Title: Recent chemical and structural studies of geometrically frustrated magnets, Dirac Semimetals, and topological insulators.

Date: Apr 30, 2015 01:30 PM

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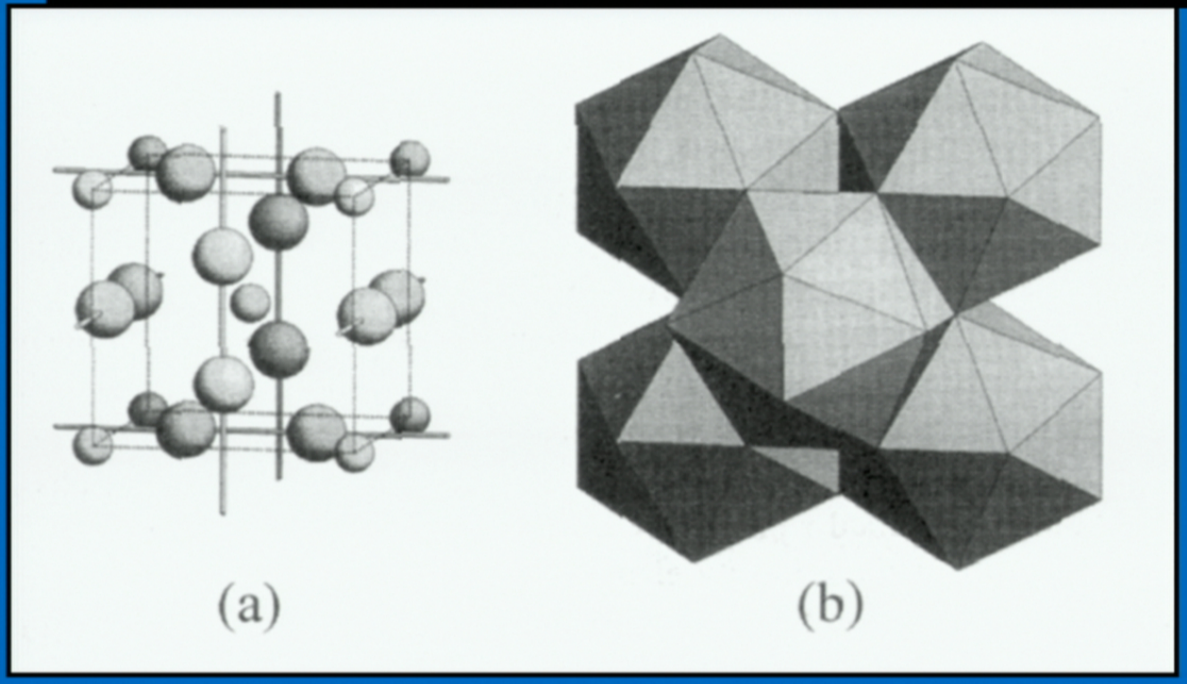
Abstract: Our search for new materials of (hopeful) relevance to materials physics is wide ranging. One of our primary interests is in finding new geometrically frustrated magnets and working on their structure-property relations. In this context in recent years we have found and grown crystals of a new class of pyrochlore magnets based on fluorine instead of oxygen. This chemical difference allows pyrochlores to be made with magnetic transition metals on the â€œB sitesâ€•, and non-magnetic ions on the A sites, which results in stronger magnetic coupling than is seen in the rare earth pyrochlores. This therefore provides the ability to probe magnetic frustration on the pyrochlore lattice at more easily accessible temperatures. Some of our initial work on these emergent materials, NaCaCo2F7 is an example of one of them, will be described. We have also been exploring the edges of the Dirac semimetal materials space and have recently gotten some interesting results on the Dirac semimetal superconductor Au2Pb. I will describe this material and a recent finding in Ca3P2, a material most often encountered in rat poison. Finally, if time permits, I will describe recent results in our search for the perfect topological insulator.

Topic 1 Searching for new superconductors using perspectives from both chemistry and physics

First project
Superconducting NbRuB
designed by the fragment formalism

Postdoc
Weiwei Xie

Lets start with
The classic intermetallic superconductor Nb_3Sn

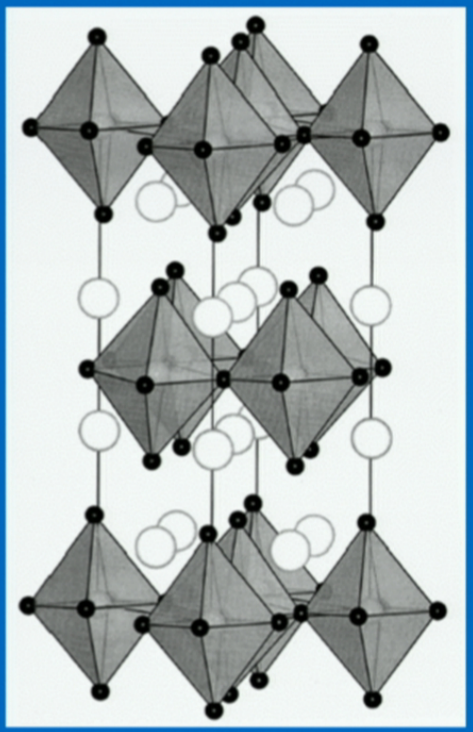


BCC Sn with Nb chains on the faces running along <100> (a)
(Or Friauf polyhedra (b))
…superconducts due to contented electrons in *k* space.
Physics rules.

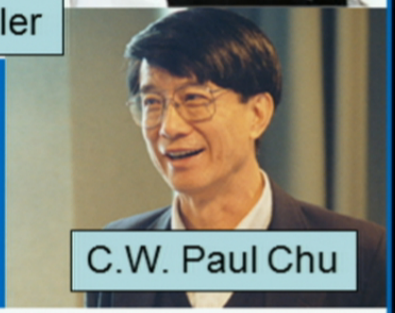
But then came along
$La_{2-x}Ba_xCuO_4$ and
$YBa_2Cu_3O_7$…
and charge transfer
(i.e. chemistry) matters!

J.G. Bednorz and K.A. Mueller

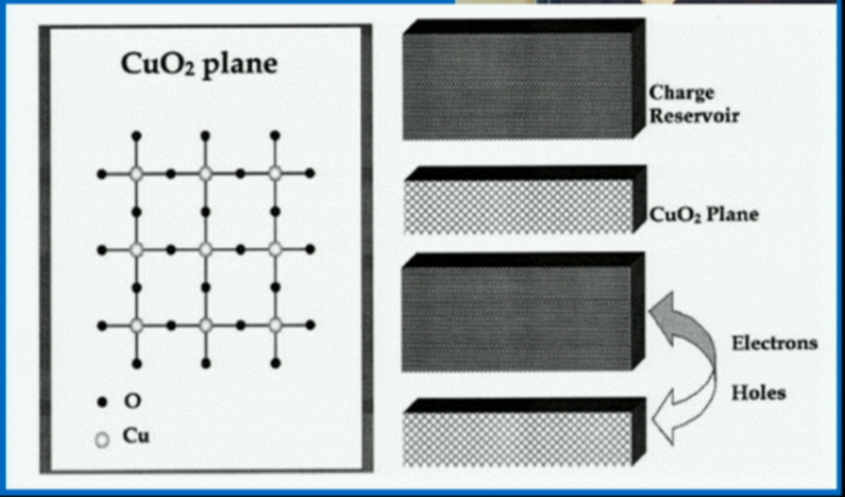
M.K. Wu

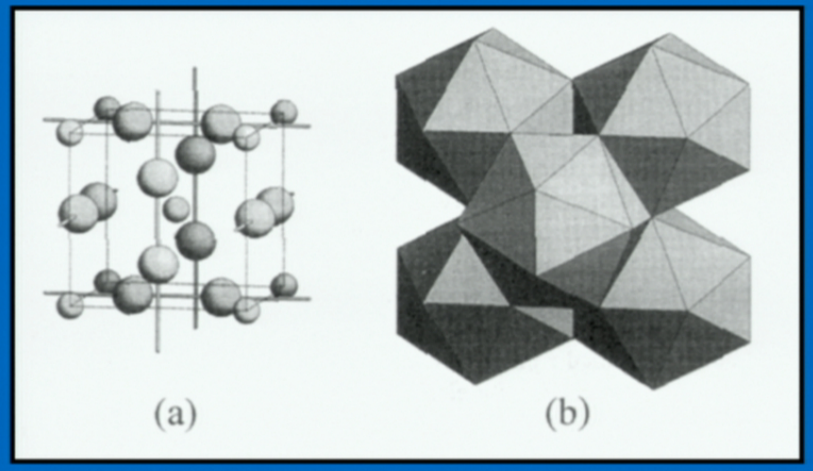


In the language of this talk
High Tc Cuprates are made
from donor and acceptor
structural fragments



C.W. Paul Chu





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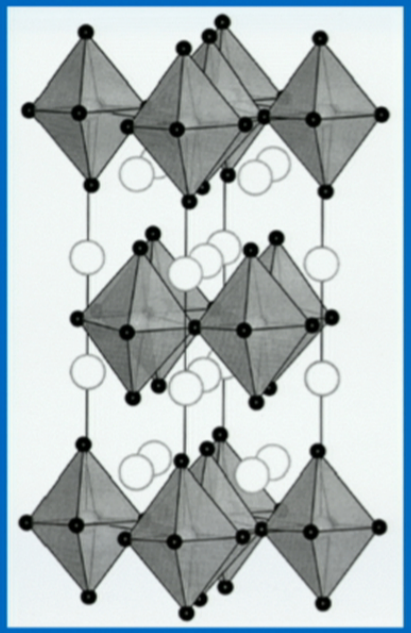


In compounds like Nb_3Sn made from metallic elements one usually doesn't think of charge transfer
but it must be there in some form.
because the metals have different electronegativities

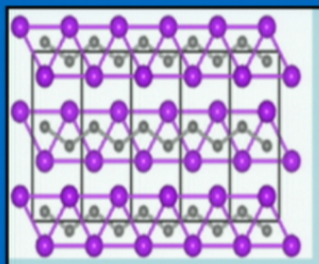
Can we take advantage of this blind spot to find a new superconductor?

Our idea: Look for an intermetallic structural fragment that supports superconductivity and put it into a different crystal structure and chemical system.

Charge will have to be balanced by a donor-acceptor relation with another fragment to yield chemical stability.

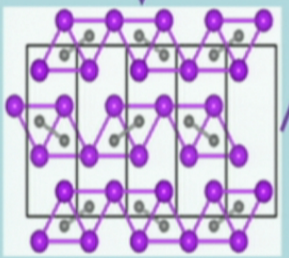
and hopefully superconductivity.

Starting from Re_3B the result was NbRuB



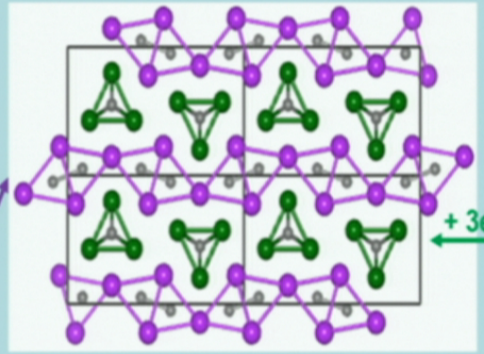
Nb_3B_3

- $3e^-$ (B)



"Nb_3B_2"

Nb_3B_2 fragment
3 electrons more than NbB
(could donate)



+ $3e^-$

NbRuB = "Nb_3B_2""Ru_3B"

Ru_3B fragment
same structure but
3 electrons less than
Re_3B (Ru is one
column to the left of
Re. could accept)

Re_3B a 4 K
superconductor

Second project
Polymorphism, Polytypism and superconductivity in $TaSe_{2-x}Te_x$

Chemical tuning of the structural stability of dichalcogenides through an isoelectronic substitution

In layered dichalcogenide superconductors, electronically 2D materials,

should the third dimension matter?

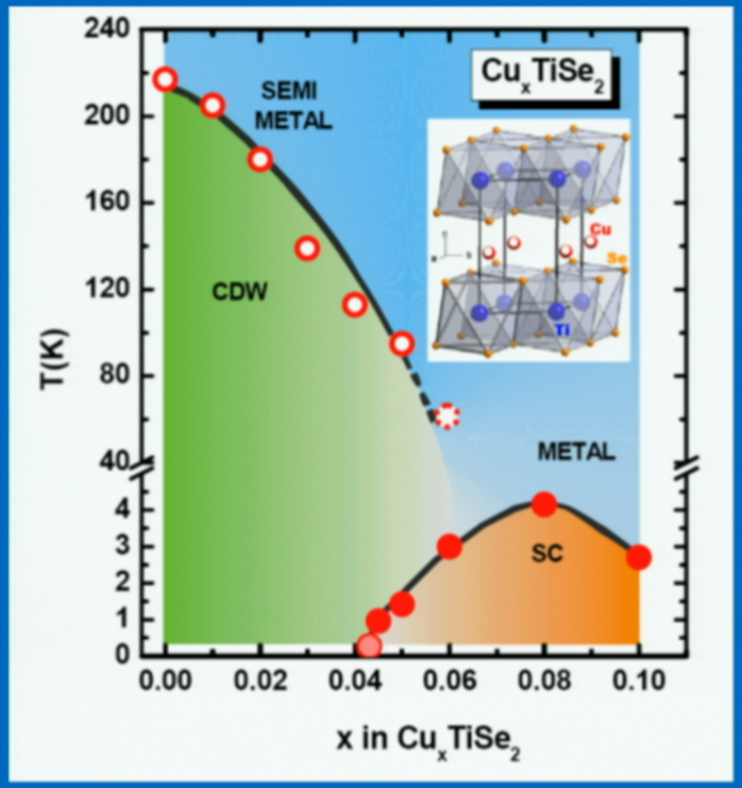
Postdoc Huixia Luo

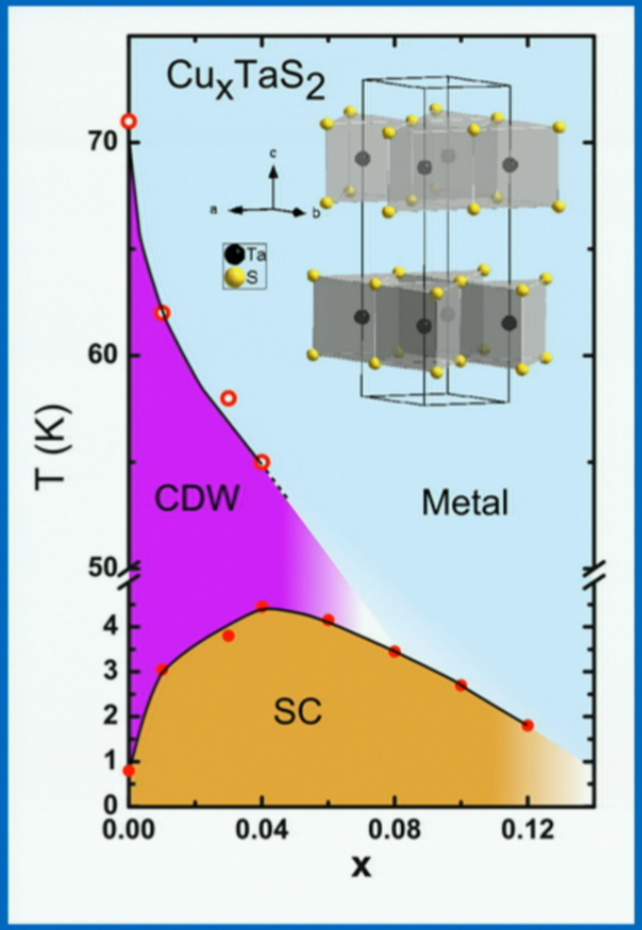
Polymorphs - different crystal structures of the same compound

Polytypes -a special kind of polymorph in layered compounds. They differ only in the stacking sequence.

with Weiwei Xie, Jing Tao, Hiroyuki Inoue, András Gyenis, Jason Krizan, Ali Yazdani, and Yimei Zhu

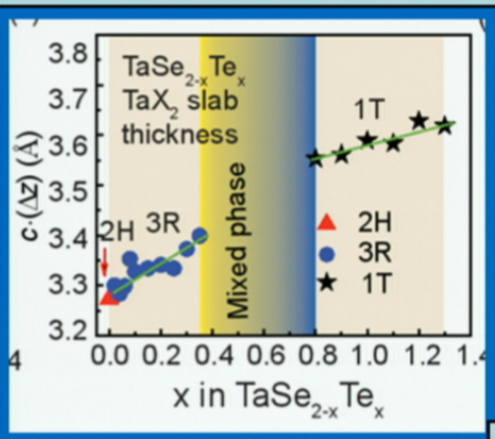
Some things we found previously
-some CDW- Superconductivity Phase Diagrams
Changing the competition between CDWs and superconductivity
through electron doping



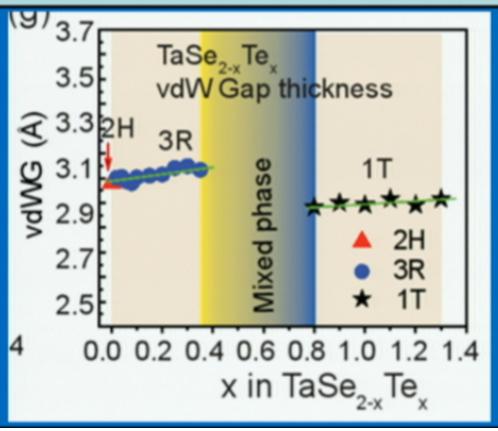


But electronically, the different Contributions may matter

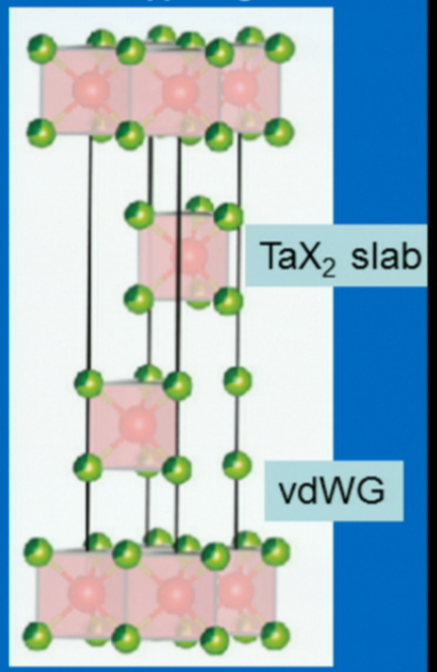
Thickness of individual layer



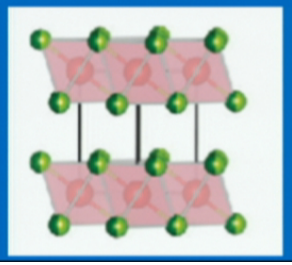
Van der Waals gap thickness



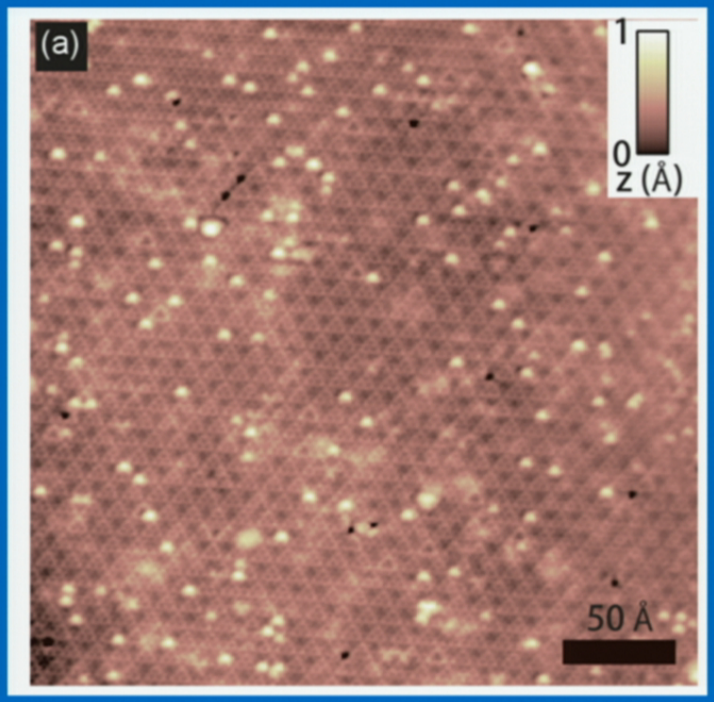
3R structure
n = 3



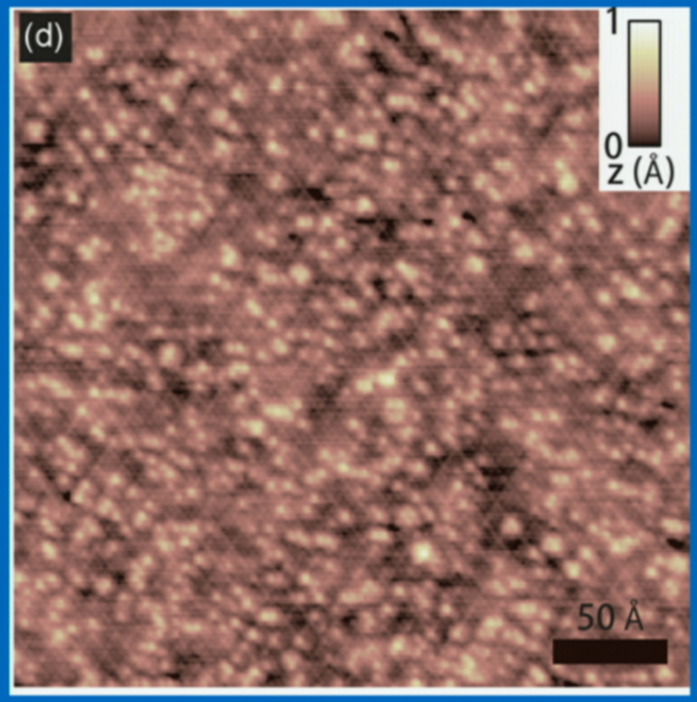
1T structure
n = 1



But maybe there is something different locally.
you can look locally at the CDW state with STM
It is clearly there, and commensurate for both 3R and 1T forms



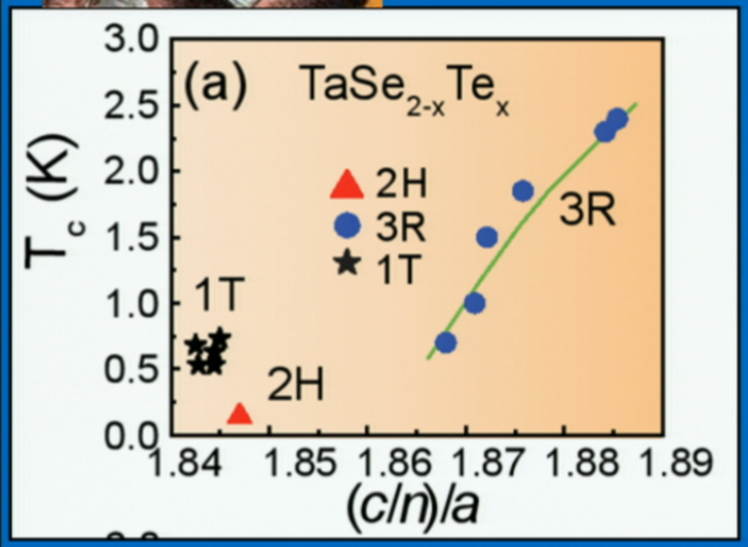
3R form (50 K)



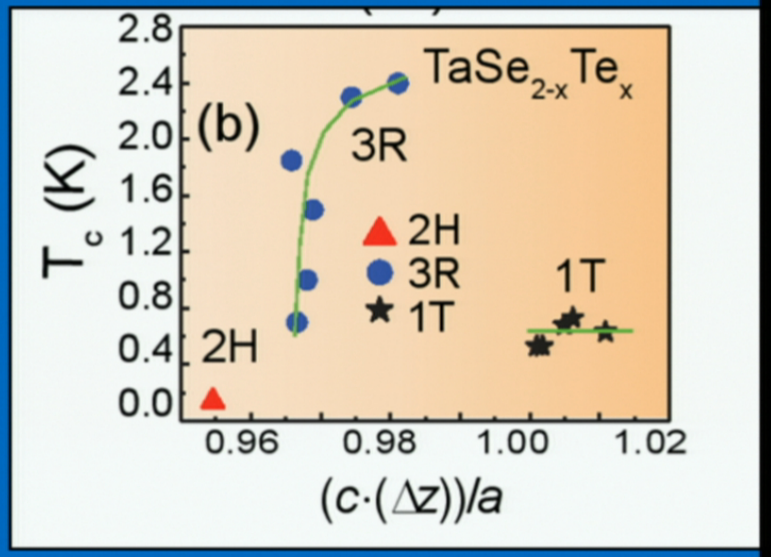
1T form (30 K)

In spite of the disorder from the substitution (Te bright dots),
the CDW is very well developed.
(Even in superconducting samples.)

"But you didn't really show that the polytype/polymorph matters… the behavior doesn't look continuous with Se to Te ratio but maybe it is anyway"



Tc vs. the character of the overall layered Structure (the *c/a* ratio)

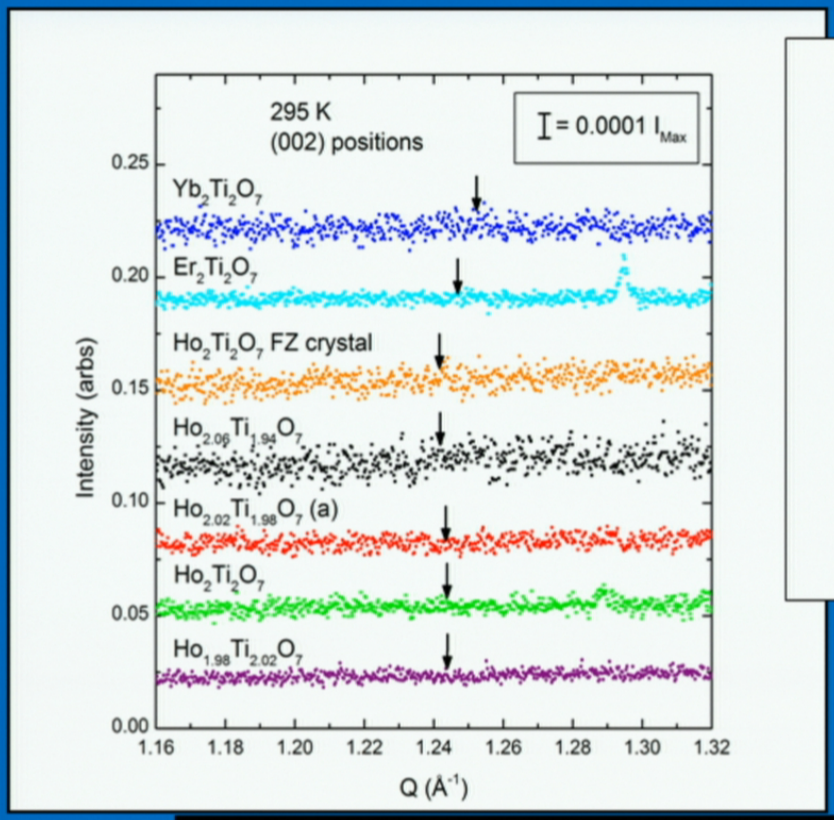


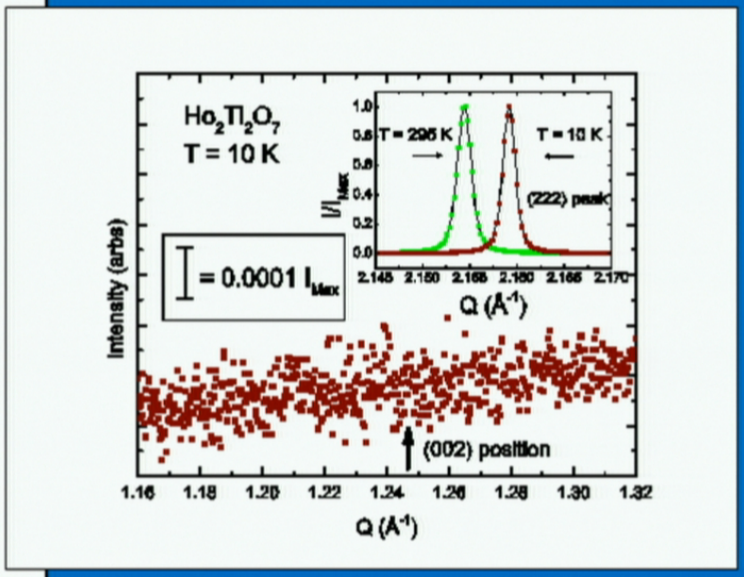
Tc vs the characteristic shape of the MX_2 layers (the layer *c/a* ratio)

No continuous variation of T_c with anything across the whole series.
Therefore *the polymorph and polytype (the third dimension) matter*.

Look in detail at the region where the 002 reflection is expected

We tested different pyrochlores, lightly "stuffed" ones, and a crushed FZ single crystal





The space group is Fd3m

There is no 002 peak to one part in 30,000

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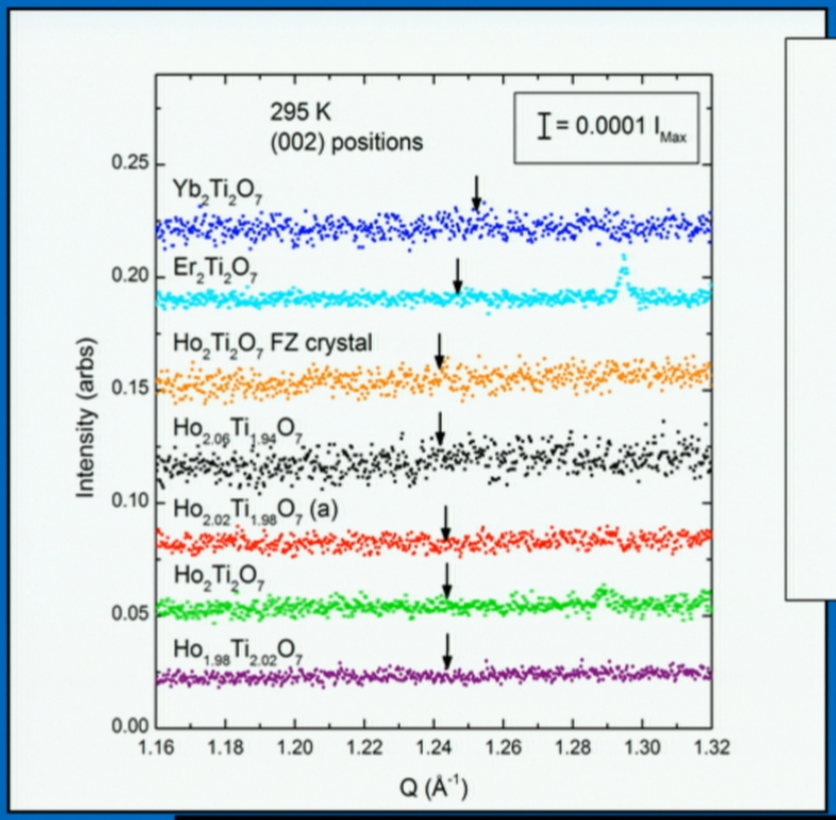

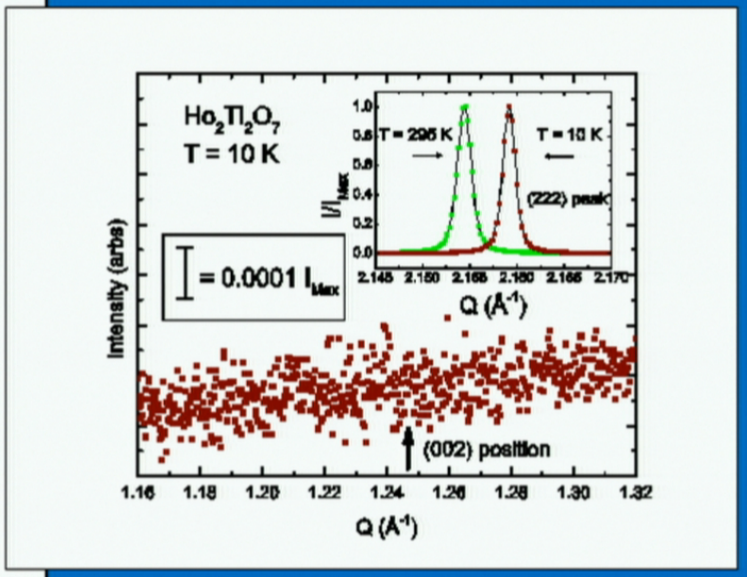

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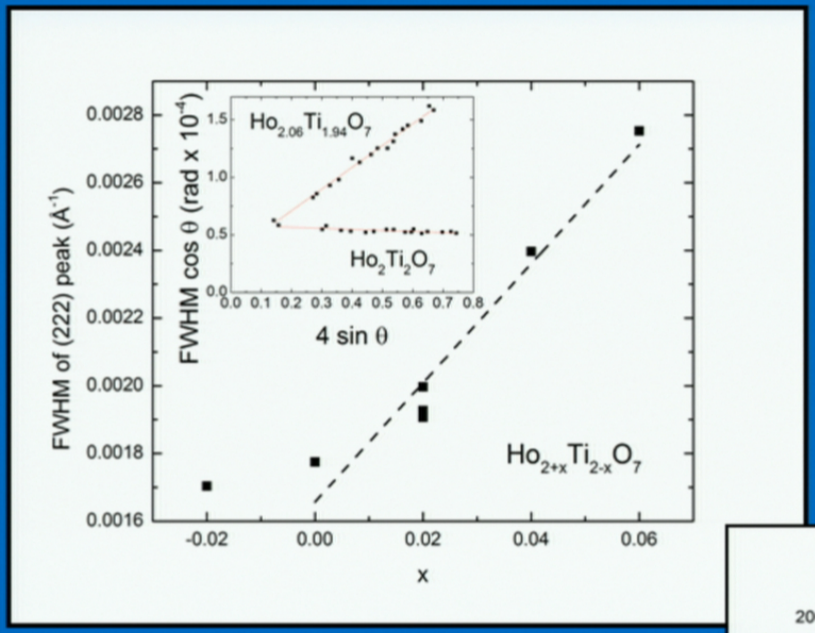
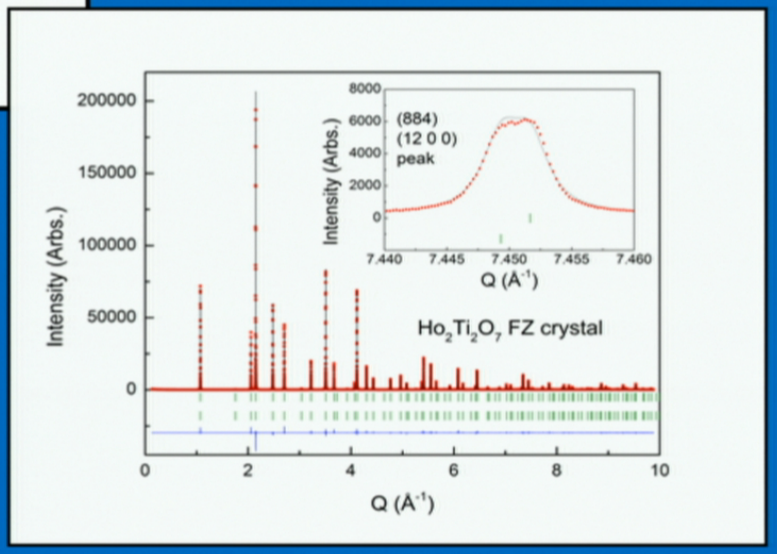


2. It also allows you to characterize local strain

(through the peak widths)

3. It allows you to see very subtle composition inhomogeneity

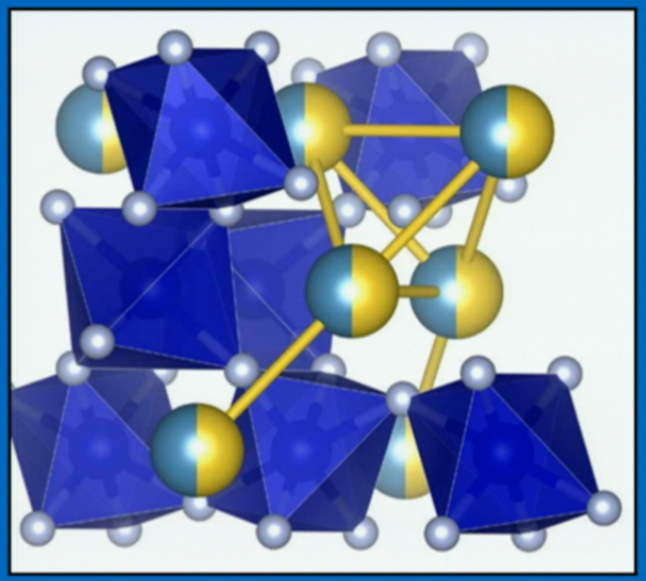


Project 2 transition metal flouride pyrochlores

Motivated by several theorists –

"can you make a pyrochlore with stronger interactions than 1 K?"

Eventually, yes…By putting transition metals on the B sites.
But you need to balance the charge



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

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

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

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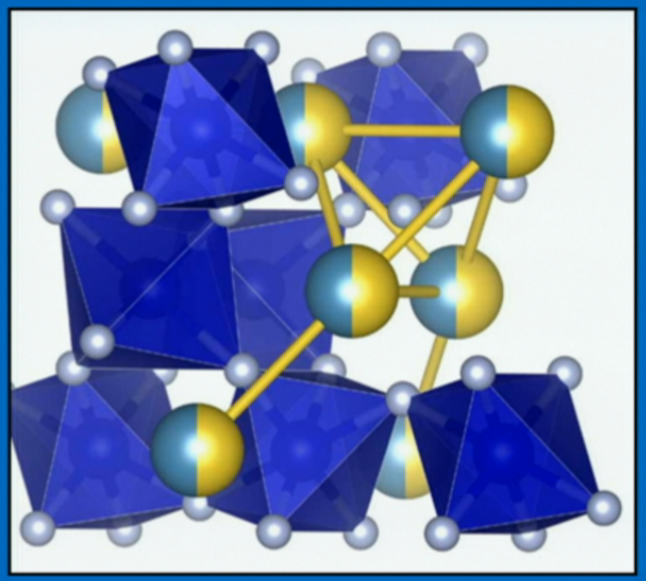

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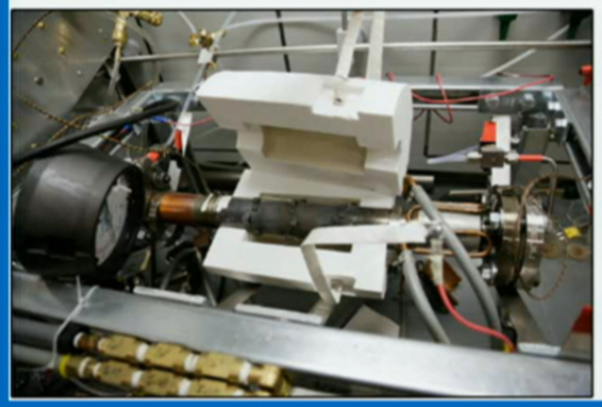
$$\overset{1+}{A'}\ \overset{(2+)}{A''}\ \overset{2\,(2+)}{B_2}\ \overset{7(1-)}{F_7} = 0$$

But there's a reason that (almost) nobody works on fluorides any more

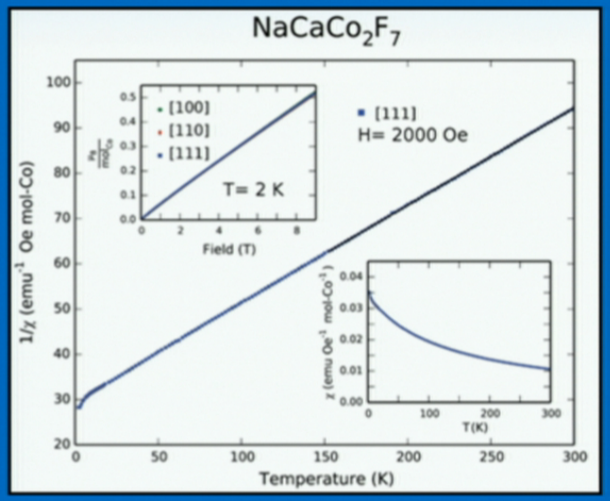
Jason Krizan

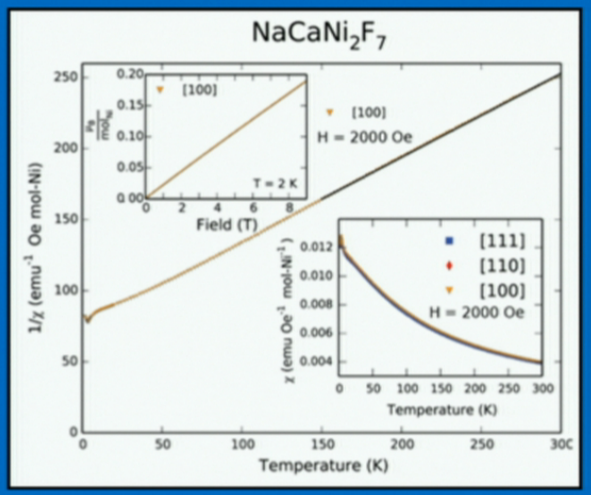


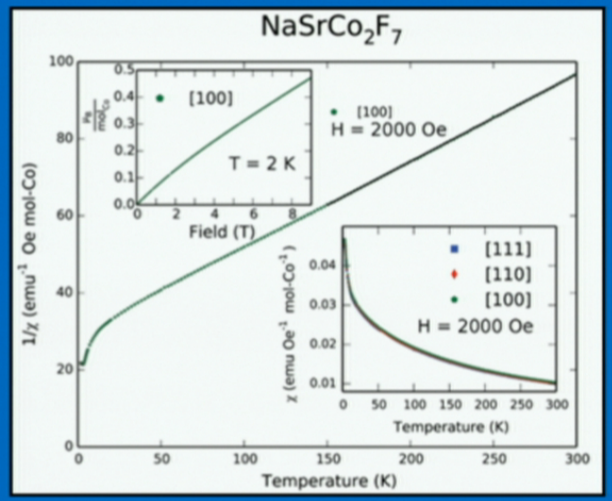
Built an in-situ HF generator

With a reaction chamber that can be transferred to a glove box. Needed for starting materials purification and pre-reaction.

All display nice Curie Weiss law behavior



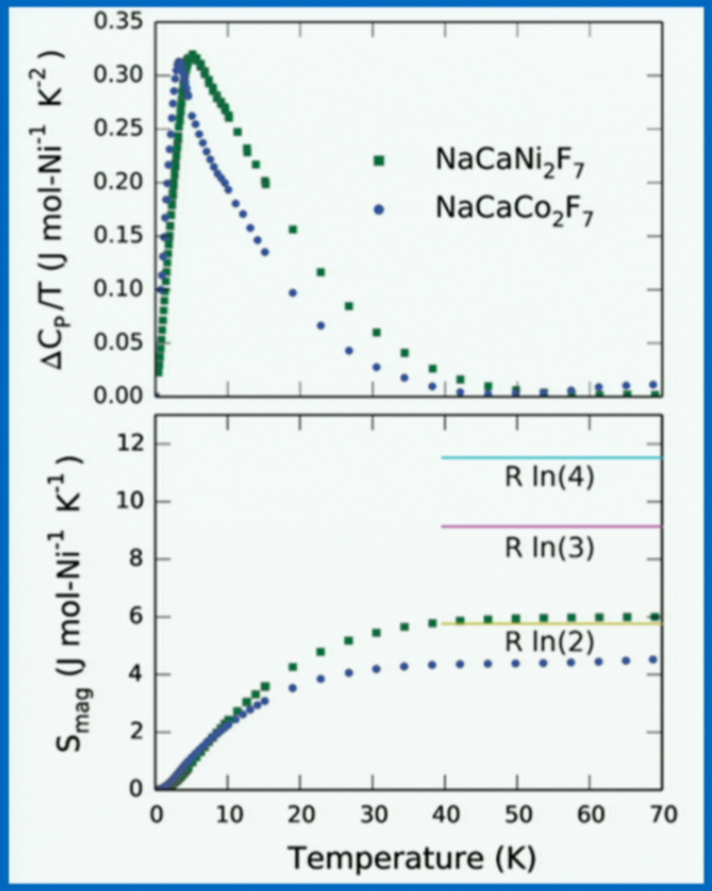


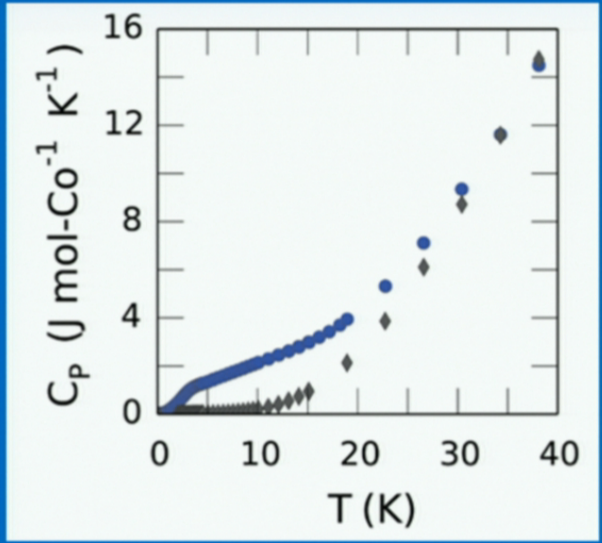


Curie-Weiss Fit:	θ (K)	p_{eff} (μ_B)
$NaCaCo_2F_7$	-139(1)	6.1(1)
$NaSrCo_2F_7$	-127(1)	5.9(1)
$NaCaNi_2F_7$	-129(1)	3.6(1)

All have a magnetic transition 2-3 K so are highly frustrated

The non-magnetic analog $NaCaZn_2F_7$ allows us to determine the entropy lost at the magnetic transition





Is on the order of R ln2
not the Heisenberg numbers
R ln(2s+1)

These are very new.
More detailed work is in progress

Topic 3

Topological Insulators and Dirac semimetals

Satya Kushwaha

Quinn Gibson

Lilia Xie

Leslie Schoop

Mazhar Ali

The search for the perfect Topological insulator.

Four primary requirements:

- Very high bulk resistivity so that the transport of charge is dominated by surface states.
- Surface Dirac point energy isolated from the bulk energies so that there is no interference from bulk electrons.
- The mobility of the topological surface state electrons should be high.
- The material must be reasonable and reproducible to fabricate

We used the vertical Bridgman crystal growth method.

The search for the perfect Topological insulator.

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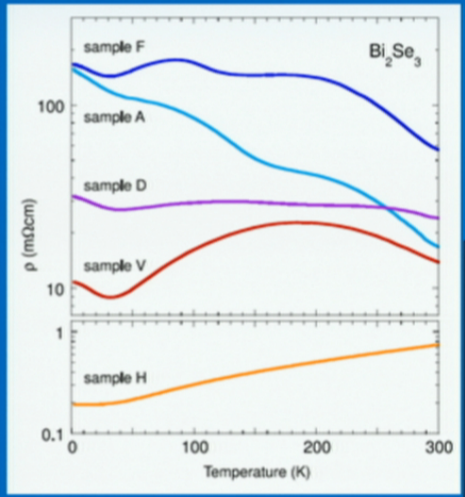
We used the vertical Bridgman crystal growth method.

Our strategy has been to learn how to control the defects that give rise to the bulk conductance in the TI family.

Other strategies:

1. Studying something simple. "Toward true bulk insulating behavior in a stoichiometric TI " (Bi_2Se_3) Dec. 2014.



Three orders of magnitude more conducting. Interest is that it is simple. Nice idea. But simple things often don't work.

Our Progress in raising the bulk resistivity ρ

2008: ρ (4 K) = 0.1 mΩcm (Bi_2Se_3)
2010: ρ (4 K) = 10 mΩcm (Bi_2Te_3)
2010: ρ (4 K) = 6 Ωcm (Bi_2Te_2Se)
2012: ρ (4 K) = 20 Ωcm (Sn-Bi_2Te_2Se)
2015: ρ (150 K) > 100 Ωcm (Sn-$BiSbTe_2S$)

we have 6 orders of magnitude improvement - one of the criteria is met. Lets look at others

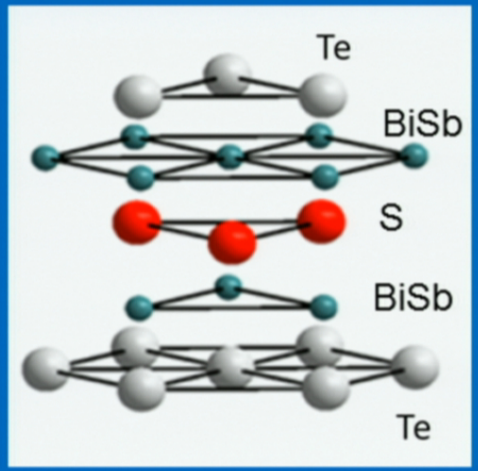
2. (Bi,Sb) $TeSe_2$ thin films - **Very nice results** but composition not fixed by structure or chemistry. Materials maker has to control too much.

In the past year we put together what we know so far to come up with $BiSbTe_2S$
- the best topological insulator known

Firstly it easily grows large crystals by the vertical Bridgeman method

This new material has more elements than physicists are comfortable with.

But it self-selects a stable composition.
S in middle layer
Bi-Sb ratio by size match.



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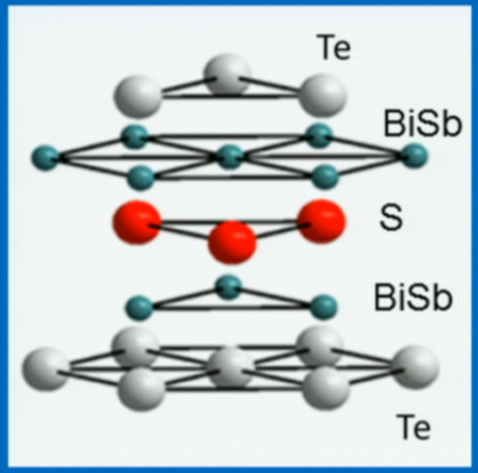
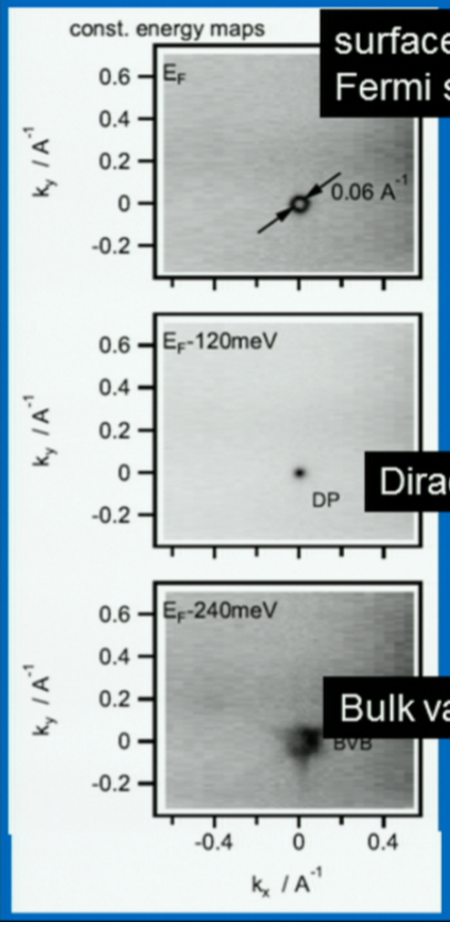
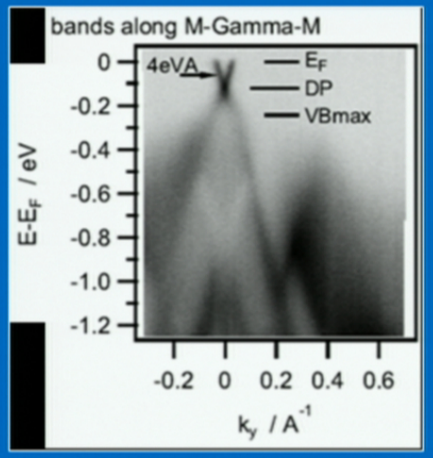
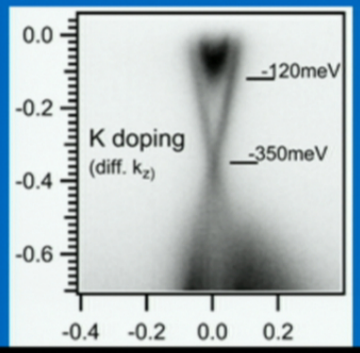


Thirdly ARPES shows that the Dirac point is isolated in energy from all bulk states for $BiSbTe_2S$

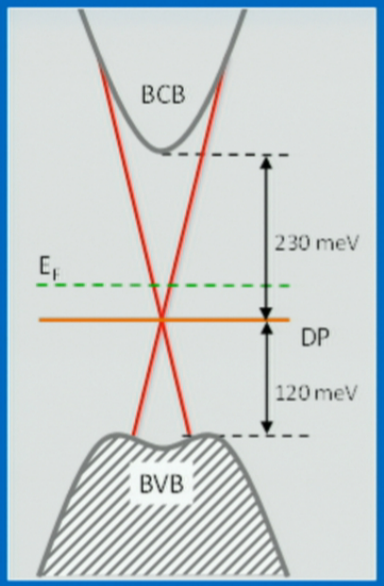
only surface states are at E_F





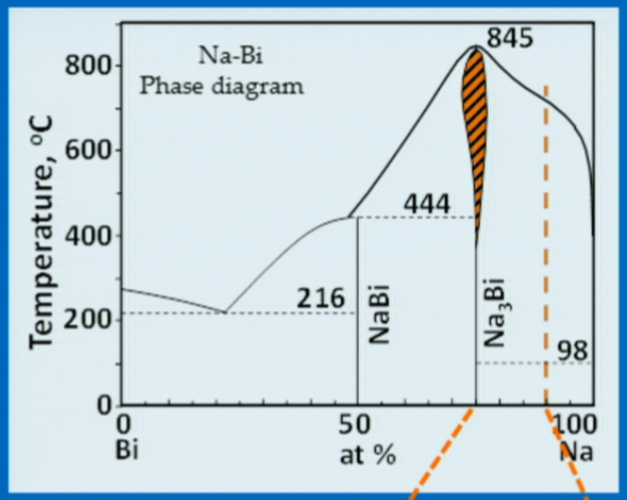


K deposition on surface donates electrons and allows conduction band to be seen



Analysis of the ARPES spectra shows that the Dirac point in In the gap! Isolated from all other states

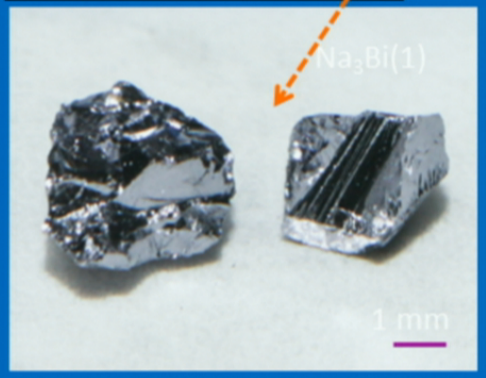
Dirac semimetals 1: Na_3Bi crystal growth



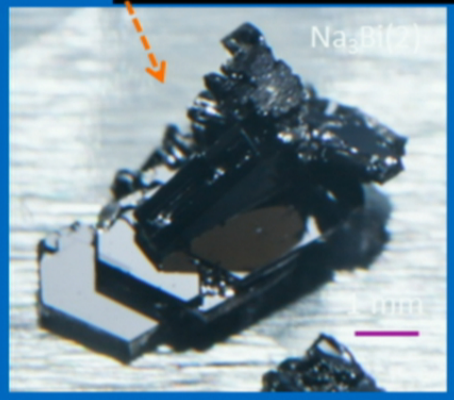
Steel tubes (304 L)

Cooling rate ~1.5 °C/h
Crystal annealed for 4 weeks
Extremely air sensitive
Crystals are processed in Ar dry box

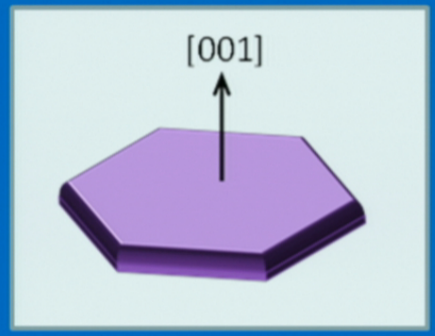
Stoichiometric cooled

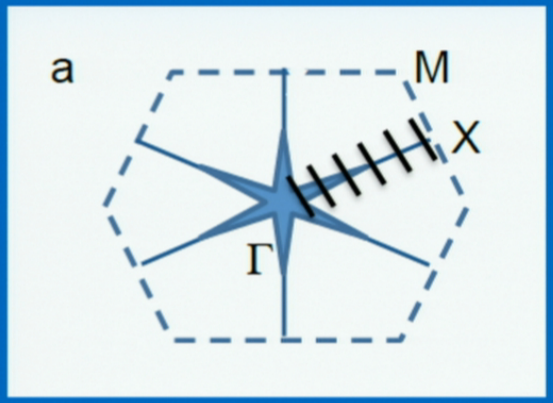


Flux grown (90% Na)

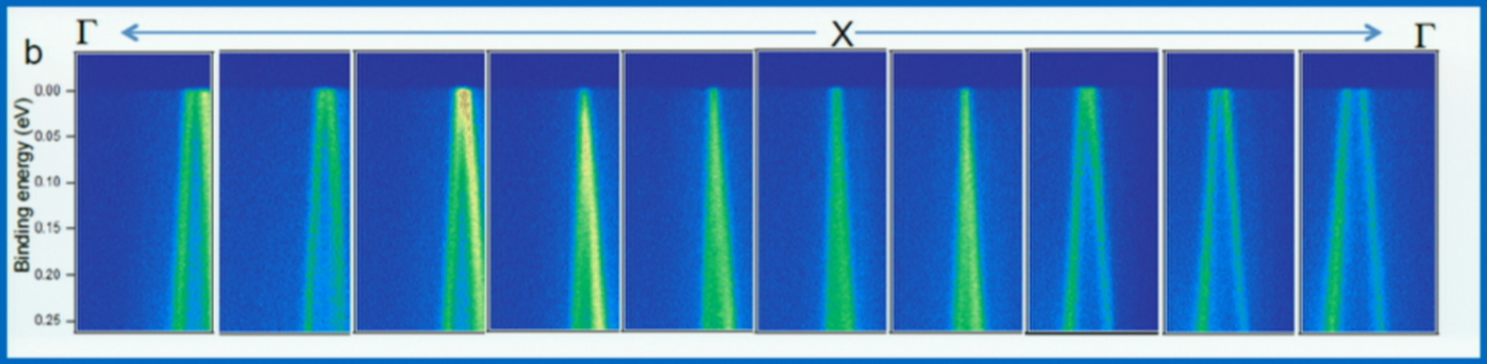


Crystal morphology





Now take a series of E vs. *k* cuts
Along one of the arms of the
(6 arm) starfish



A series of Dirac cones

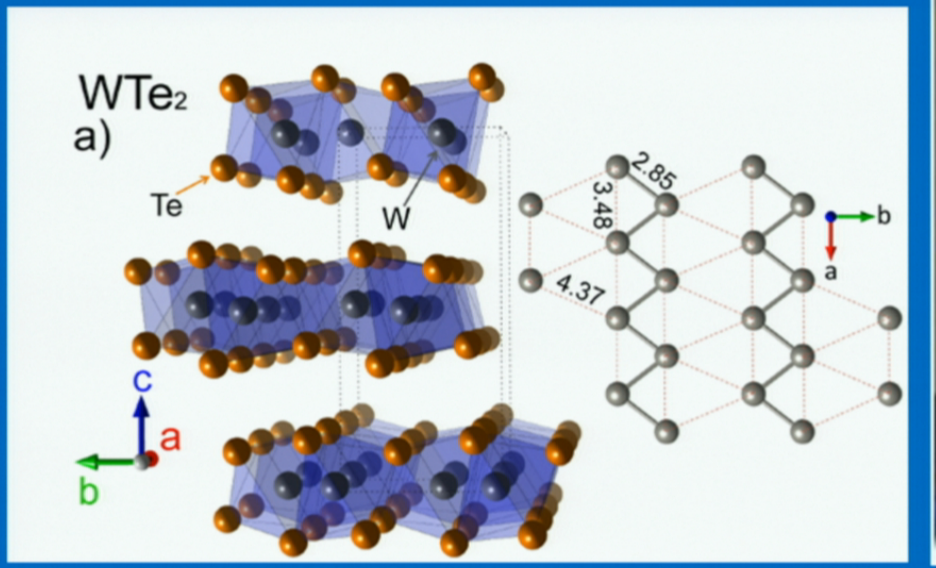
Dirac point is above E_F at Γ, at E_F near X

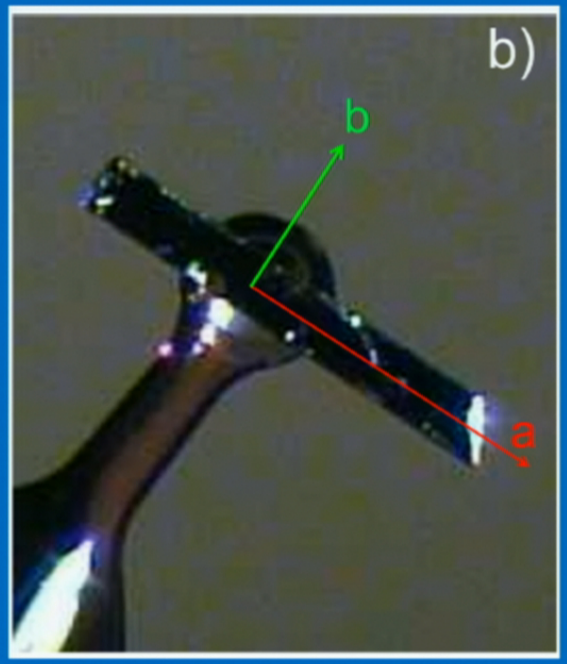
2. A recent new material – WTe_2

Ludicrous magnetoresistance in WTe_2

Titanic magnetoresistance in WTe_2

The WTe_2 crystal structure





A classic layered dichalcogenide structure
- like MoS_2 $TiSe_2$ etc.

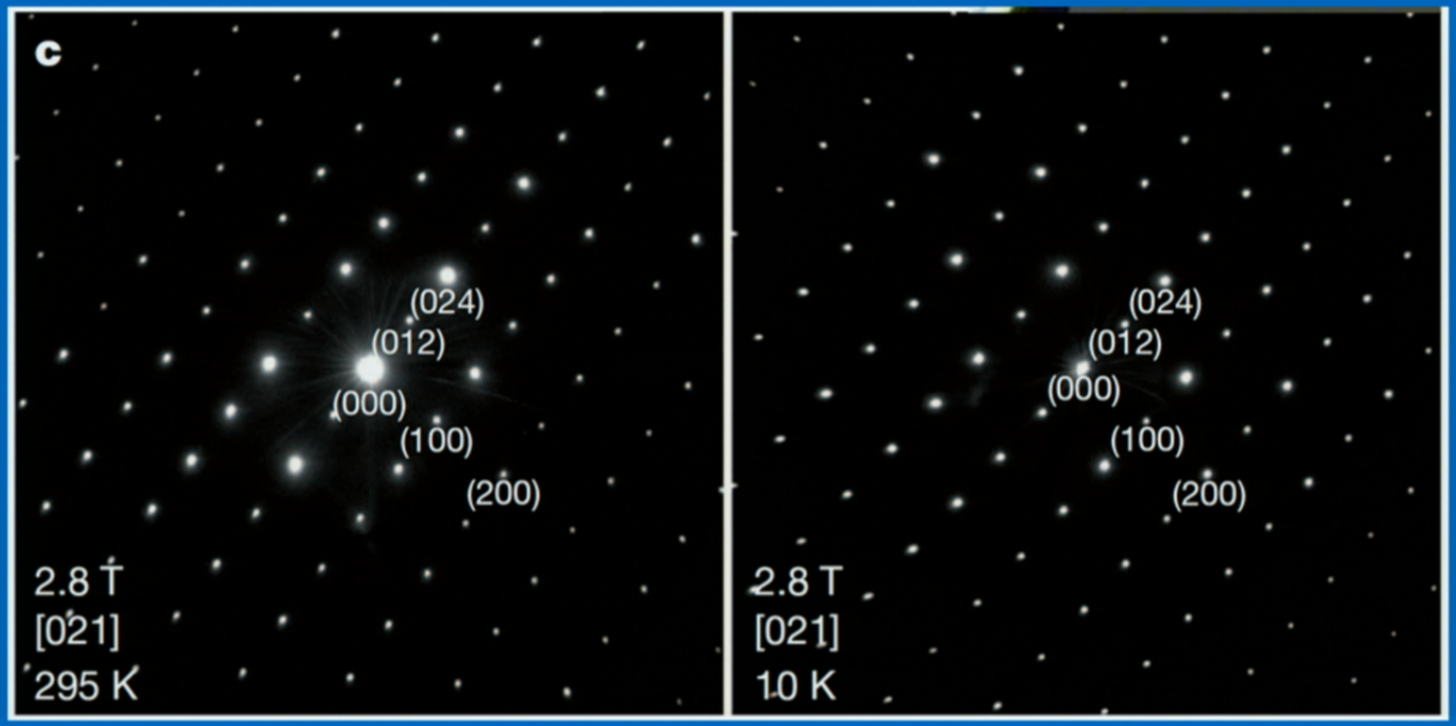
But it uses its 2 electrons per site
to form bonds to 2 neighboring W
making chains and (almost) a semiconductor.

Forms crystal ribbons along chains

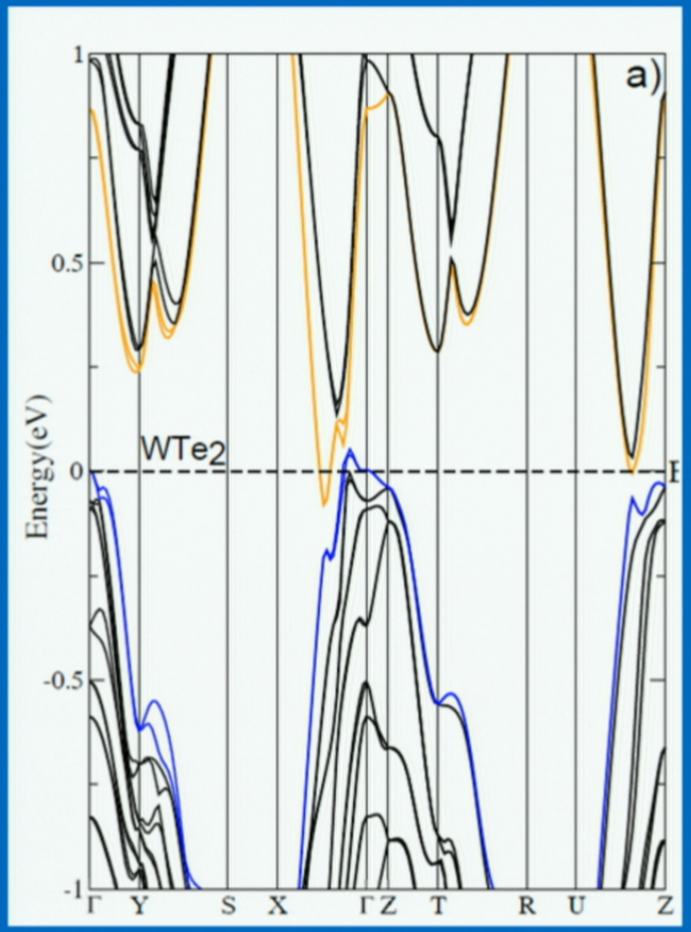
It is easily cleaved and exfoliated

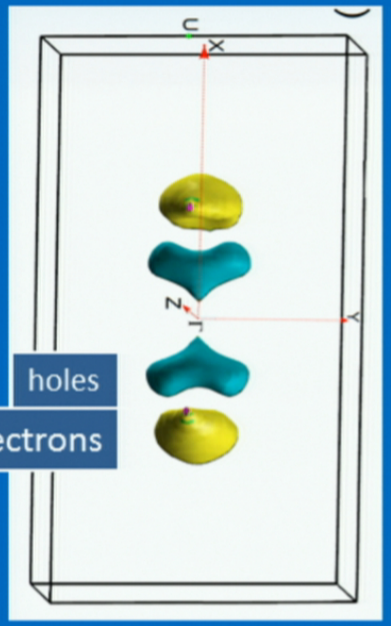
Electron diffraction performed at 10 K in 2.8 Tesla

No CDW or structural distortion to accompany the onset of the LMR



WTe_2 calculates to be a very delicate semimetal



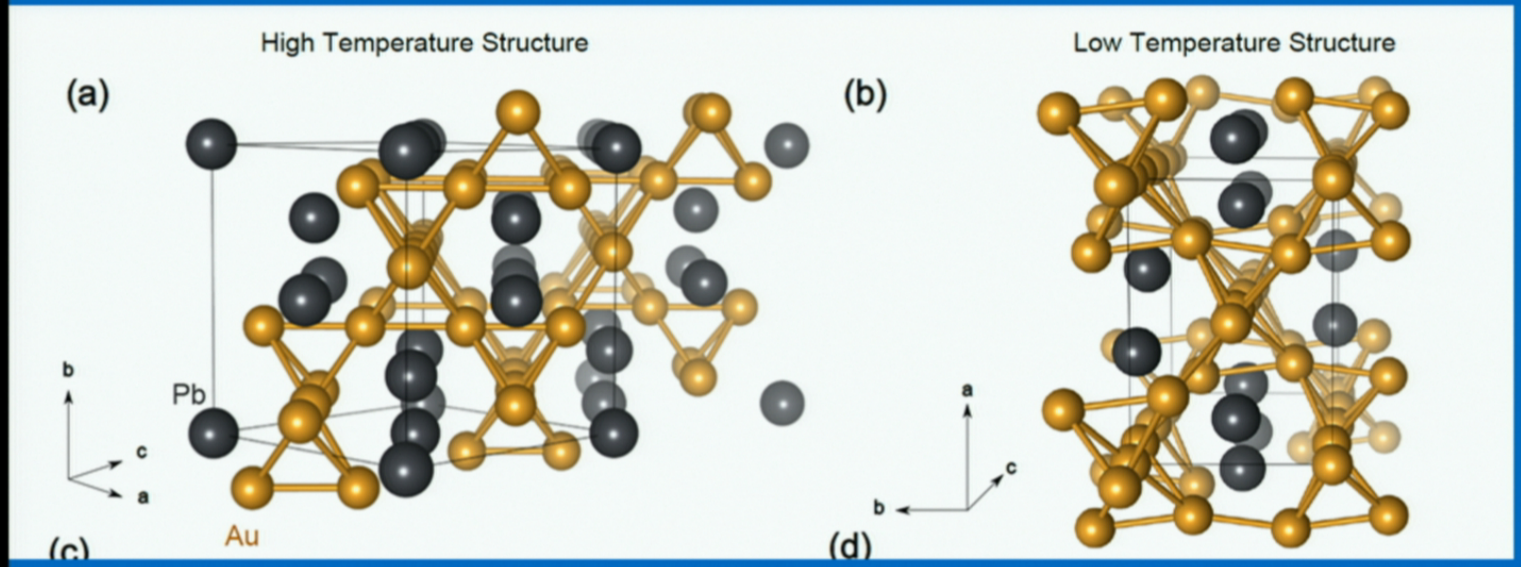


A 1D electronic structure

h and e pockets // chains.

Reminds me of the "excitonic insulator" $TiSe_2$

We found a collaborator who was interested in performing high resolution synchrotron powder diffraction at low T. (Saul Lapidus at ANL APS line 11-BM)



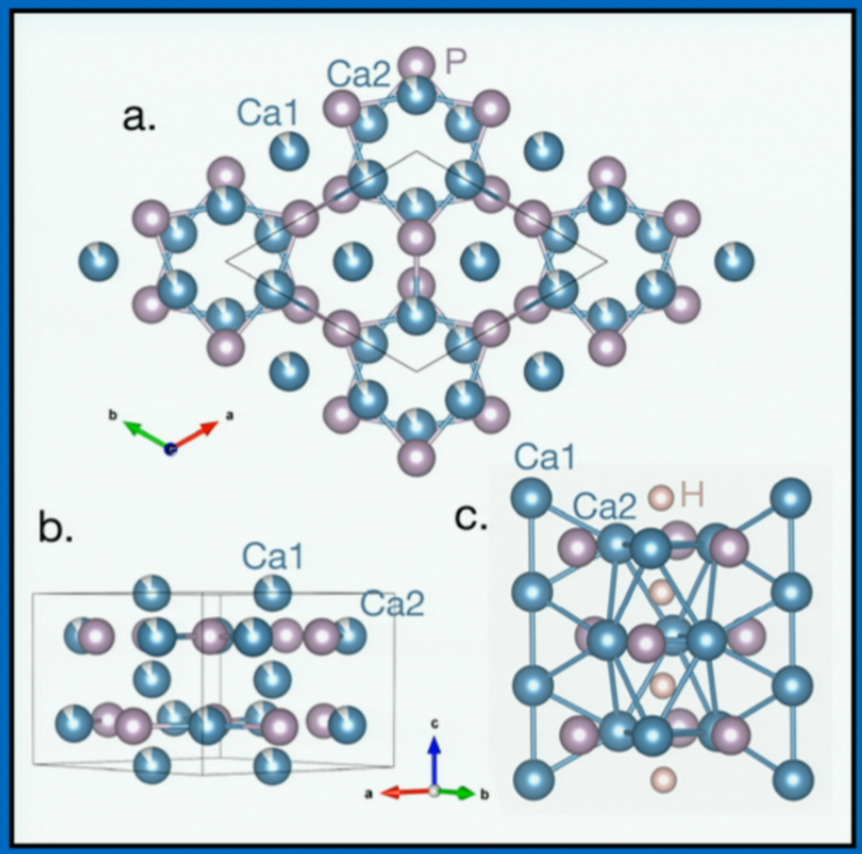
He found a phase transition from the cubic Laves phase at high T to a new kind of distorted Laves phase at low T

4. Another surprise

Topological rat poison

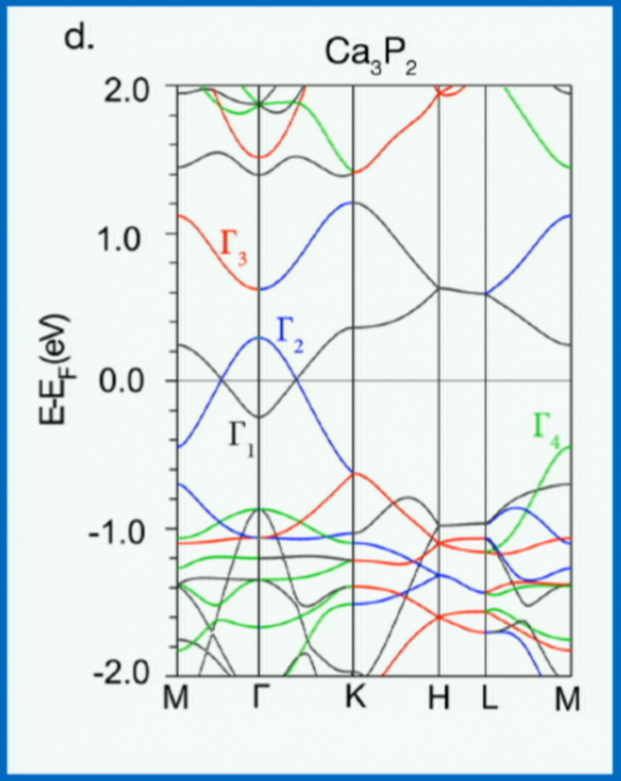
A crystalline
Version of
Ca_3P_2

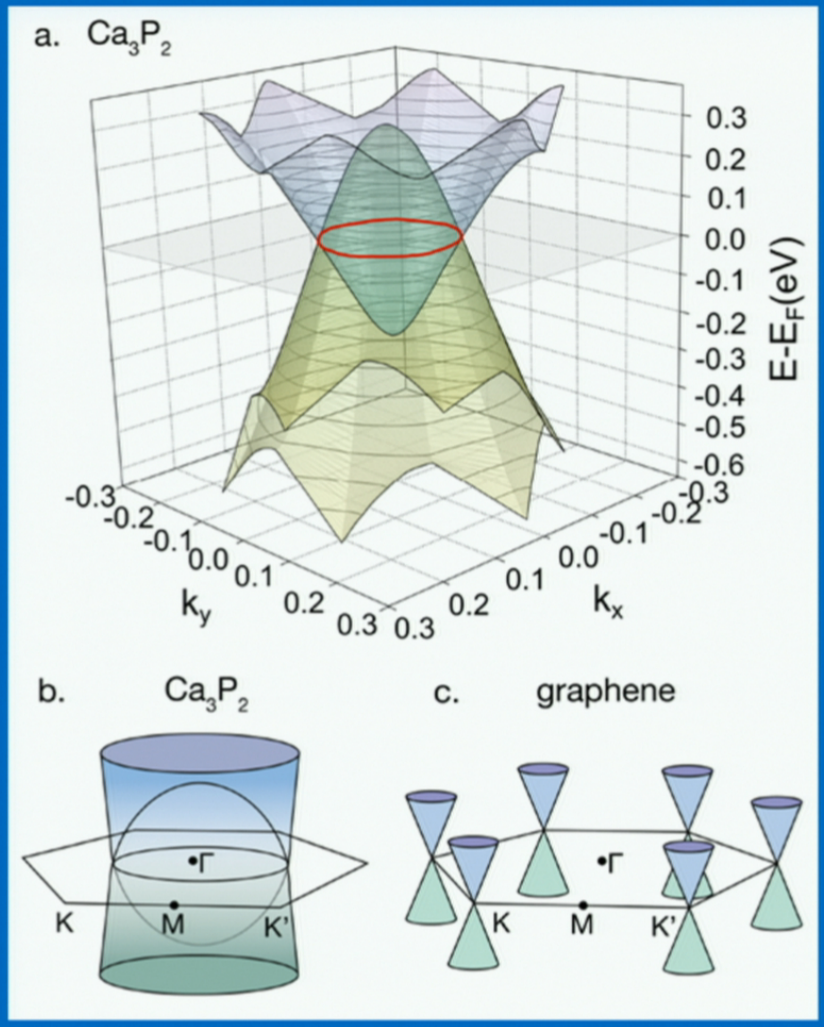
(releases
phosphine
In wet air,
which kills things)



From: $2\ Ca_5P_3H \rightarrow 3\ Ca_3P_2 + Ca + H_2$ oxidation of H, reduction of Ca

A *real* material
With a predicted
Dirac Ring





Conclusions

Chemistry has well developed formalisms to explain the stability of molecules and non-molecular solids. We are now using these chemical principles and others to try to "predict" new superconductors. Sometimes it works.

The layered dichalcogenides are conceptually simple systems that are definitely worth working on in spite of (and due to) their long history.

Because theory, experiment, and new materials discovery have developed in parallel, materials have had a significant impact in the development of geometric magnetic frustration as a field. I gave some or our examples.

Topological insulators and Dirac semimetals are new physics, and so its at first not obvious how new materials can contribute,
But in this case as well, materials, theory and experiment are developing together. There's a lot of "new materials" action here.

Finally, please talk with me about cases where a new material might help to develop or prove your ideas or theories.
Or for samples to study properties of interest to you.