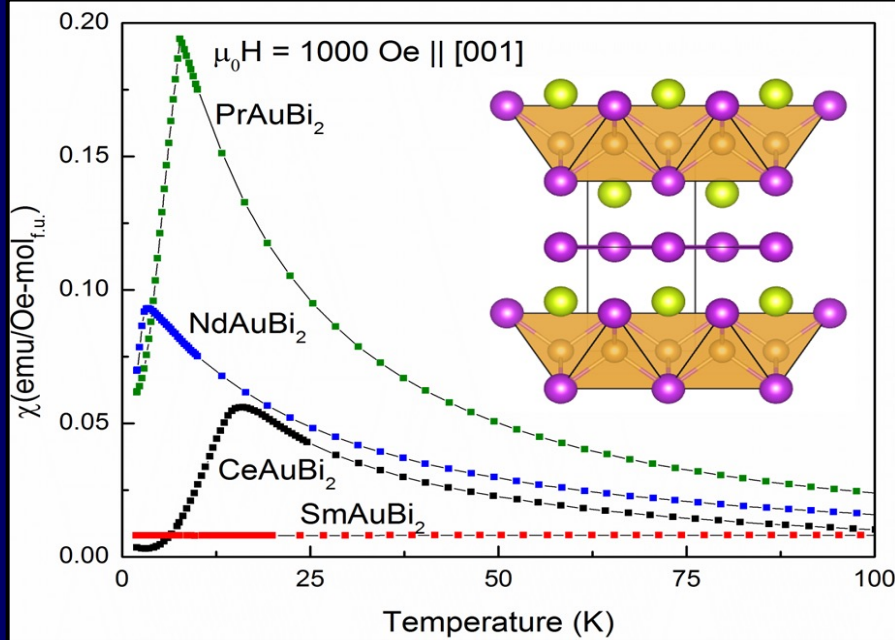
plus

an electronegative
element

To “confuse” the
Au.

First, we found
 RAuBi_2





All show magnetic behavior due to the rare earths present.

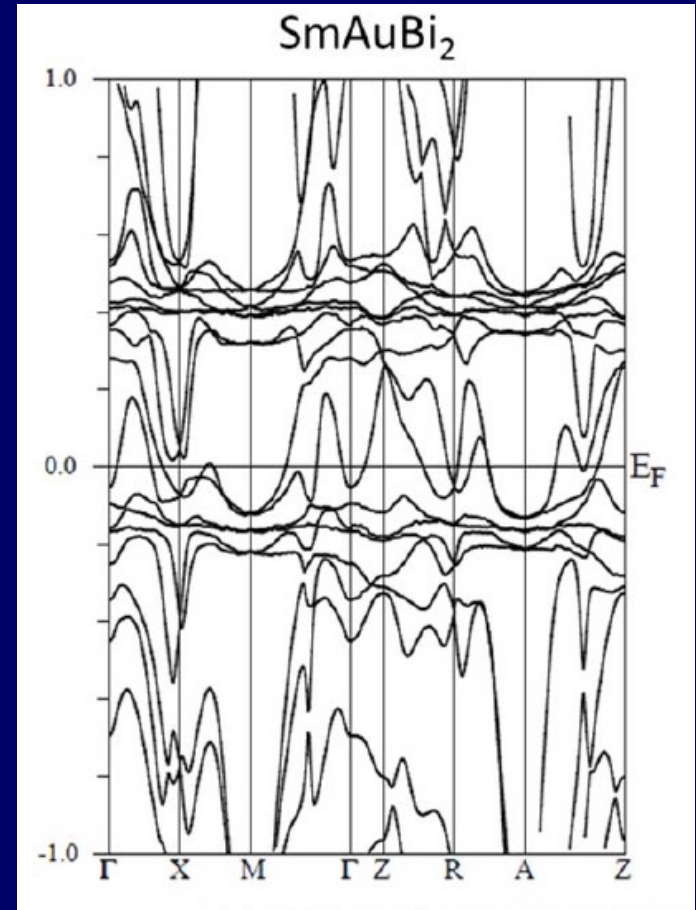
(Wien 2K, an electronic structure calculating program, is easily used, even by chemists.)

The Bi layer dominates the states at the Fermi energy

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

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)

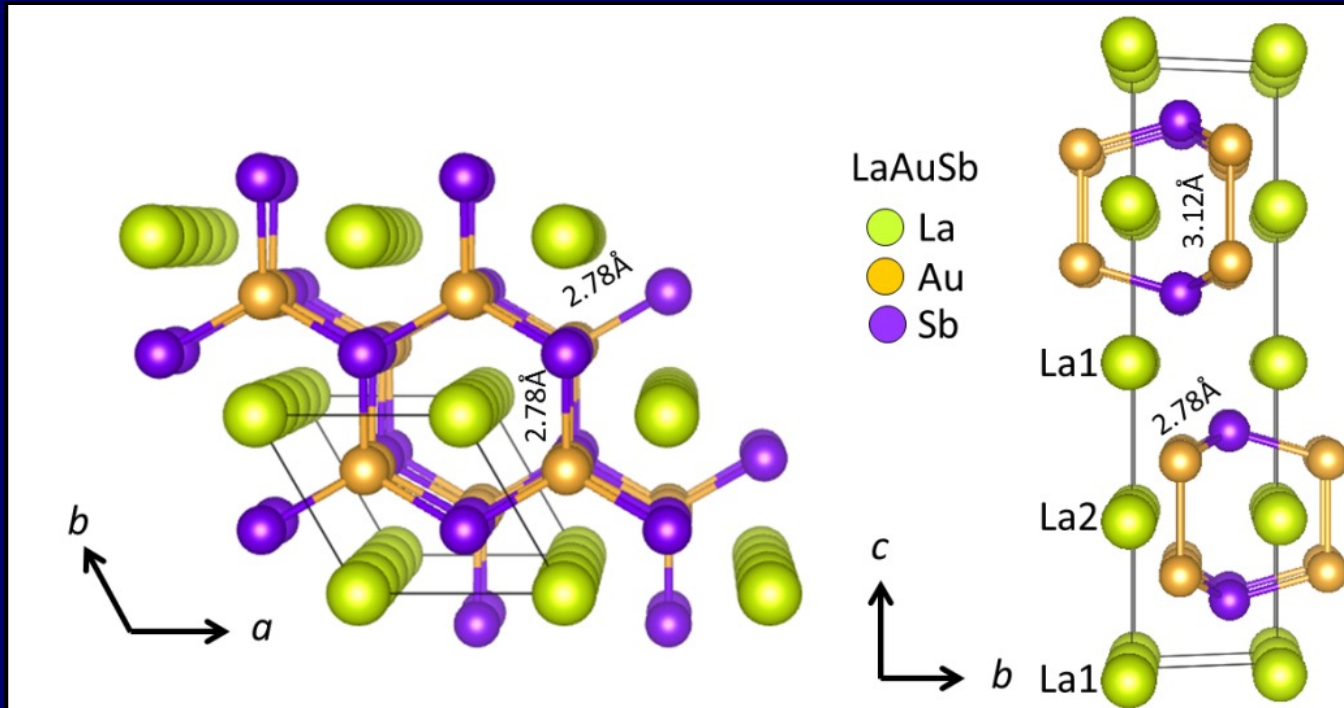
hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70 Lu 174.97	hafnium 71 Hf 178.49	tantalum 72 Ta 180.95	wolfram 73 W 183.84	reuterium 74 Re 186.21	osmium 75 Os 190.23	iridium 76 Ir 192.22	platinum 77 Pt 195.08	gold 78 Au 196.97	mercury 79 Hg 200.59	thallium 80 Tl 204.38	lead 81 Pb 207.2	bismuth 82 Bi 208.98	polonium 83 Po [209]	astatine 84 At [210]	radon 85 Rn [222]						
francium 87 Fr [223]	radium 88 Ra [226]	** 89-102 Lr [262]	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]							
		* Lanthanide series		praseodymium 58 Pr [140.91]	cerium 59 Ce [140.12]	lanthanum 57 La [138.91]	europium 63 Eu [151.96]	gadolinium 64 Gd [157.25]	terbium 65 Tb [158.93]	dysprosium 66 Dy [162.50]	holmium 67 Ho [164.93]	erbium 68 Er [167.26]	thulium 69 Tm [168.93]	ytterbium 70 Yb [173.04]									
		** Actinide series		actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]						

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.

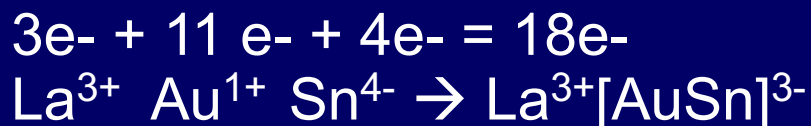
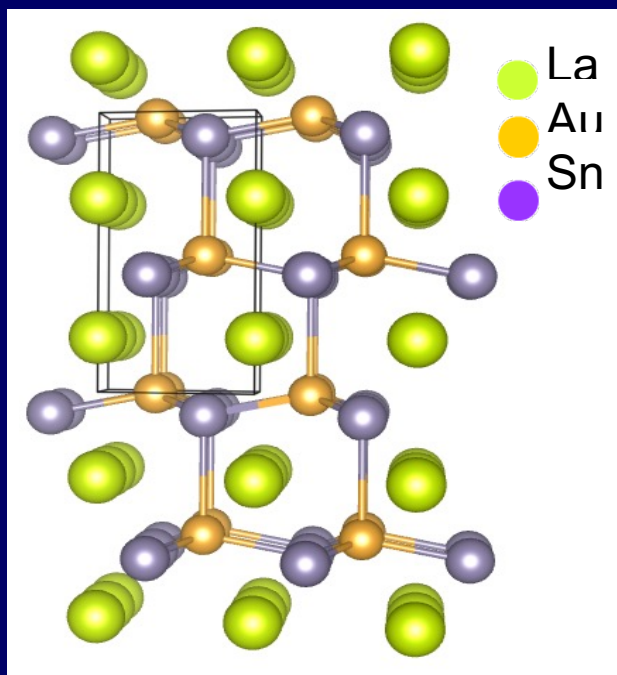


Its crystal structure has very buckled layers with the Au's pulled together— why?

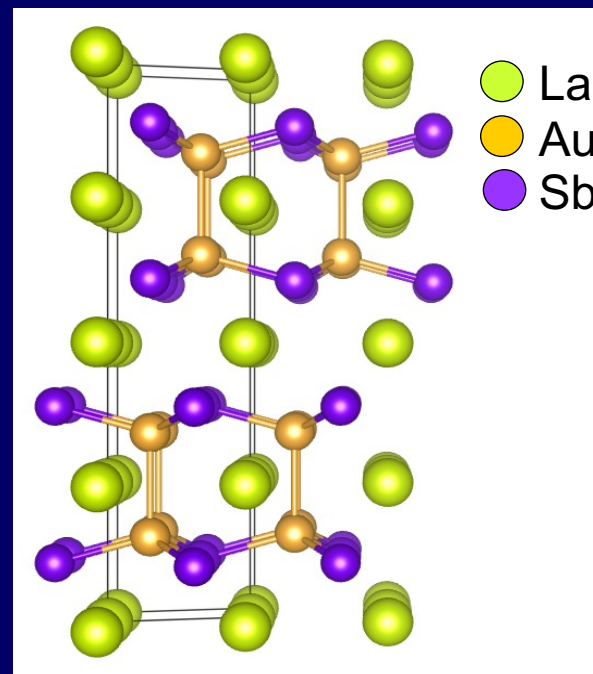
Is this an Au-Au bond in a solid?
A bond between inert atoms?

Counting the electrons

LaAuSn – a normal compound
with 18 electrons



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

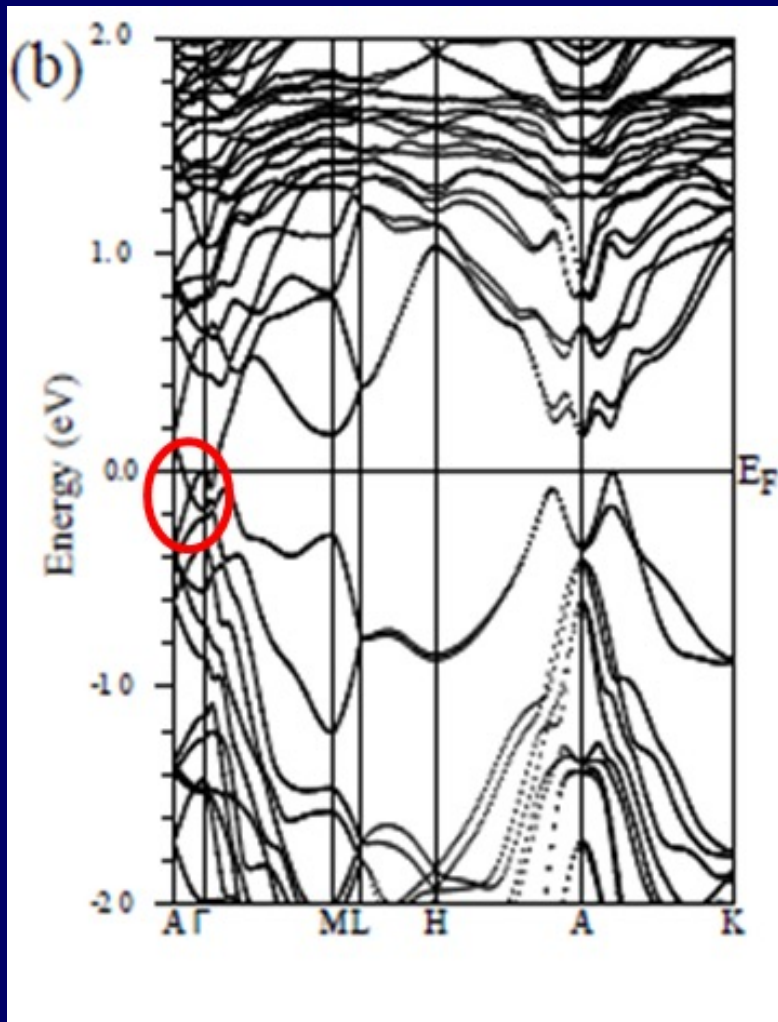


+ 1 e⁻



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

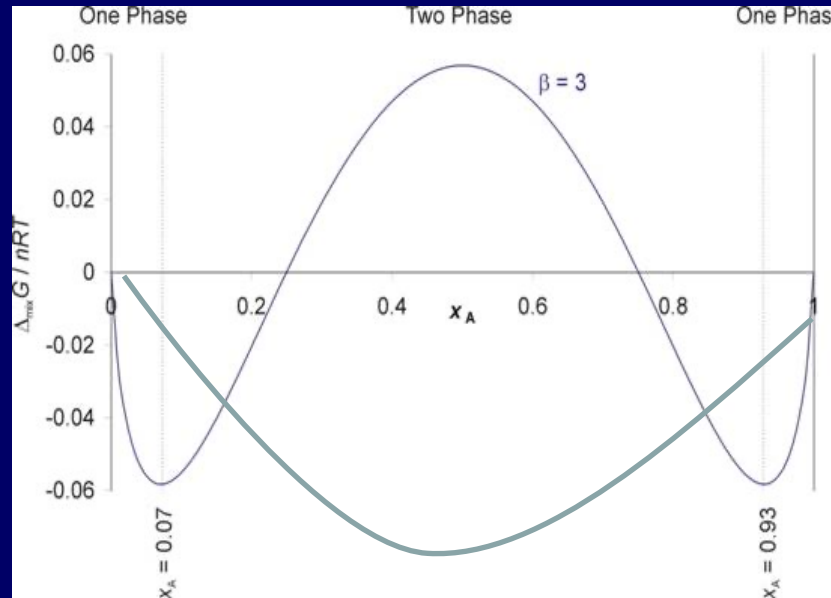


Fabian von Rohr

$$\Delta G = \Delta H - T\Delta S$$

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)

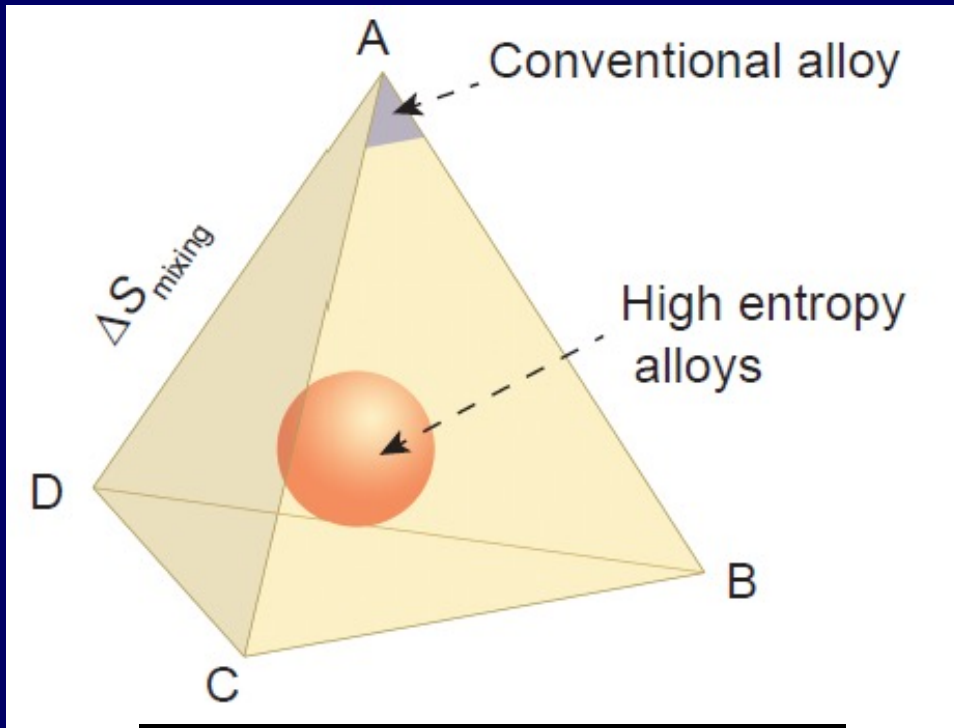


But the entropy of mixing is large in solid solutions with major fractions of mixed elements



Tomasz Klimczuk

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.

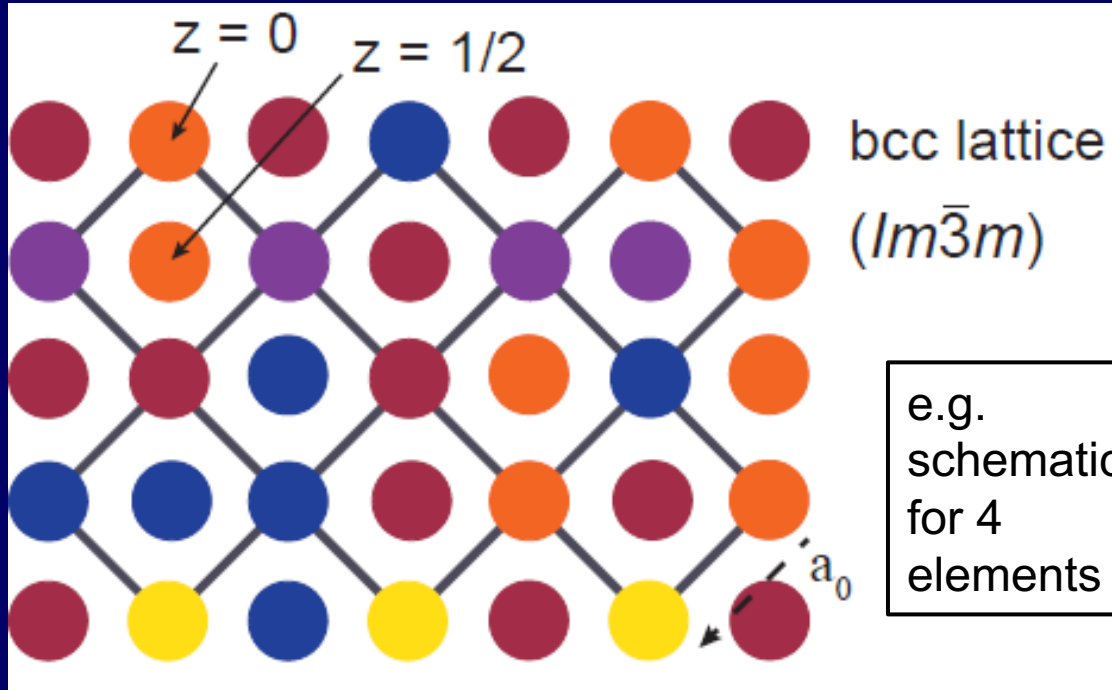
The properties of HEAs emerge as a property of the mixture of elements, which are all present in significant proportion.

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



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

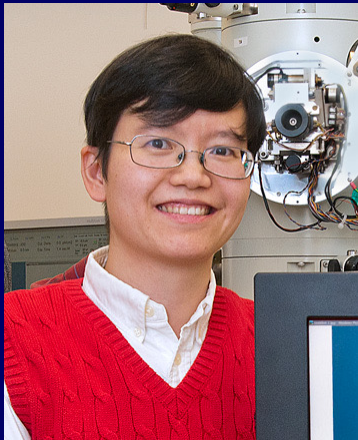
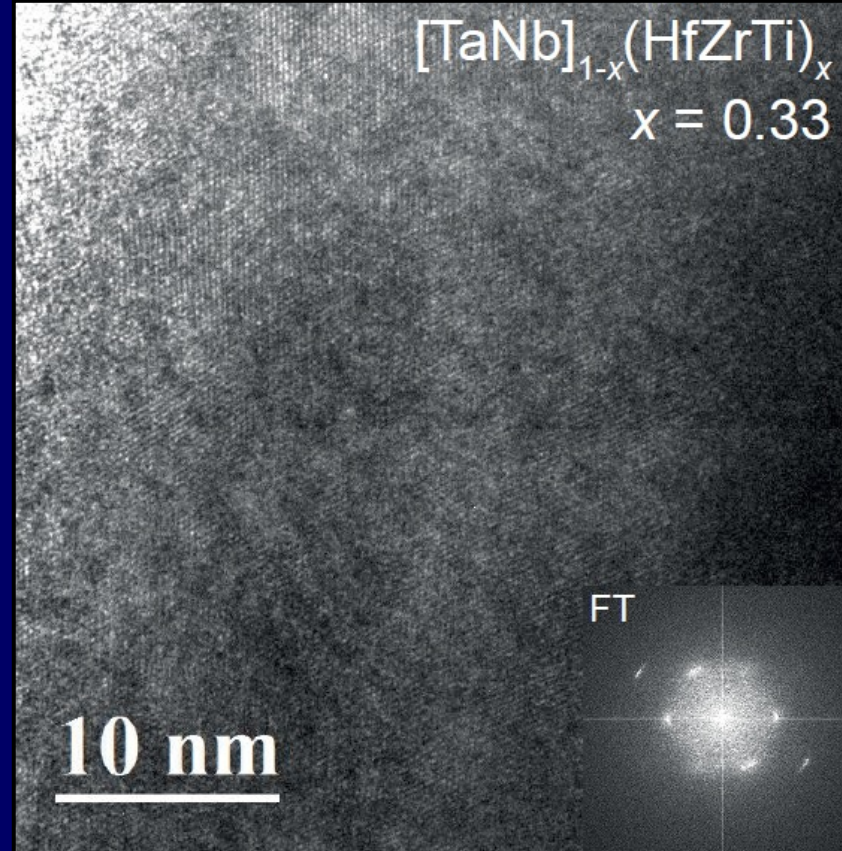
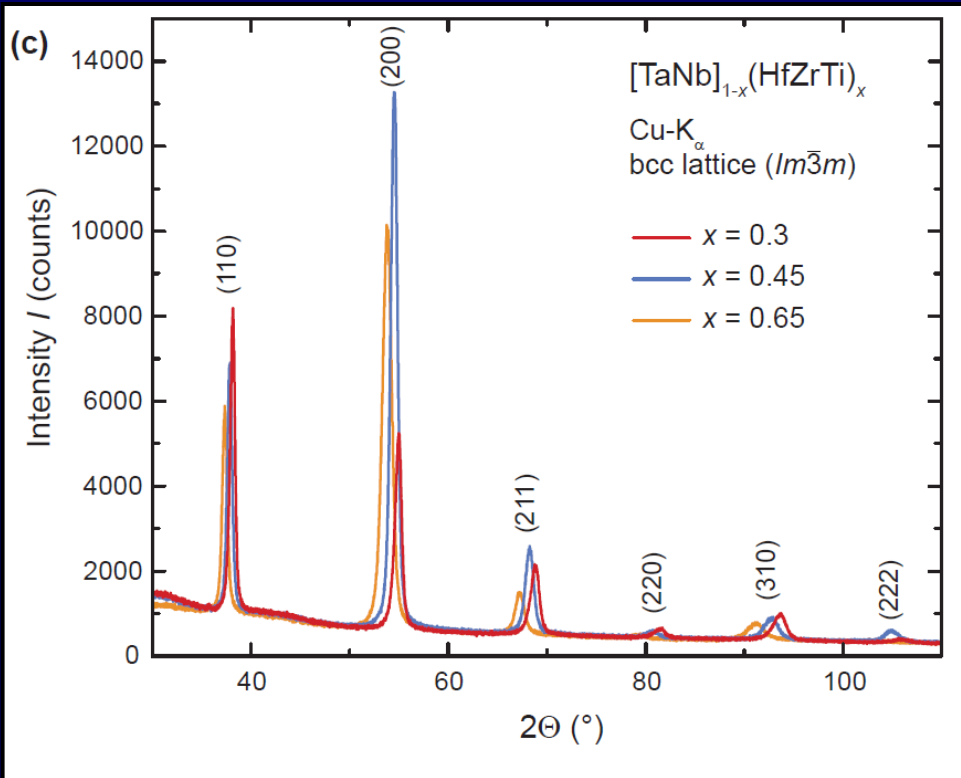
We tested the effects of electron count, alloy complexity and the elements present

The alloy of interest is $(\text{TaNb})_{1-x}(\text{HfZrTi})_x$

For example $x = 0.33$ is $\sim \text{Ta}_{33}\text{Nb}_{33}\text{Hf}_{11}\text{Zr}_{11}\text{Ti}_{11}$

$x = 0.67$ is $\sim \text{Ta}_{16}\text{Nb}_{16}\text{Hf}_{22}\text{Zr}_{22}\text{Ti}_{22}$

First, the average structure is BCC

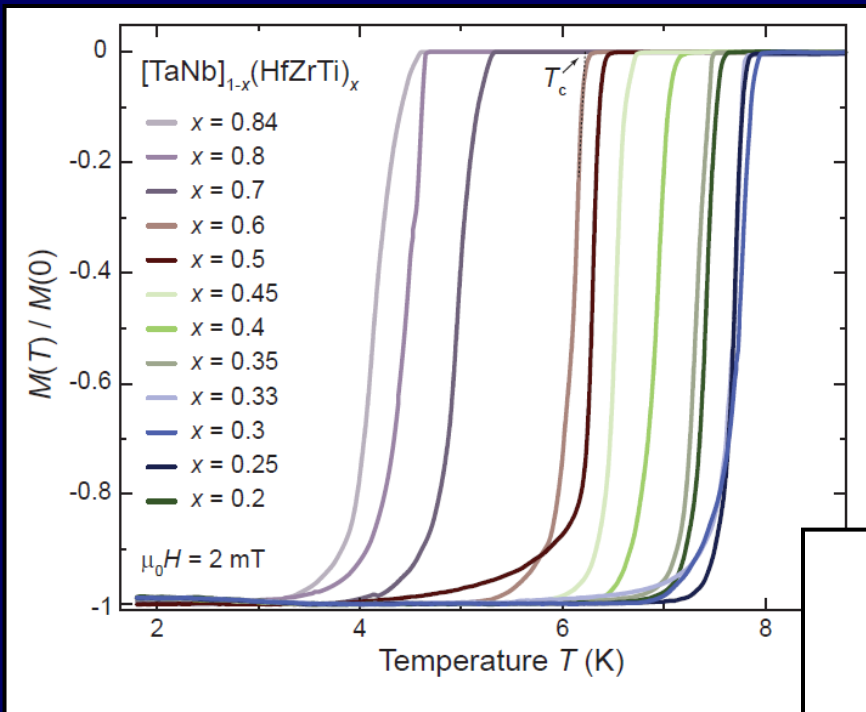


The local level structure is important. Can it really be a random mix? Looking down the [111] direction of the HEA in the HRTEM.

It's a random distribution of elements in a BCC lattice.

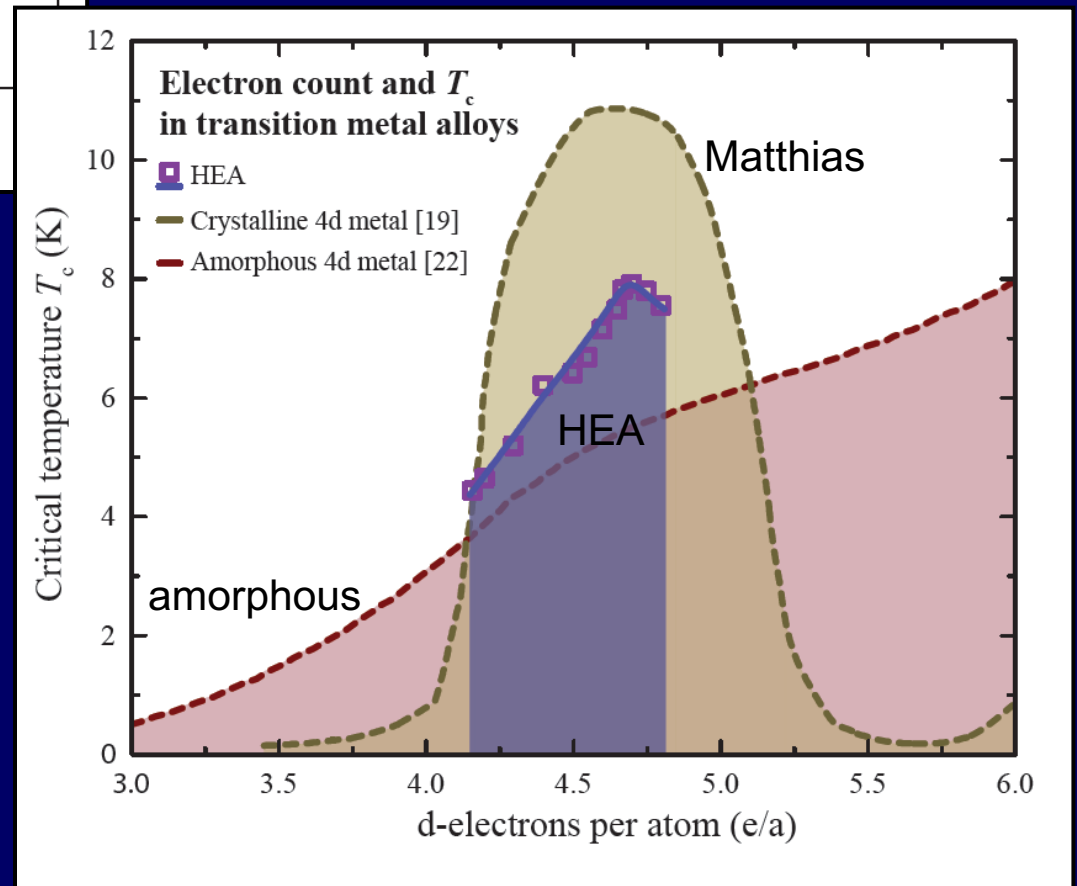
No nanometer scale clusters.

(Jing Tao at BNL now IOP)



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

The electron count variation in T_c 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!

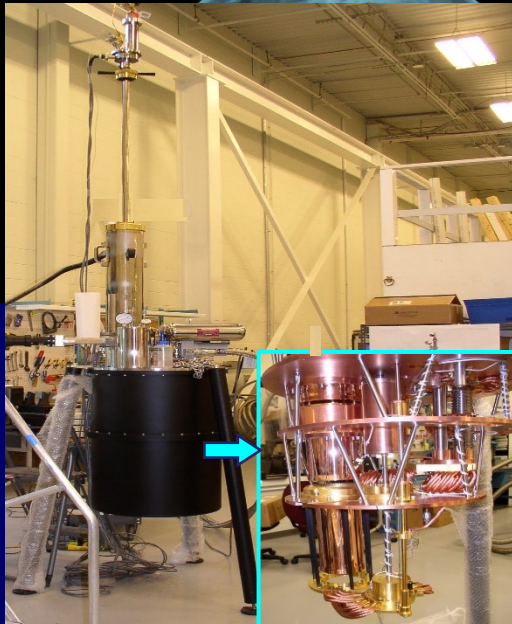
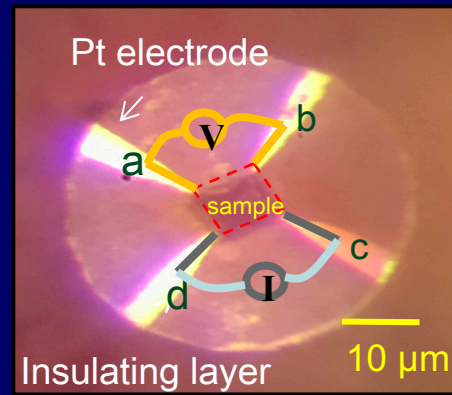
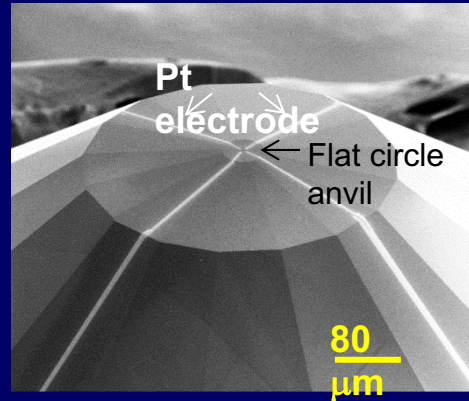
We have to flatten the samples in a roller and then snip or file off pieces to get an X-ray pattern.

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

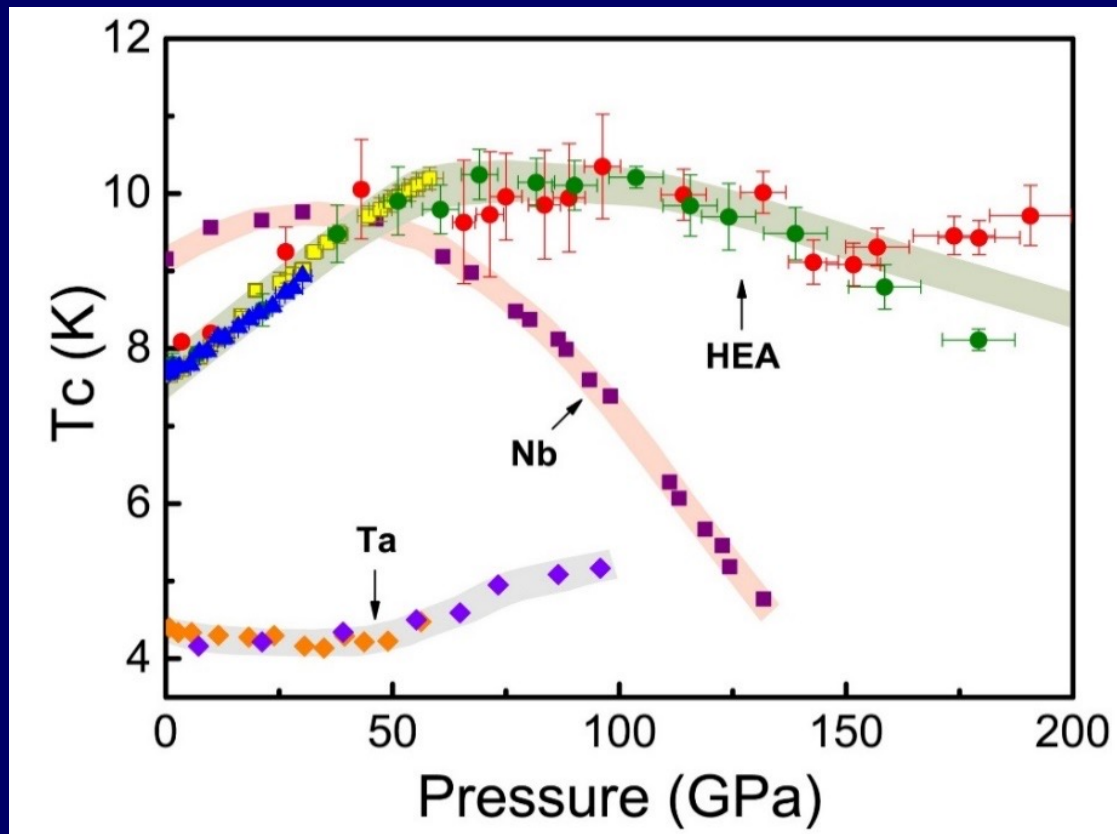


Liling Sun IOP Beijing



Jing Guo IOP Beijing

What did they find?

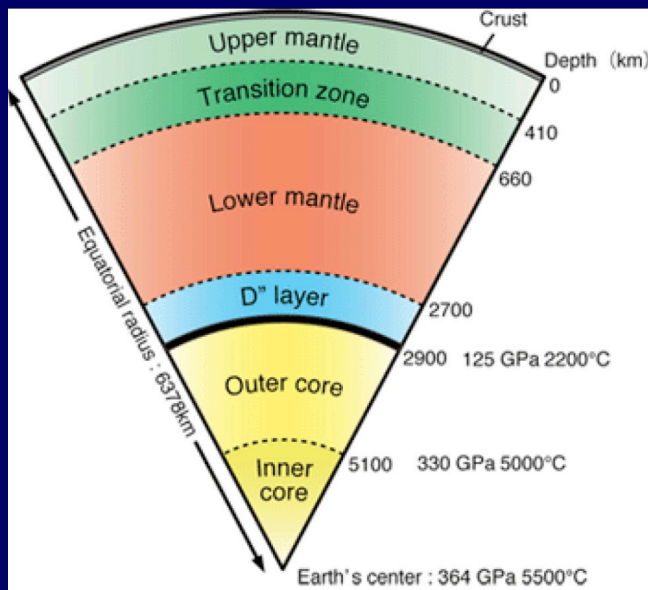


T_c vs. pressure.

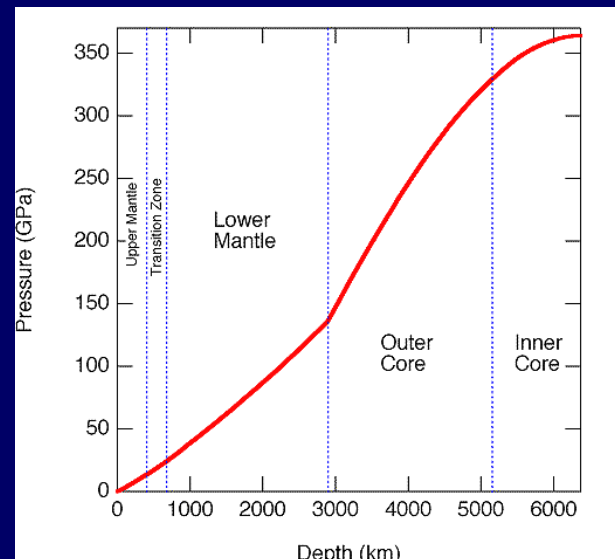
Different colors are different experiments
(they break the diamonds)

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

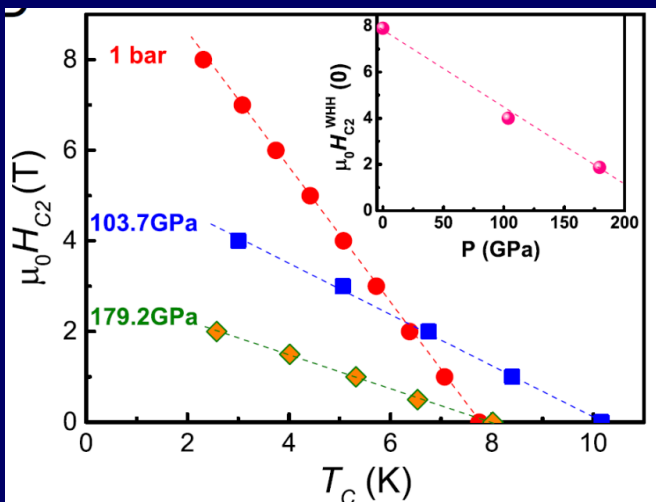
Really? Just how high is 200 GPa in pressure?



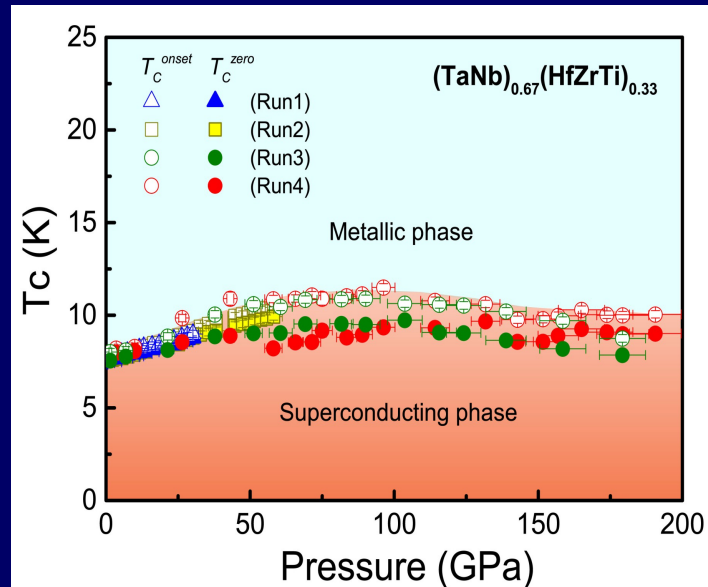
Very high



Core of the earth high



The physicists can measure H_{C2} (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.

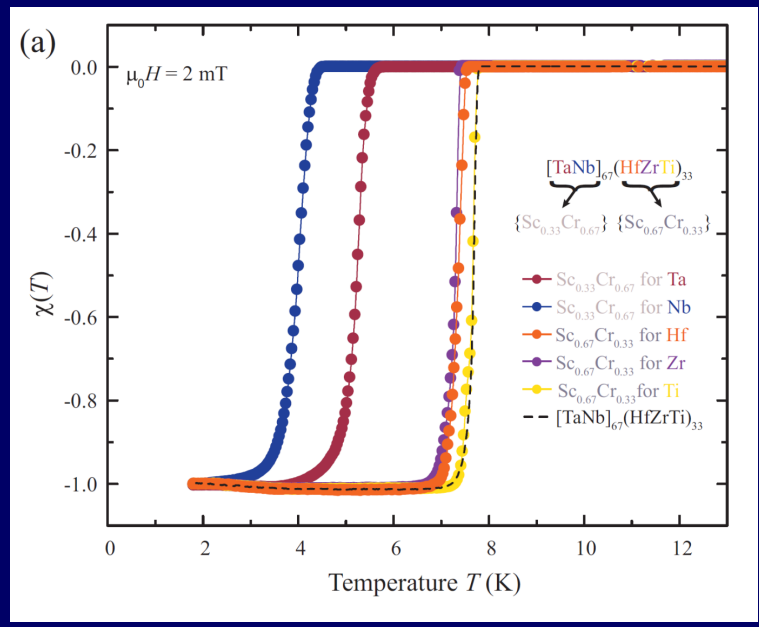
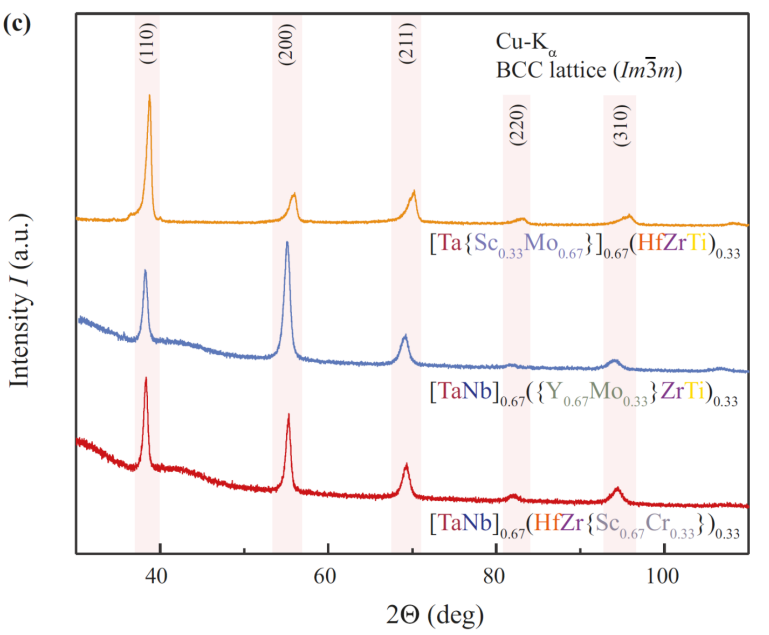
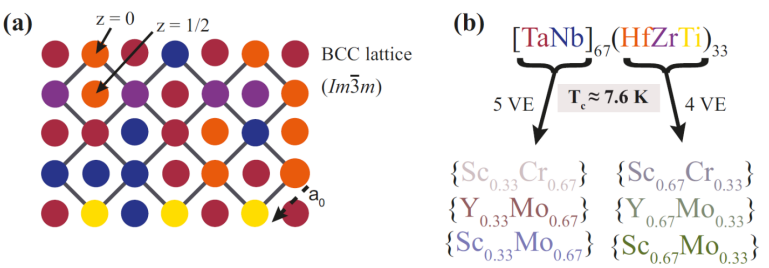
You have to be willing to try some things that don't work and not be afraid to appear stupid for trying.

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?”



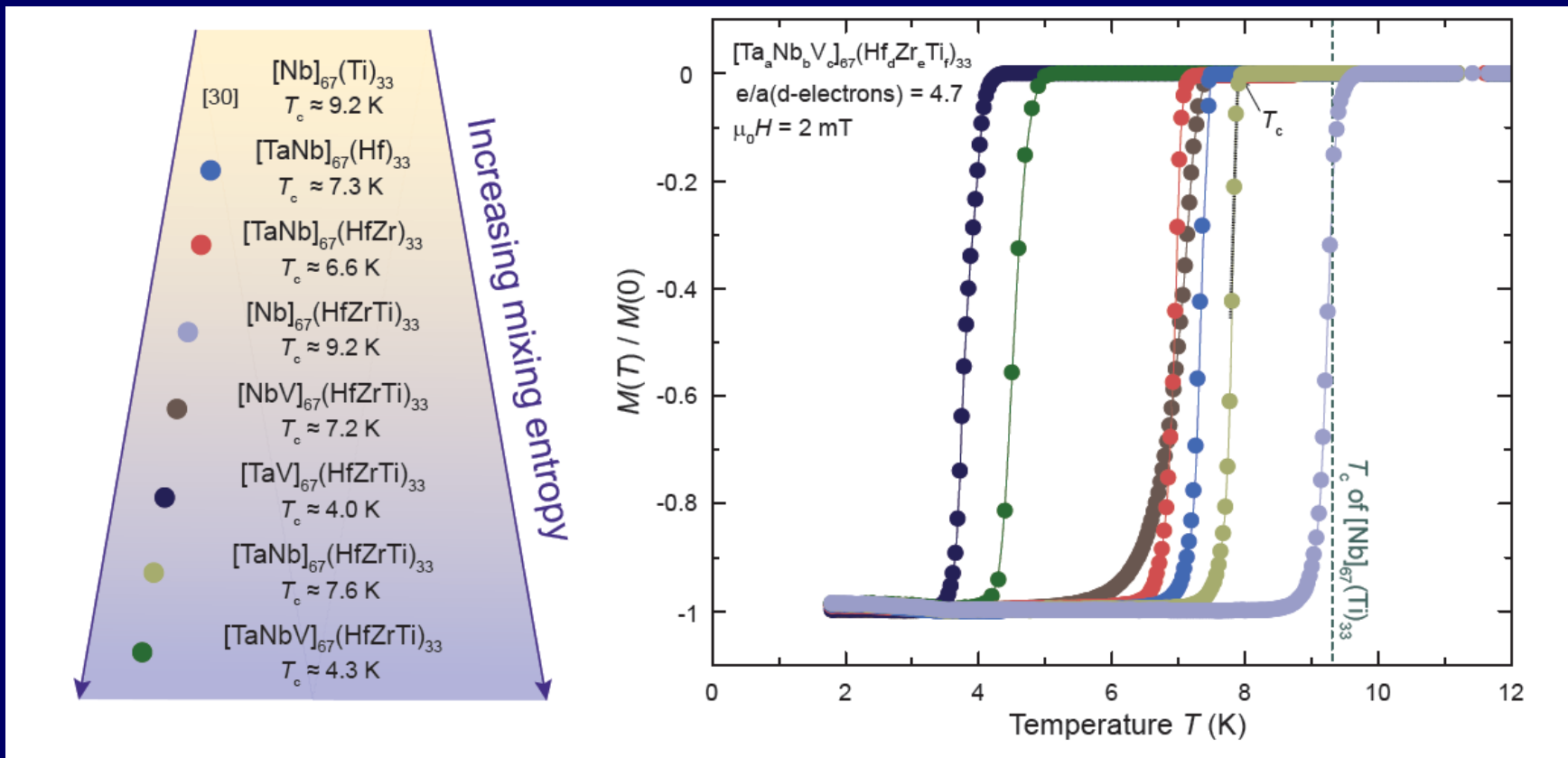
Original element / Substitution	Ta	Nb	Hf	Zr	Ti
$Sc_{0.33}Cr_{0.67}$	5.6	4.4	—	—	—
$Sc_{0.67}Cr_{0.33}$	—	—	7.5	7.4	7.6
$Y_{0.33}Mo_{0.67}$	4.7	3.5	—	—	—
$Y_{0.67}Mo_{0.33}$	—	—	7.6	6.7	7.5
$Sc_{0.33}Mo_{0.67}$	4.4	2.9	—	—	—
$Sc_{0.67}Mo_{0.33}$	—	—	7.5	6.6	7.5

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

In a high entropy alloy superconductor

– do the elements present actually matter

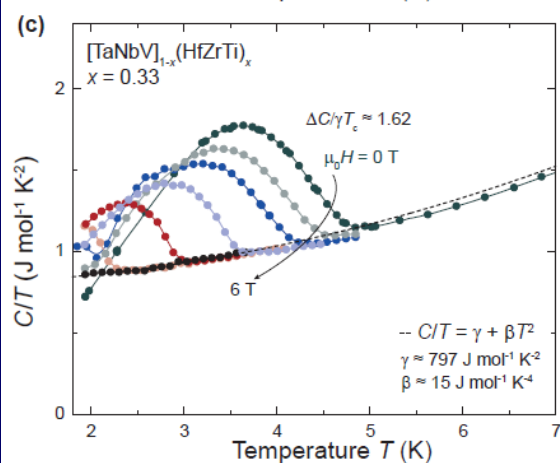
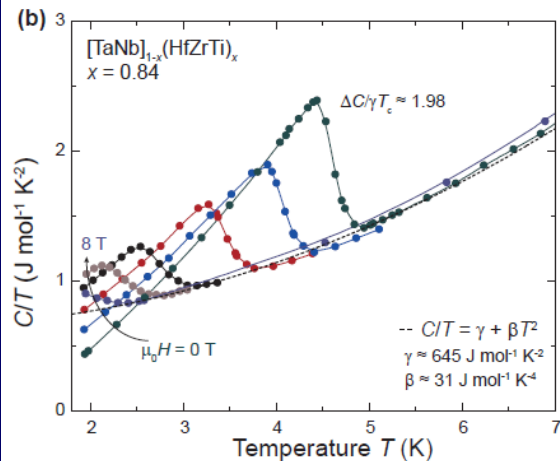
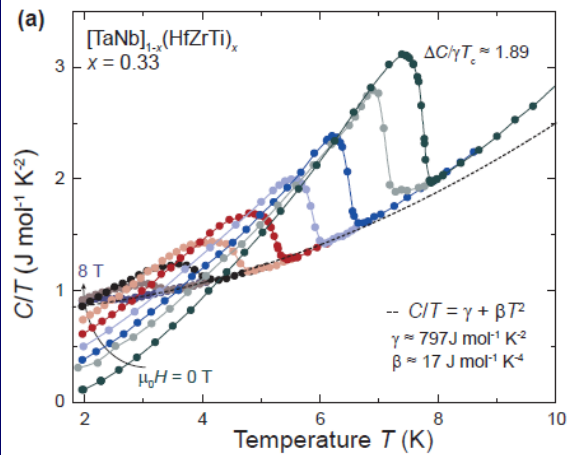
Or is it only the electron count?



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

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

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.

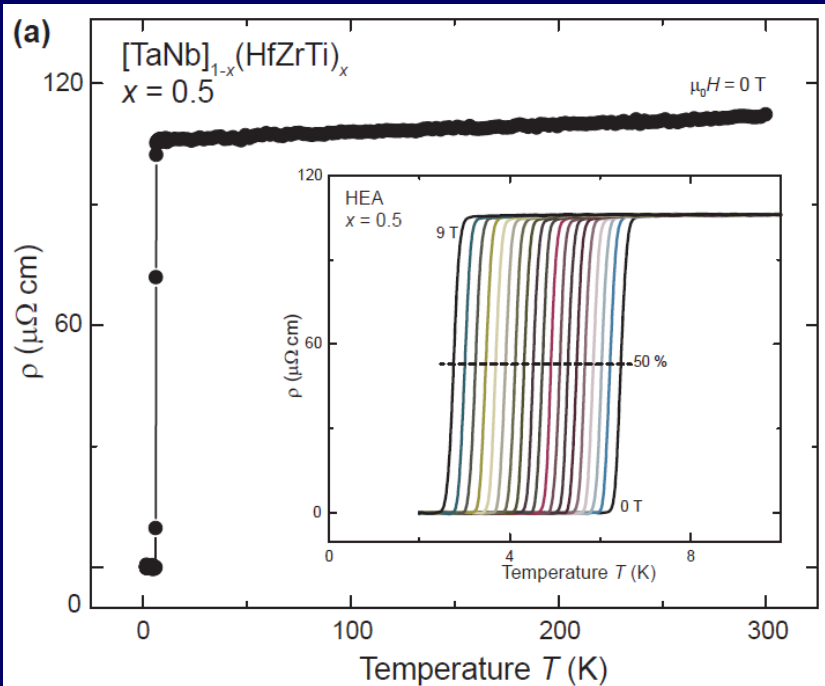
But for the V-containing HEA the electron phonon coupling is weaker.

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.

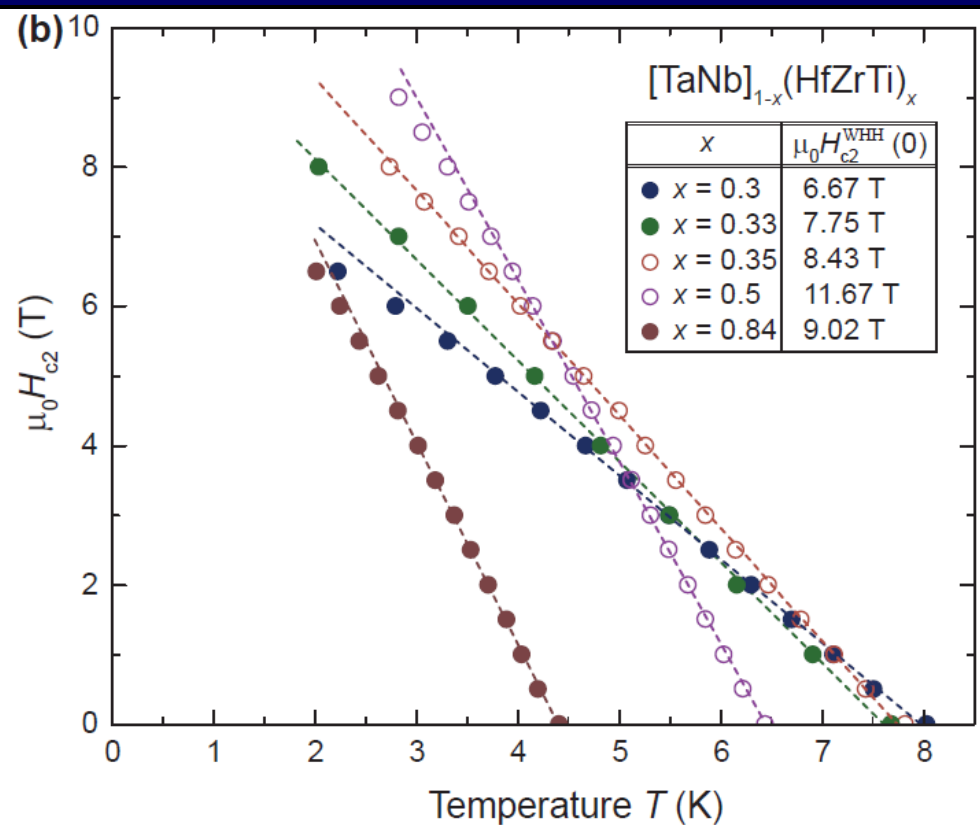
Here are some more...



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

Nice behavior

The highest T_c 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)

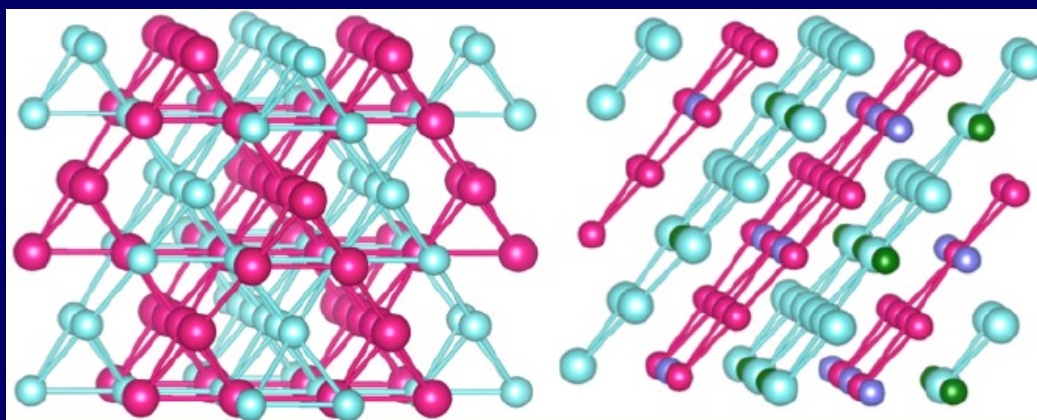
Can we compare Pyrochlores and Kagomes?

How can we make a rare earth Kagome that has a pyrochlore equivalent?

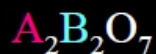


Marisa Sanders

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



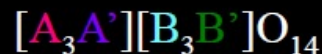
● A ● B



Pyrochlore

Fd-3m

● A ● A' ● B ● B'

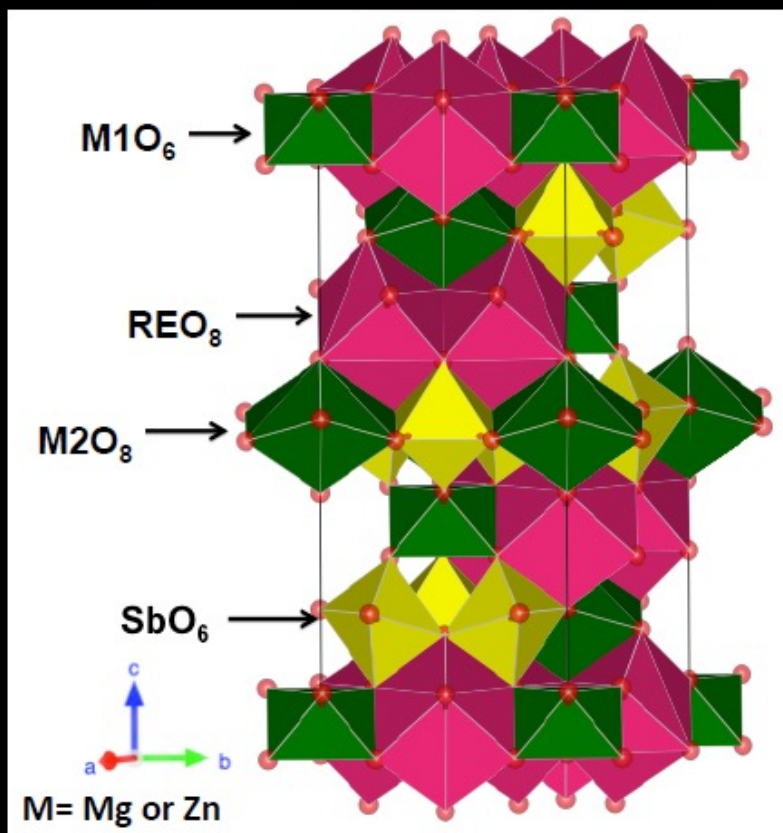


Kagome

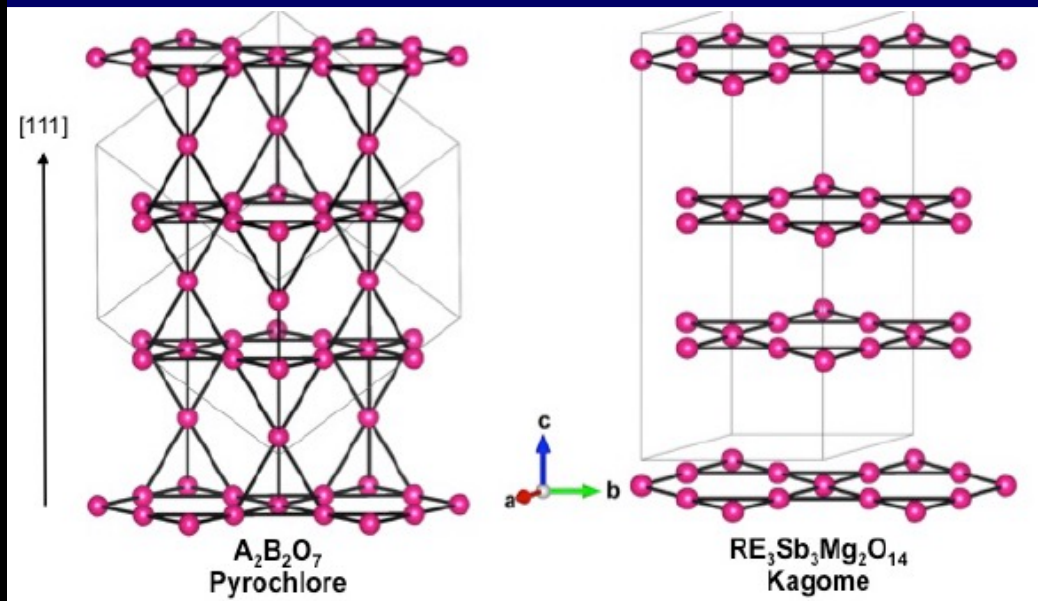
R-3m

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

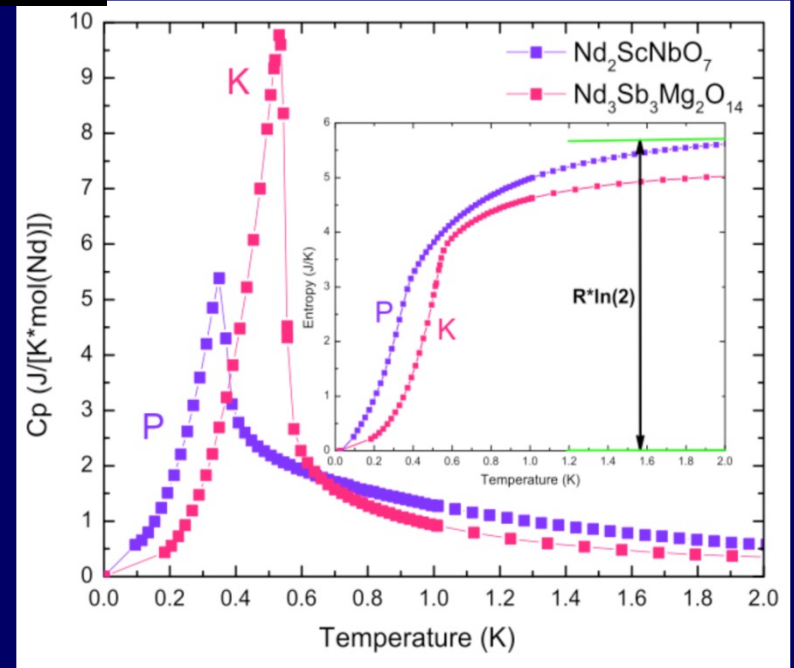
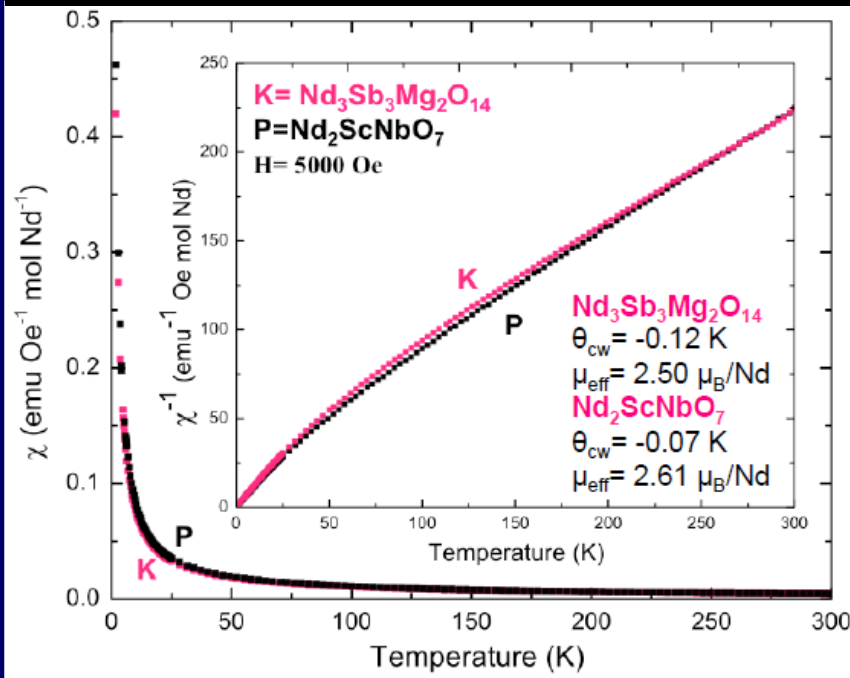
The trick, as usual, is to see the
forest through the trees

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
- θ_{CW} = Weiss Temperature
- χ = Magnetic Susceptibility
- T = Temperature in K
- C = Curie Constant
- 0 \rightarrow Paramagnetic
- + \rightarrow Ferromagnetic
- \rightarrow Antiferromagnetic

Comparison of the magnetic properties of the $\text{Nd}_2(\text{ScNb})\text{O}_7$ pyrochlore and the $\text{Nd}_3\text{Sb}_2\text{Mg}_2\text{O}_{14}$ kagome.



First comparison of its kind – no gross difference in behavior

The periodic table again again.

THE PERIODIC TABLE OF THE ELEMENTS

1 IA 1A																	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A																										
1 H Hydrogen 1.008																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180																										
3 Li Lithium 6.941	4 Be Beryllium 9.012																	11 Na Sodium 22.990	12 Mg Magnesium 24.305																	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948							
11 K Potassium 39.098	12 Ca Calcium 40.078	3 Sc Scandium 44.956	4 Ti Titanium 47.88	5 V Vanadium 50.942	6 Cr Chromium 51.996	7 Mn Manganese 54.938	8 Fe Iron 55.933	9 Co Cobalt 58.933	10 Ni Nickel 58.693	11 Cu Copper 63.546	12 Zn Zinc 65.39																	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80															
19 Rb Rubidium 84.468	20 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411																	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29															
55 Cs Cesium 132.905	56 Ba Barium 137.327																	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59																	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025																	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]																	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
Lanthanide Series		57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967																																
Actinide Series		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]																																
Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide																																							

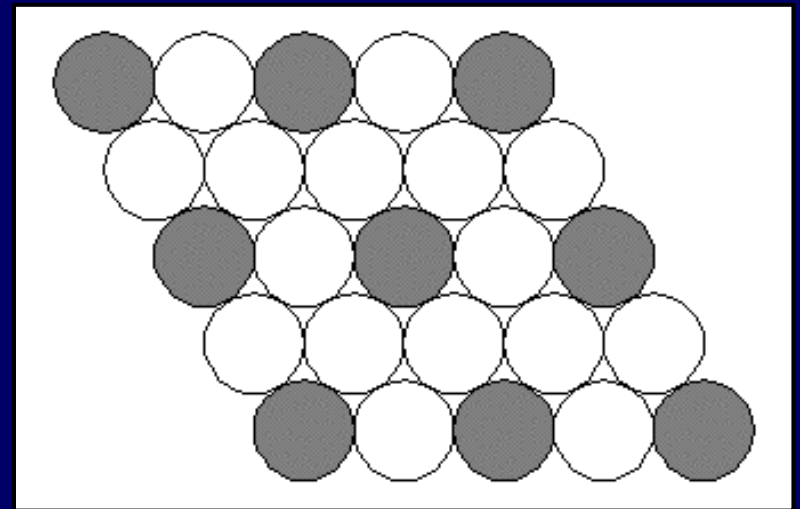
Final topic – 4. hexagonal perovskites

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.



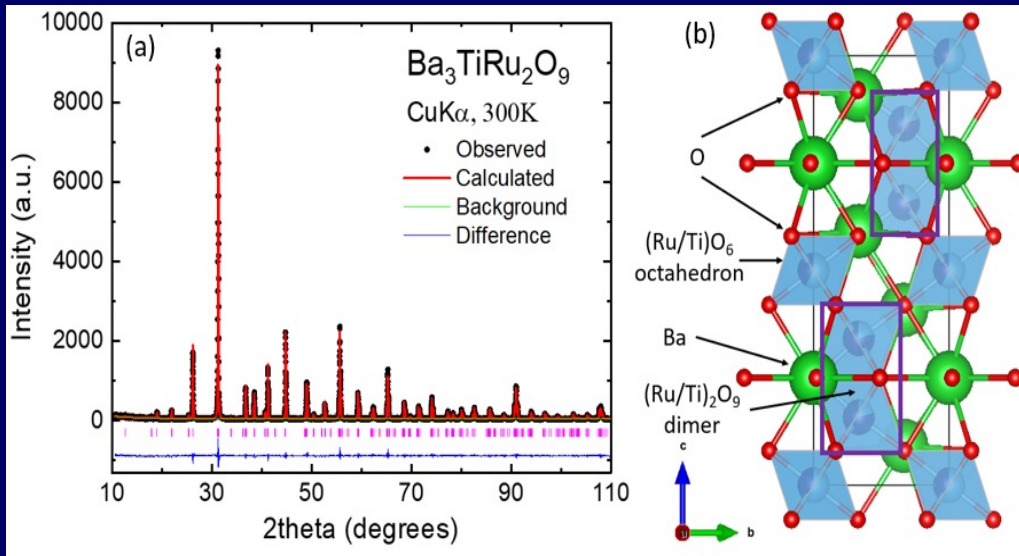
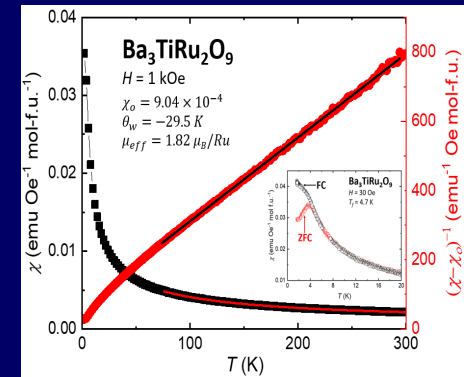
Ba^{2+} (gray) in a close packed plane of O^{2-} (white)

The first of our work on hex perovskite oxides -a dimer compound $\text{Ba}_3\text{TiRu}_2\text{O}_9$. 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.

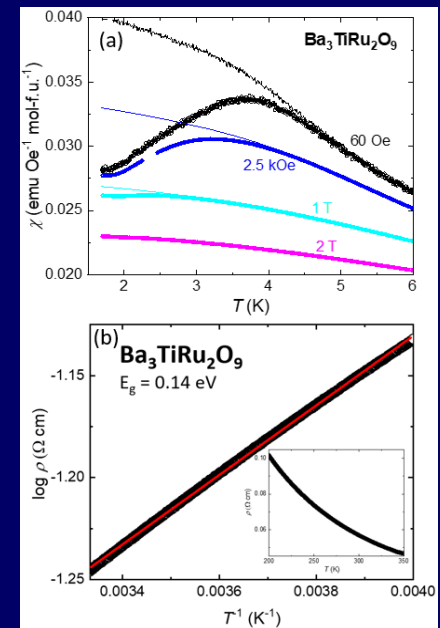
Many dimer systems have been studied by physicists. Nice but not so interesting for me because they don't directly address the issue of localized vs itinerant electrons on clusters.



Loi Nguyen

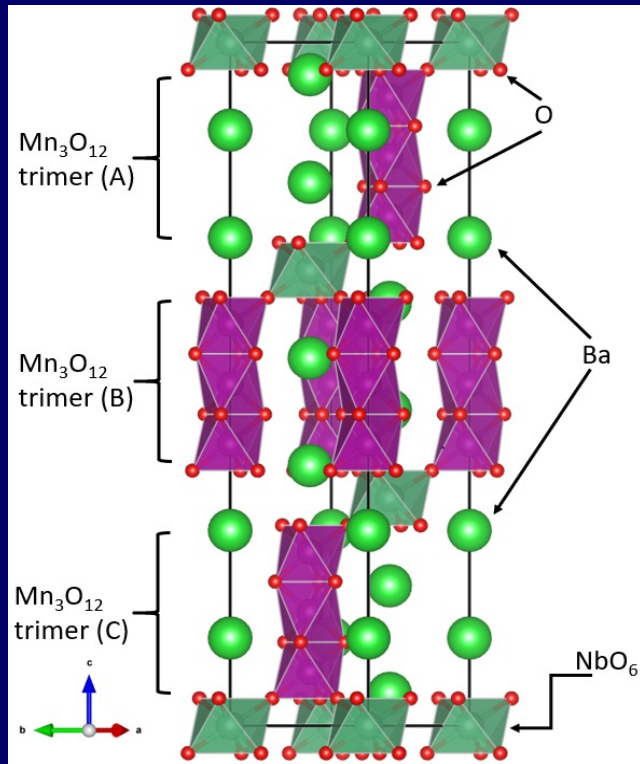


The first of our many insulators In this family

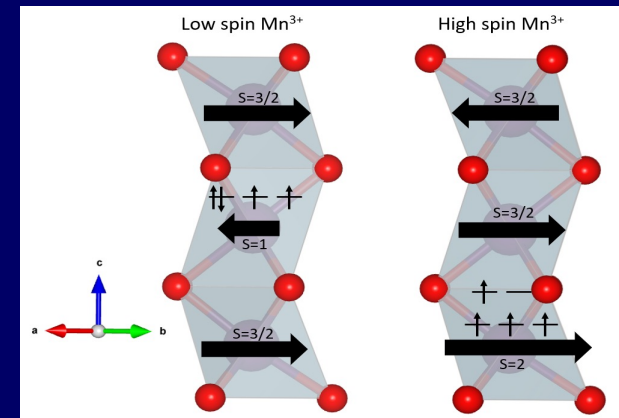
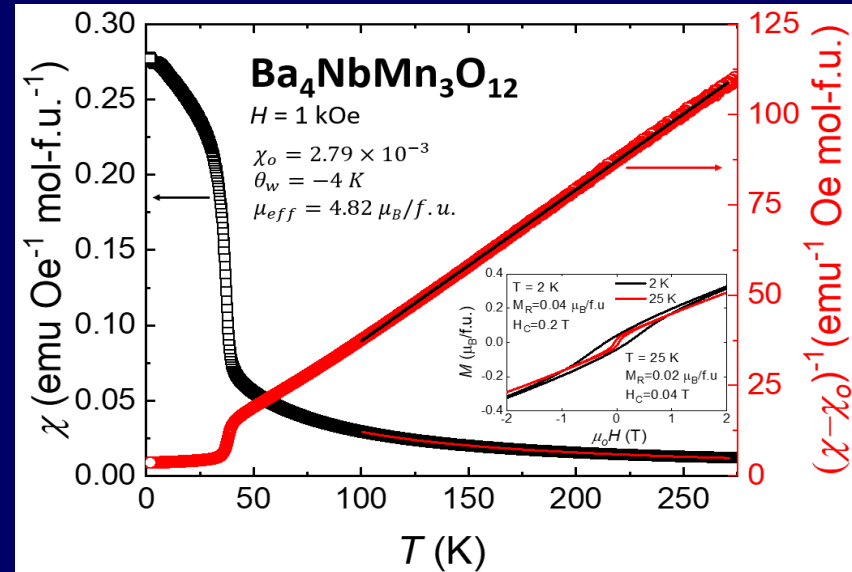


Now the first of several trimer compounds.
 First one is based on a 3d element (Mn).

I like trimers because
 “wheres the spin?”



Ba²⁺ and Nb⁵⁺ are not magnetic
 So all magnetism is from Mn.
 a 3d ion.
 Two Mn⁴⁺
 3d³
 One Mn³⁺
 3d⁴



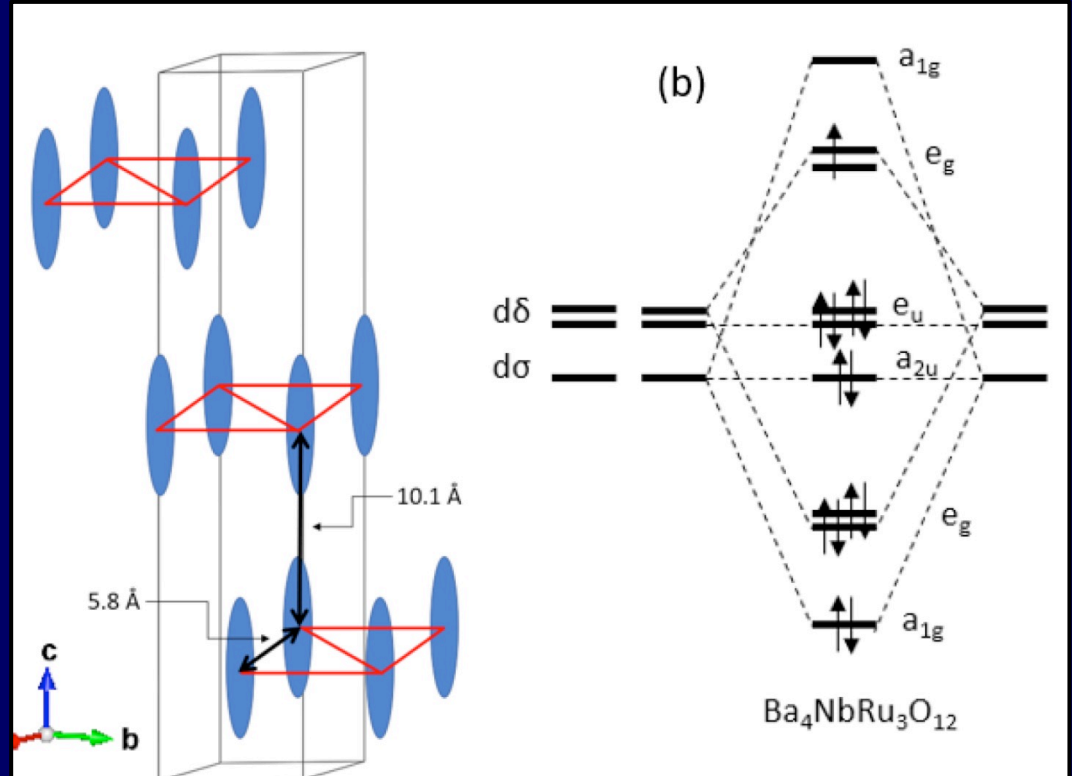
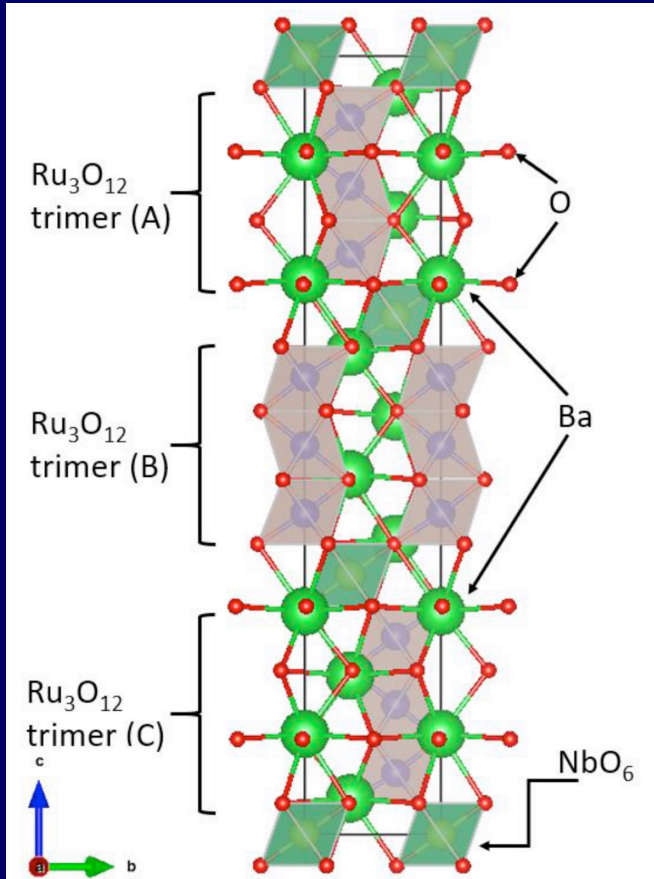
As we progress from 3d to 4d to 5d
 magnetic elements
 Does a local moment picture break
 down?

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

Now a second trimer compound $\text{Ba}_4\text{NbRu}_3\text{O}_{12}$.
Based on a 4d element that is often magnetic in oxides. (Ru)

A Geometrically Frustrated Trimer-Based Mott Insulator

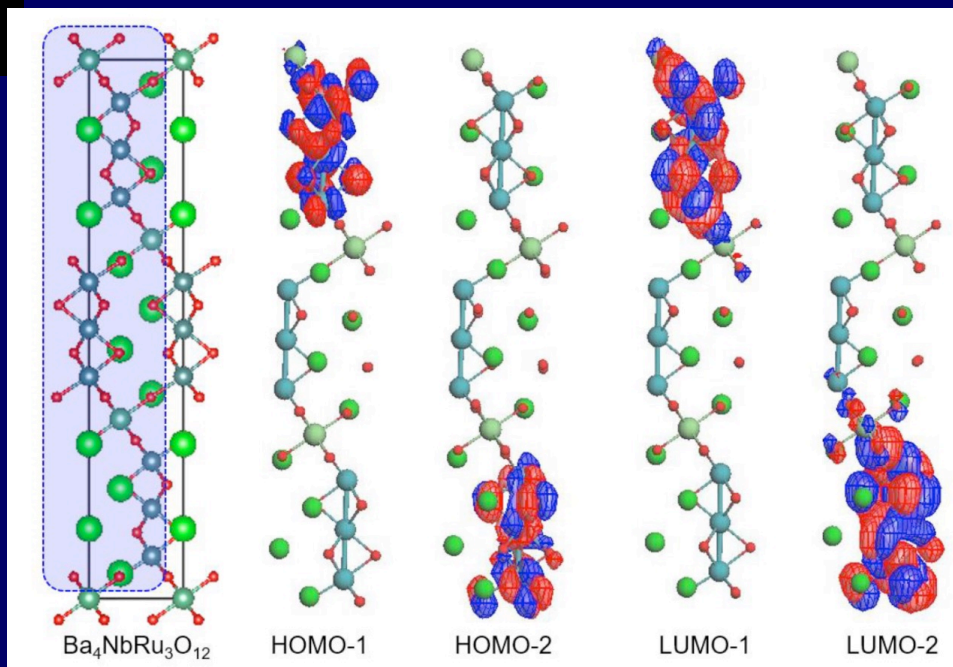
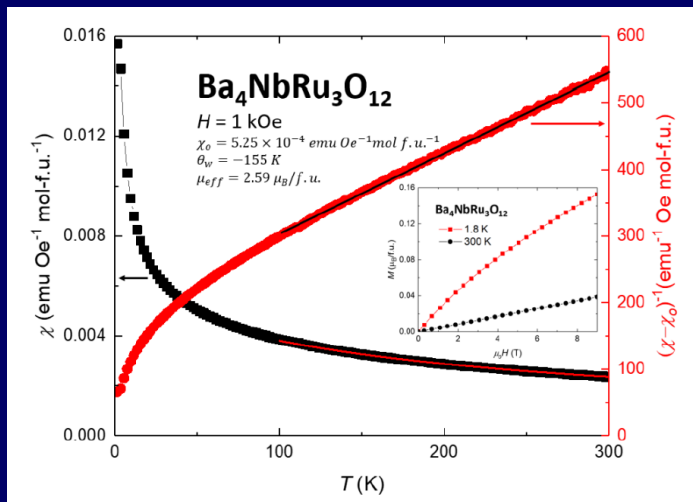
Loi T. Nguyen¹, T. Halloran², Weiwei Xie³, Tai Kong¹, C.L. Broholm² and R.J. Cava¹



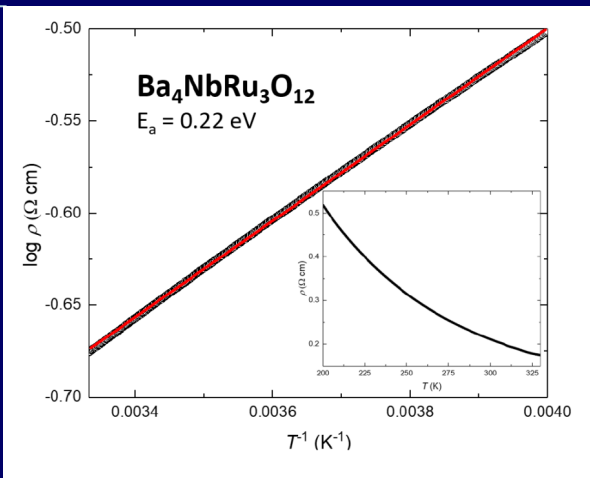
Two Ru 4+ and one Ru3+
= 13 electrons per trimer = spin $\frac{1}{2}$ per trimer
a nice spin.

Cigar-shaped spin $\frac{1}{2}$ 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 χ 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?

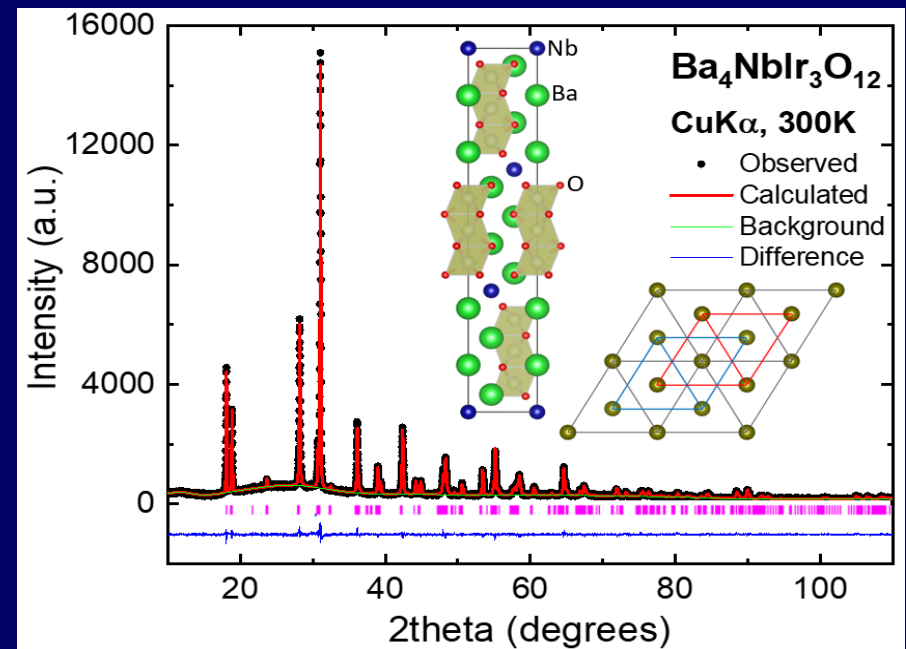
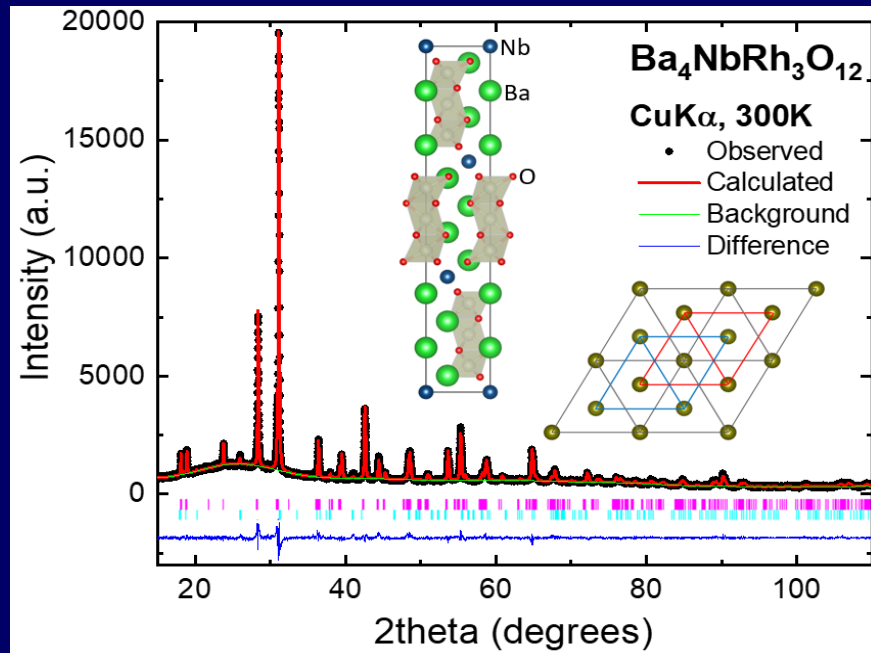
Two more: with Ir_3O_{12} and Rh_3O_{12} trimers in the new materials

$\text{Ba}_4\text{NbRh}_3\text{O}_{12}$ and $\text{Ba}_4\text{NbIr}_3\text{O}_{12}$.

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

Note its Co - Rh - Ir down the column.

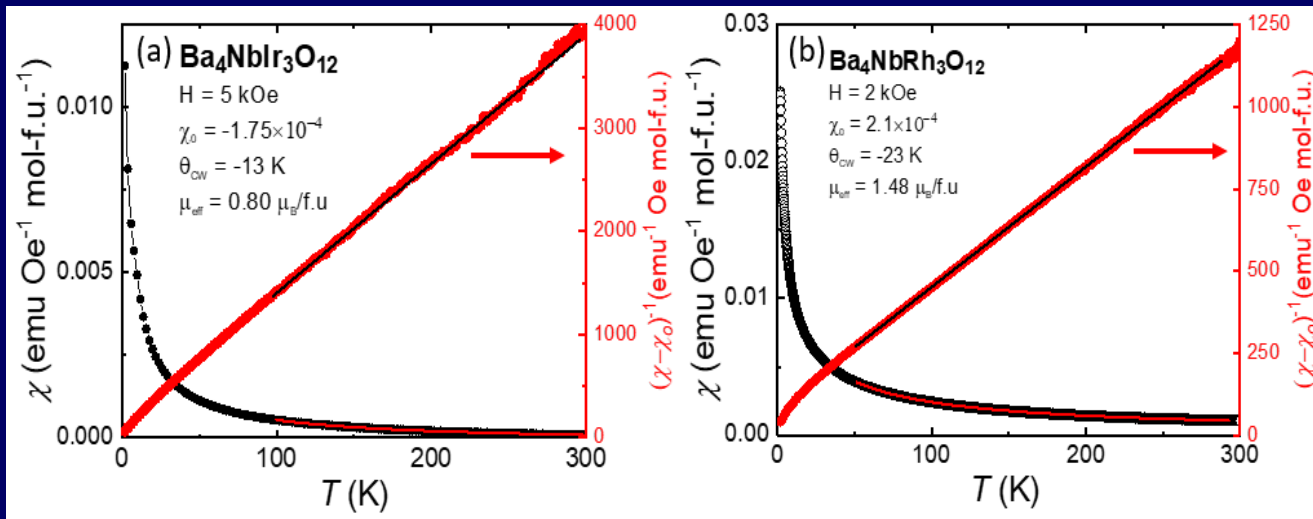
The Co one makes an annoying disordered cubic perovskite.



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

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

Now lets look at their magnetism



To 1st order they seem very similar magnetically

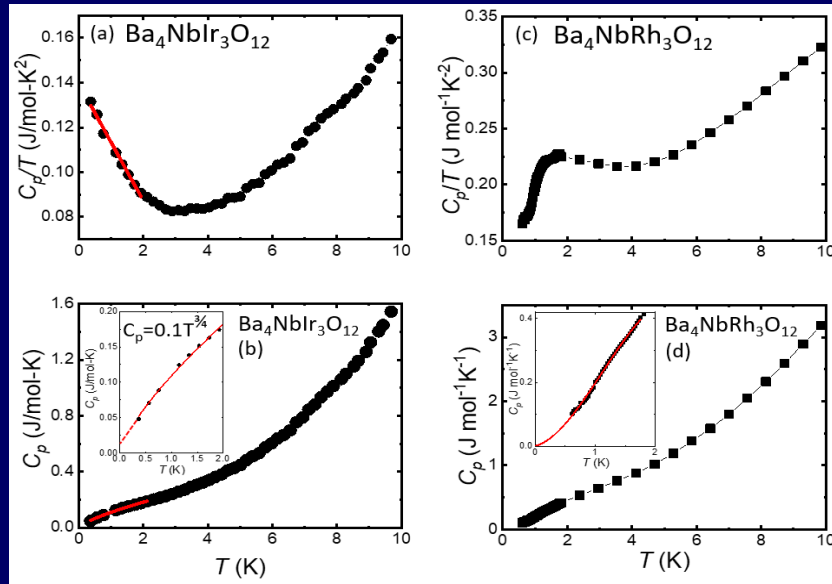
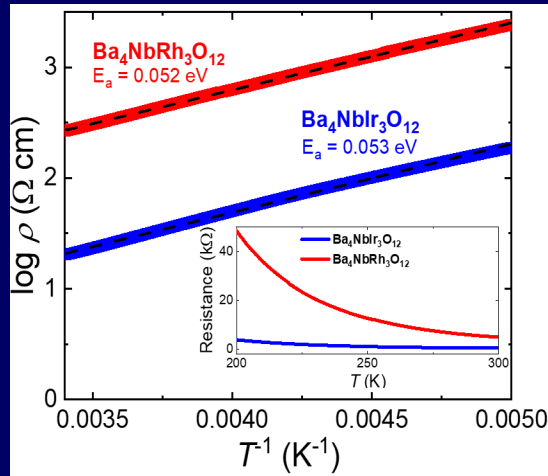
Very small moments - both effective moments are less than spin $\frac{1}{2}$ per trimer, and the Θ_{CW} are in the -15 to -25 K range

And there is no sign of magnetic ordering above 2 K

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

Rh³⁺ and Ir³⁺ are d^6 and possibly boring.
Rh⁴⁺ and Ir⁴⁺ 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?

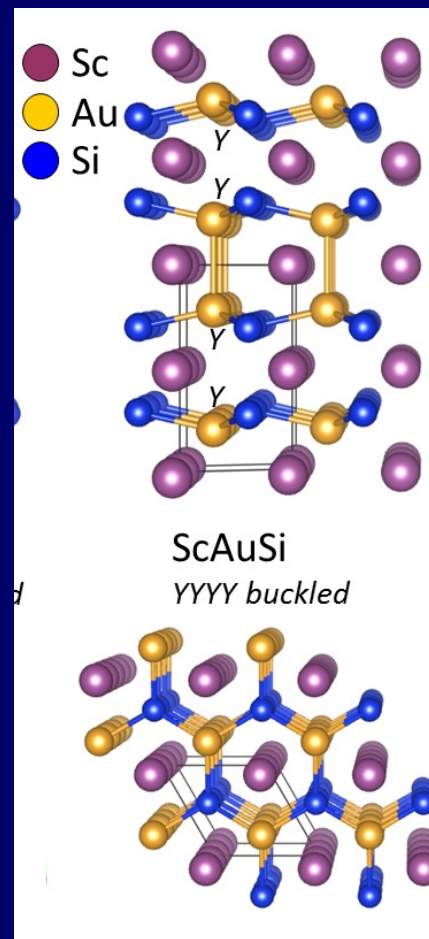
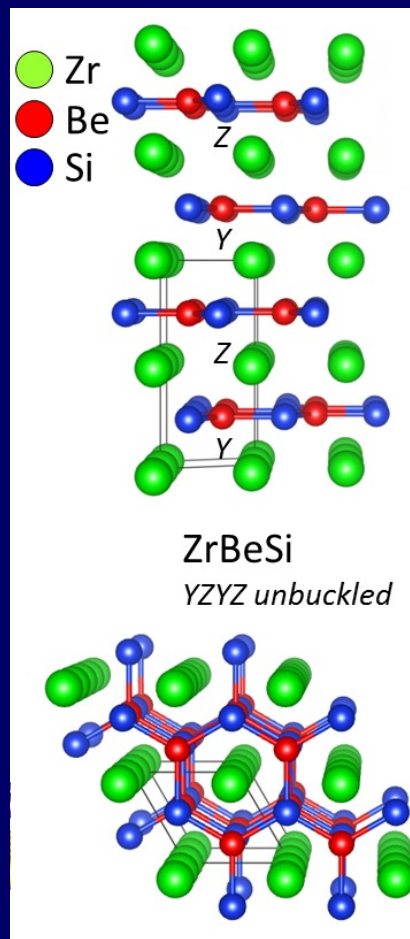
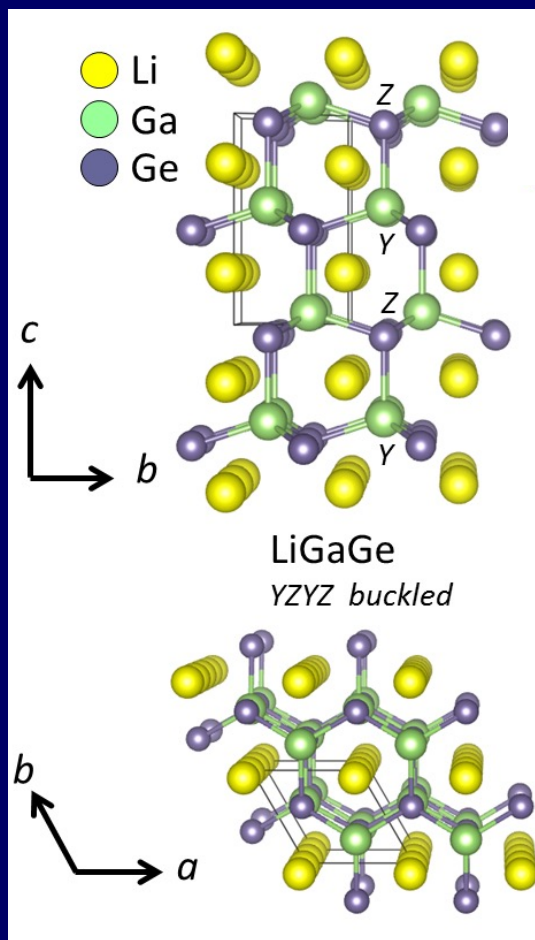
Ba₄Nblr₃O₁₂ is doing something strange. No magnetic phase transition, Cp/T continues to rise down to 0.35 K and does not extrapolate to 0 at T = 0.

Ba₄NbRh₃O₁₂ 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.

