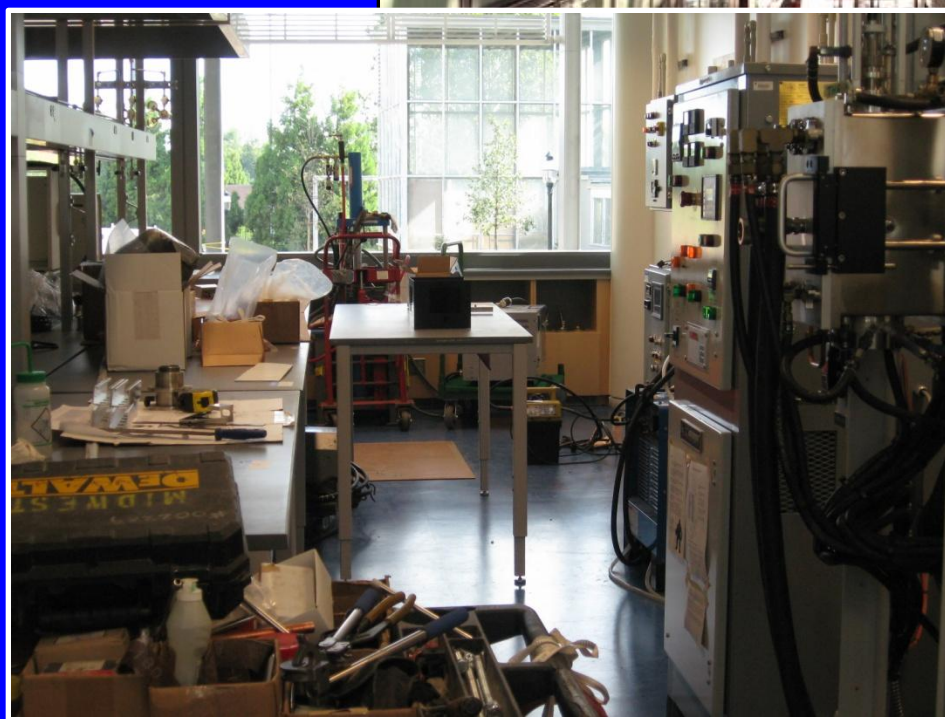# Stoichiometry, Structure, Bonding and the Electronic properties of Fe and Co pnictides

We have moved into a new lab



Bob Cava
with **Shuang Jia**

Funded by DOE BES
Solid State Chemistry

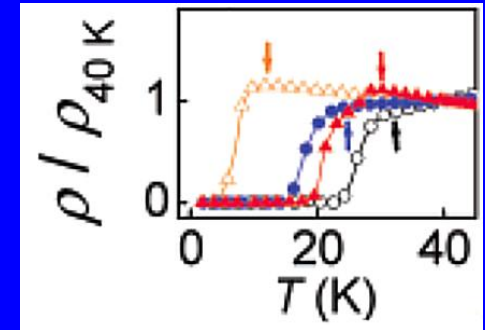# The iron arsenide superconductors
## first reported in January 2008

- Earlier Iron superconductors:
  - $U_6Fe$ ($T_c$ = 3.9 K),     1958
  - $Th_7Fe_3$ ($T_c$ = 1.9 K),   1961
  - $Lu_2Fe_3Si_5$ ($T_c$ = 6.1 K), 1980
  - $LaFe_4P_{12}$ ($T_c$ = 4.1 K),  1981

- But they are rare: magnetic states usually trump superconductivity.

  Fe usually makes magnets. Max Tc near 55 K

# The superconductors have layered crystal structures.
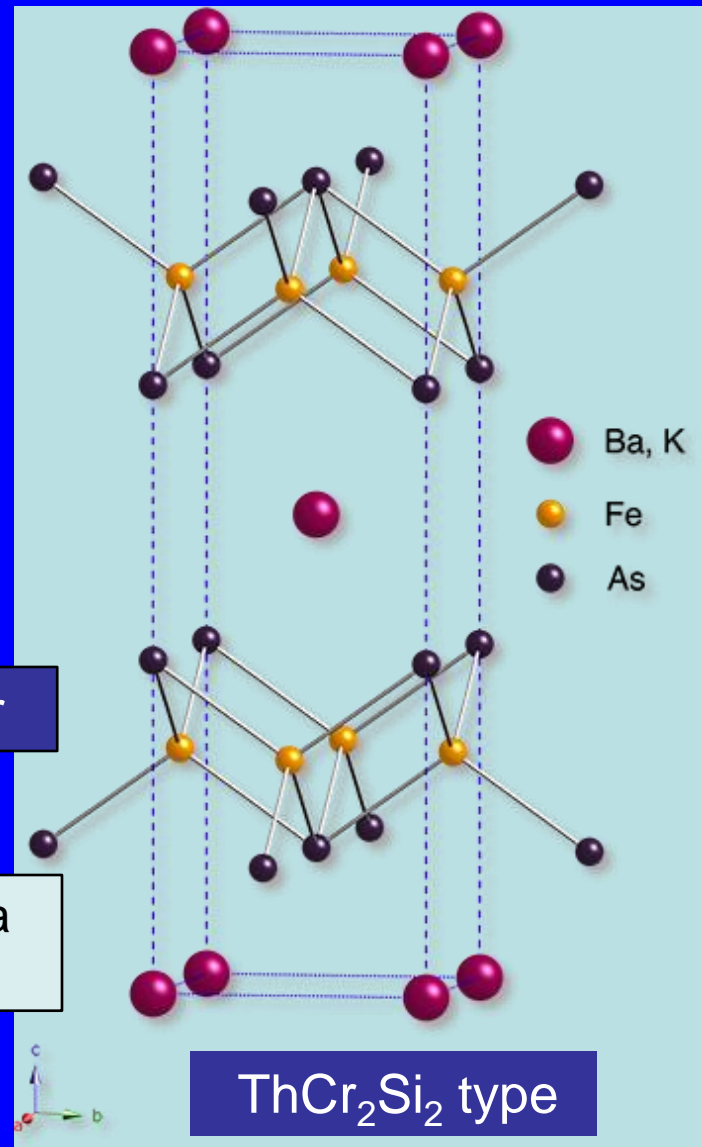
## Unusual oxypnictides were first,
## Then came $ThCr_2Si_2$-type phases



La

O

Fe

As

Ba, K

Fe

As
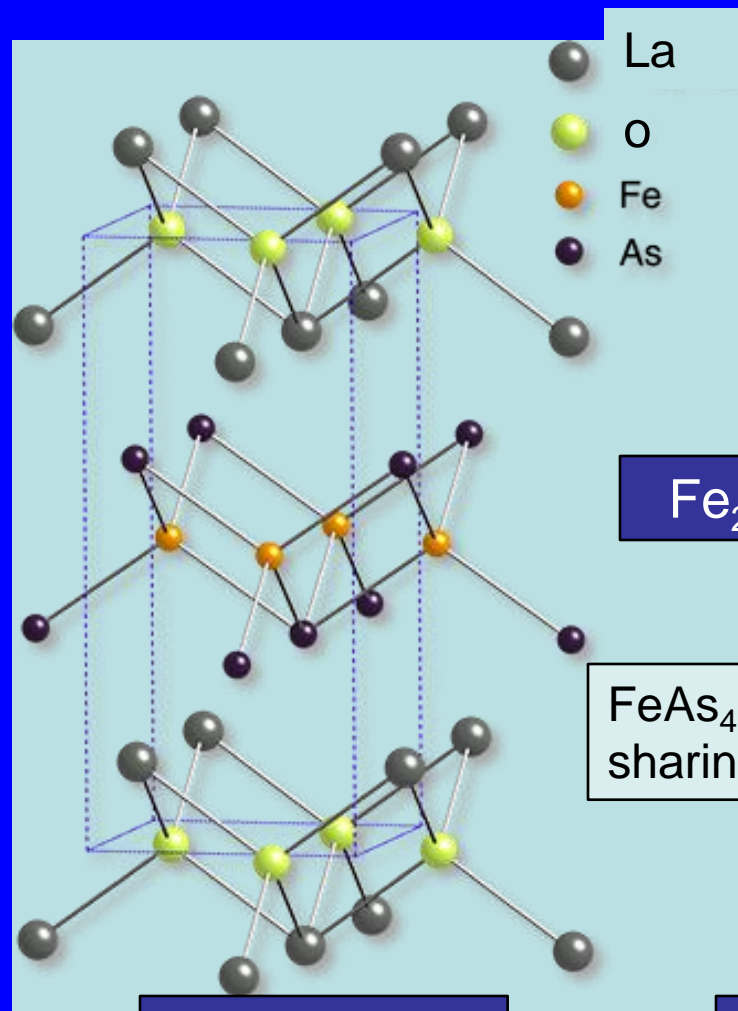
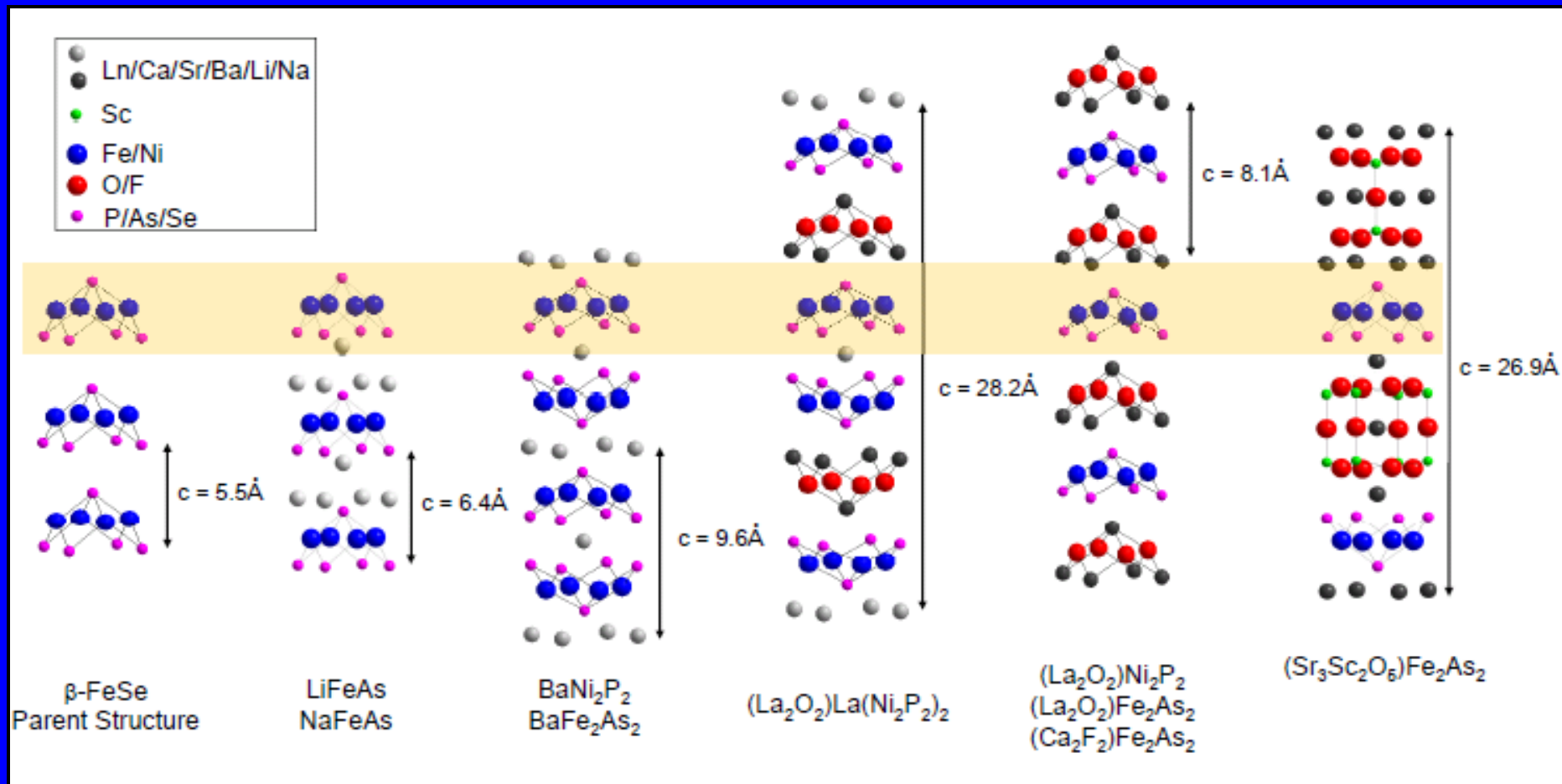$Fe_2As_2$ layer

$FeAs_4$ tetrahedra sharing edges

$ThCr_2Si_2$ type

oxypnictide

both types are difficult to make well

# The family of superconducting phases expanded rapidly, fueled by "Condmat posting fever":



## Square $M_2X_2$ layers (highlighted) + charge reservoir layers

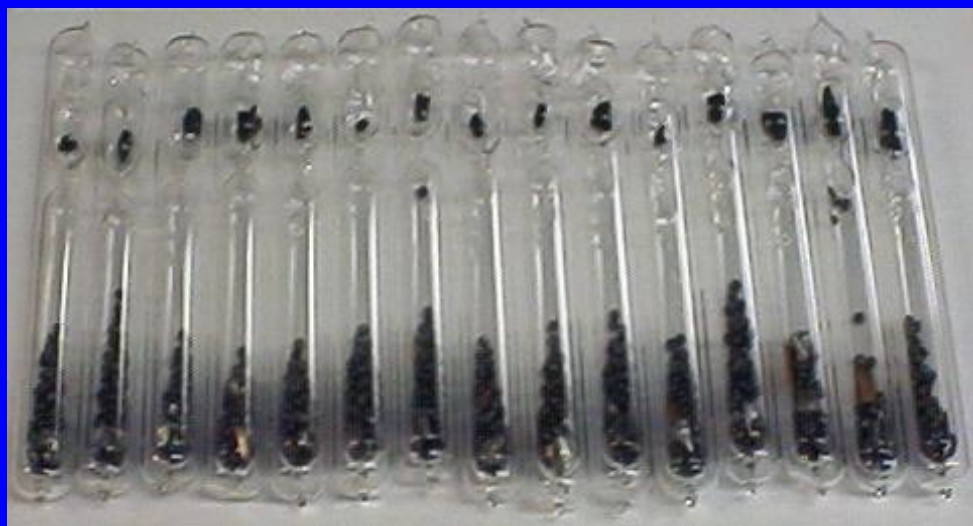Structural complexity beyond LaFeOAs does not improve the superconductivity

# An example of how we make these - FeSe



**High Density Carbon** (oxygen getterer)

**Double-Sealed** dried silica

**Polished Iron & Selenium Pieces**

(both sealed under vacuum)

# For the physics community:
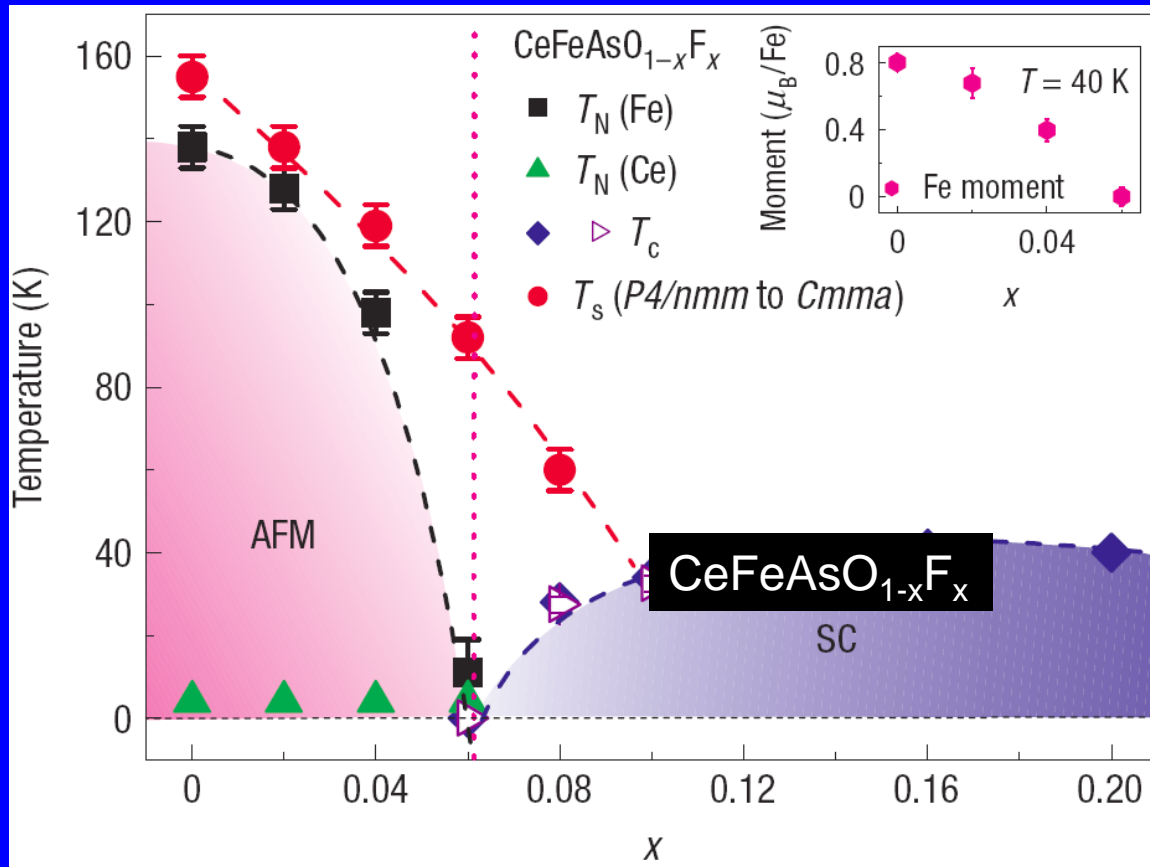


How does magnetism evolve into superconductivity?

Is the superconductor itself exotic or conventional?

Why is Tc so high?

For the materials scientist – how do the structure and chemistry determine the properties ?

The superconductors are based on Fe-As, Fe-Se, and Fe-P

And except for FeSe include an electropositive element …e.g.  La, Ba, Li



While not clearly ionic there are significant differences in electronegativity among constituent atoms  e.g. in $BaFe_2As_2$   and LaFeAsO
So they are not clearly intermetallic either.

# Do structure and chemistry actually matter?

To see, we are going to look at some non-superconducting analogs.

Many of the superconductors have the $ThCr_2Si_2$ structure:

# ThCr$_2$Si$_2$



Si

Cr$_2$

Si

Th

Ba, K
Fe
As
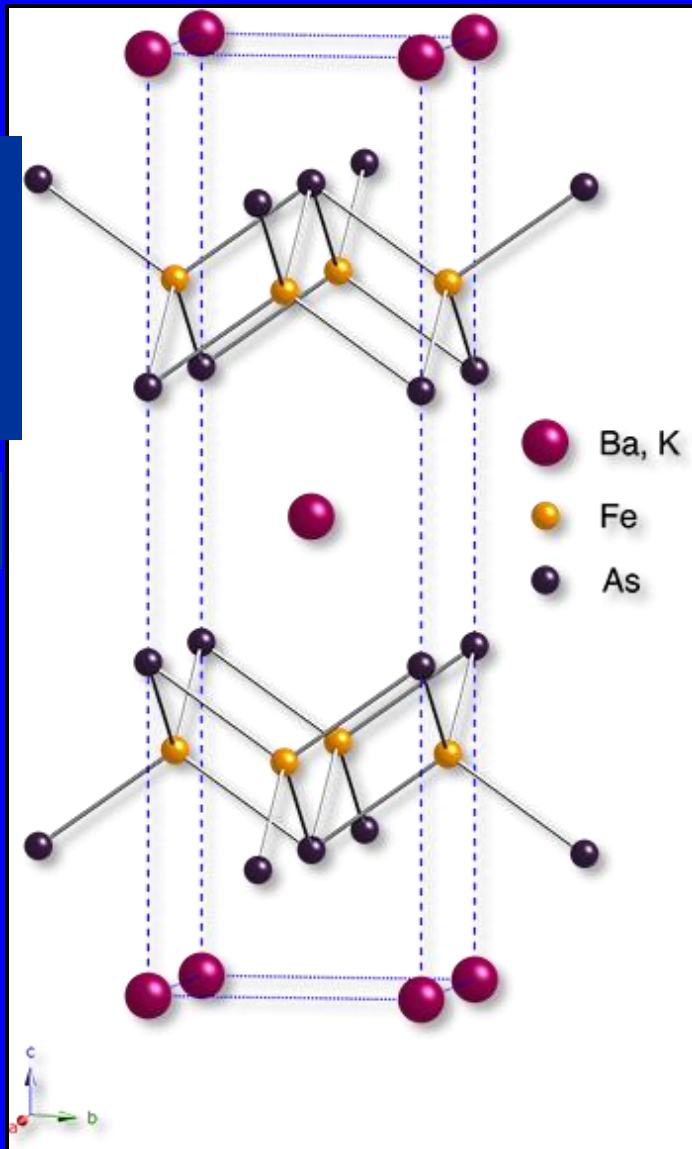
The most common ternary intermetallic structure type

forms for borides, aluminides, gallides, silicides, germanides, stannides, phosphides, arsenides, antimonides, sulfides, and selenides.

It usually lives in the perfect, happy world of intermetallic physics:

- Very interesting properties
- Very simple structure
- Chemistry doesn't matter

But Roald Hoffman (Nobel prize in chemistry) noticed in the 1980s that $AM_2P_2$ phosphides are a special case:

If the large A atom is not large enough, you can get P-P bonding between the $M_2P_2$ layers
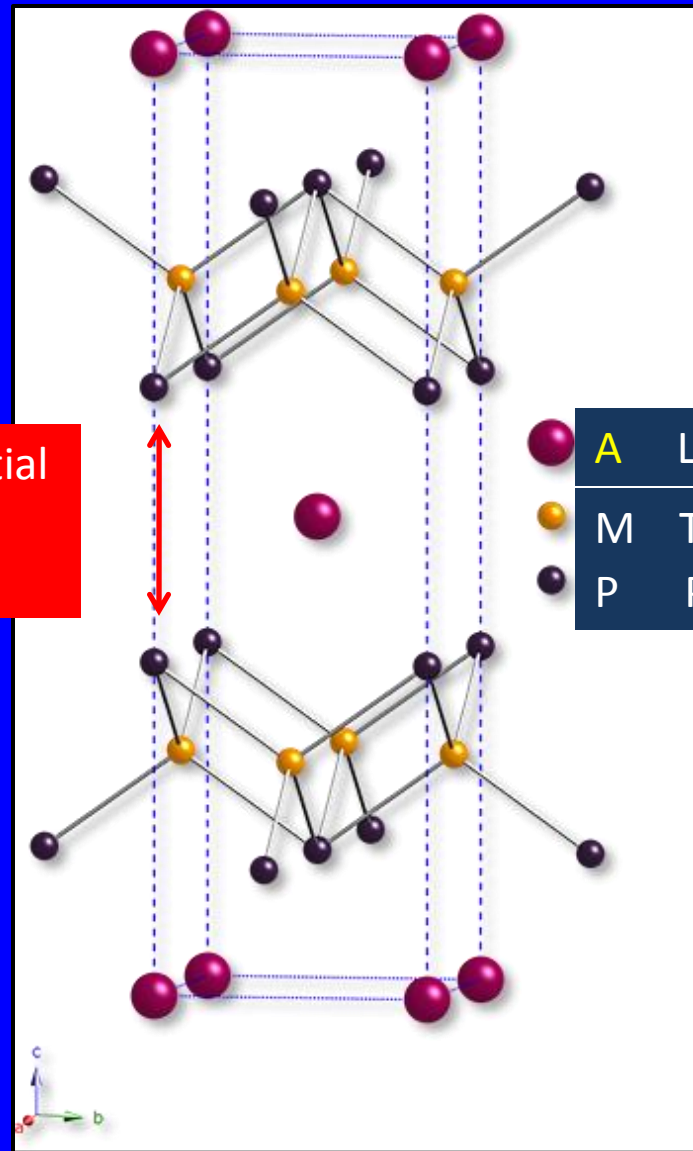
In fact you can have $P_2^{3-}$ for large A atoms and $(P-P)^{4-}$ for small A atoms



Potential P-P bond

| A | Large element |
|---|---|
| M | Transition element |
| P | Phosphorus |

# Brief Tutorial on bonding and antibonding bands and dimer formation:

Antibonding orbitals

$\sigma^*$

Add 6e  no dimer

Add 4e still have dimer

P

P

Bonding orbitals

$\sigma$

$P_2$

isolated

dimerized

$P^{3-}_2$

$(P_2)^{4-}$

P – P distance tells you what you have
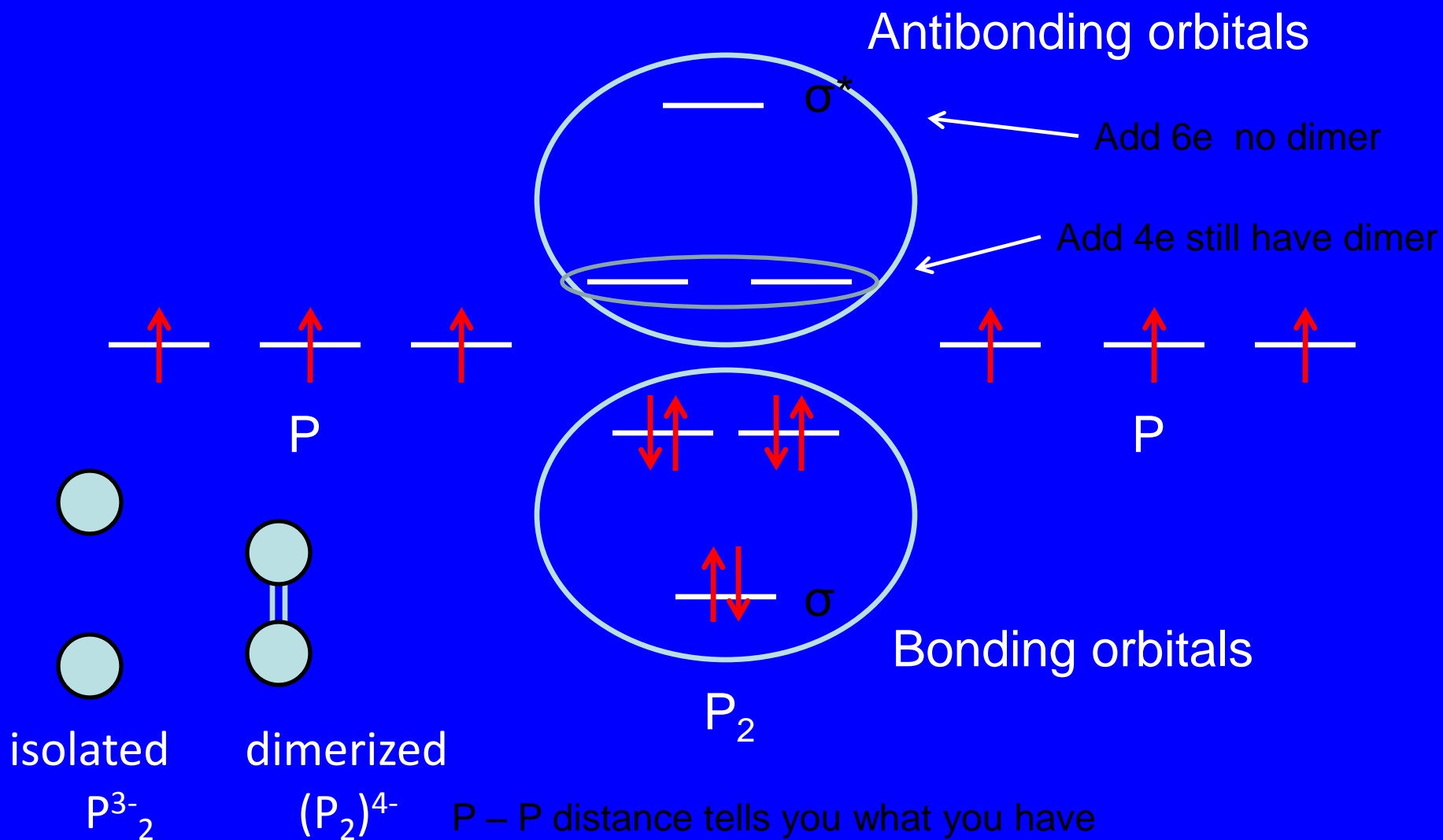
# Hoffman's observation about the P-P bonding explains some surprising structural characteristics of $AM_2P_2$ compounds

But no property implications until recently

Then in 2009 $CaFe_2As_2$ was found to superconduct under pressure near a structural phase transition
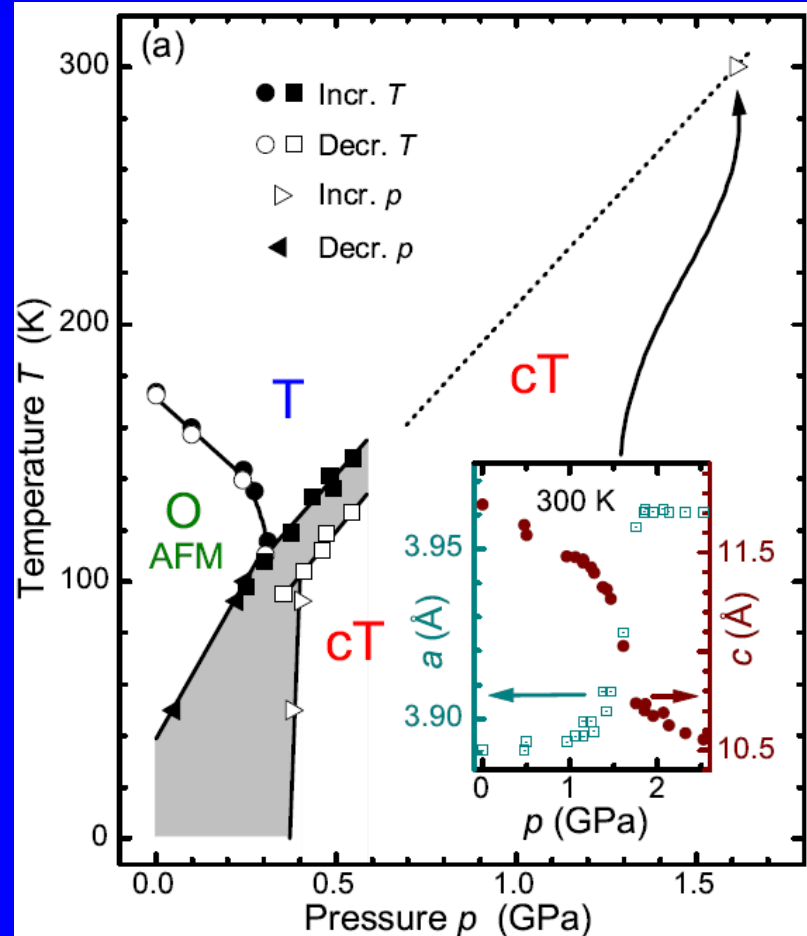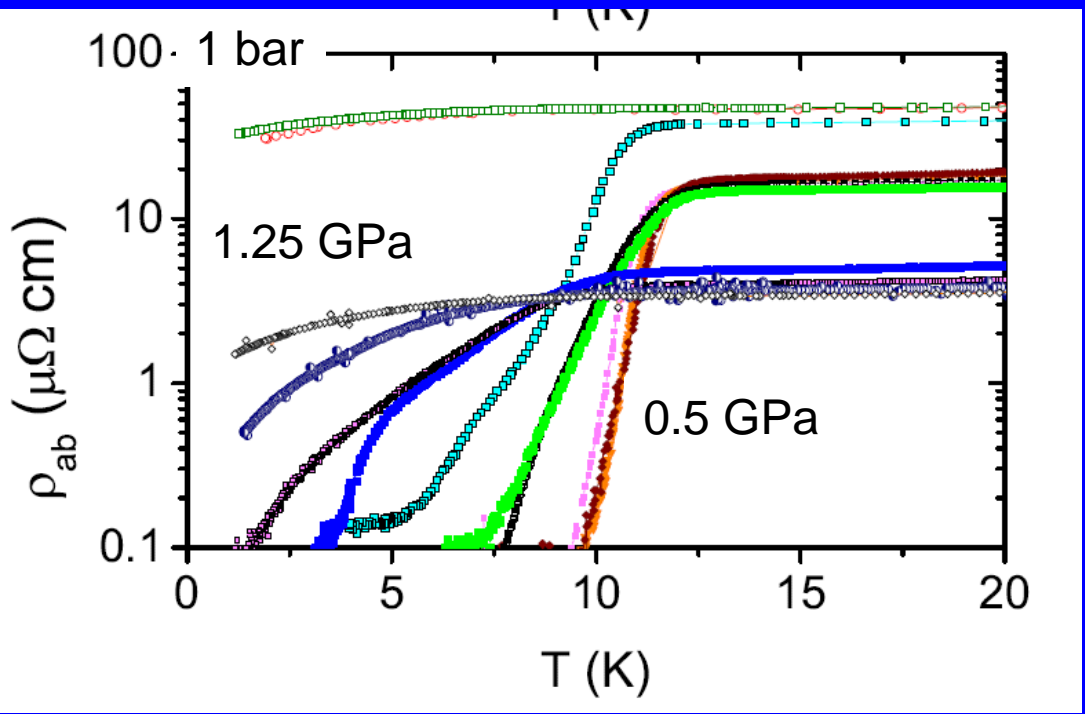


T = tetragonal, cT = collapsed tetragonal

From Los Alamos and Ames Laboratory

Physicists concentrated on the pressure dependent properties

But a chemist can ask - Does the formation of As-As bonds drive the collapse?

Can we use "chemical pressure" instead of applied pressure to control the crossover from the non-bonded to the bonded state?
Yes, in the related phosphides



Ba, K
Fe
As

$c$

$a$
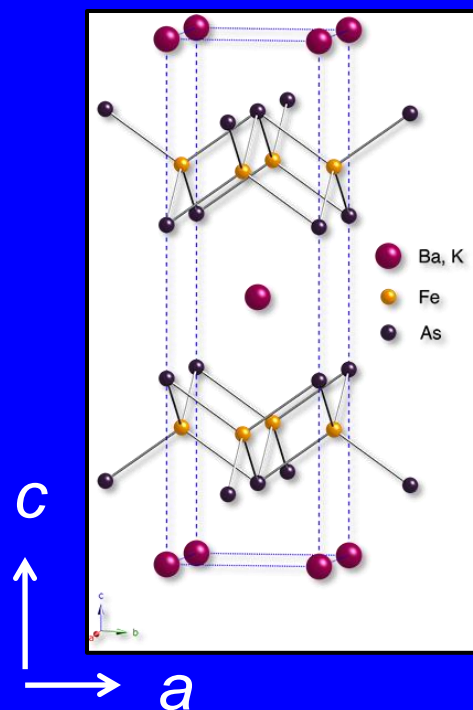
$SrCo_2P_2$ and $CaCo_2P_2$ are anomalous :

$SrCo_2P_2$   $a =$  3.79    $c =$  11.6

$CaCo_2P_2$   $a =$  3.85    $c =$   9.6

- The $a$ axis **grows** on going from Sr to Ca, and there is a large decrease in $c$.

Does a non-bonded $P^{-3}_2$ to bonded dimer $P_2^{4-}$ transition occur in the $Sr_{1-x}Ca_xCo_2P_2$ solid solution?   Do the properties change?

Ca$^{2+}$ is much smaller than Sr$^{2+}$
in the Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ solid solution...
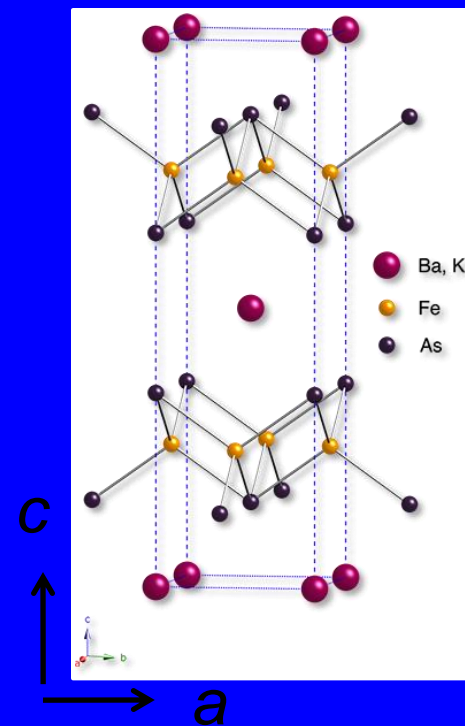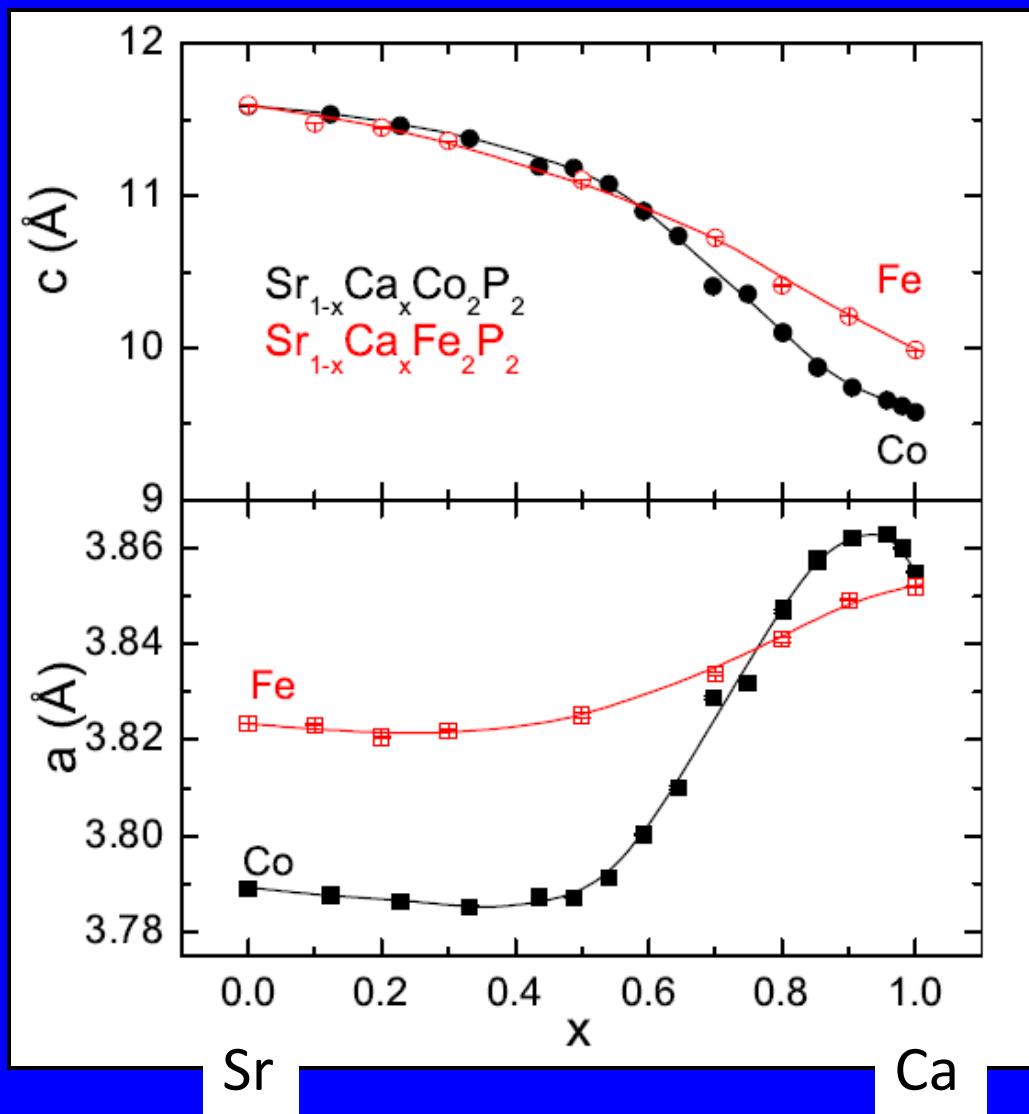




It should be a simple mixing of different size spheres on one site. so linear shrinking in all directions is expected

But it isn't .

Similar but less pronounced for Fe

# The P-P bond length changes continuously



Crossover between $P_2^{6-}$ and $(P_2)^{4-}$ (Hoffman)
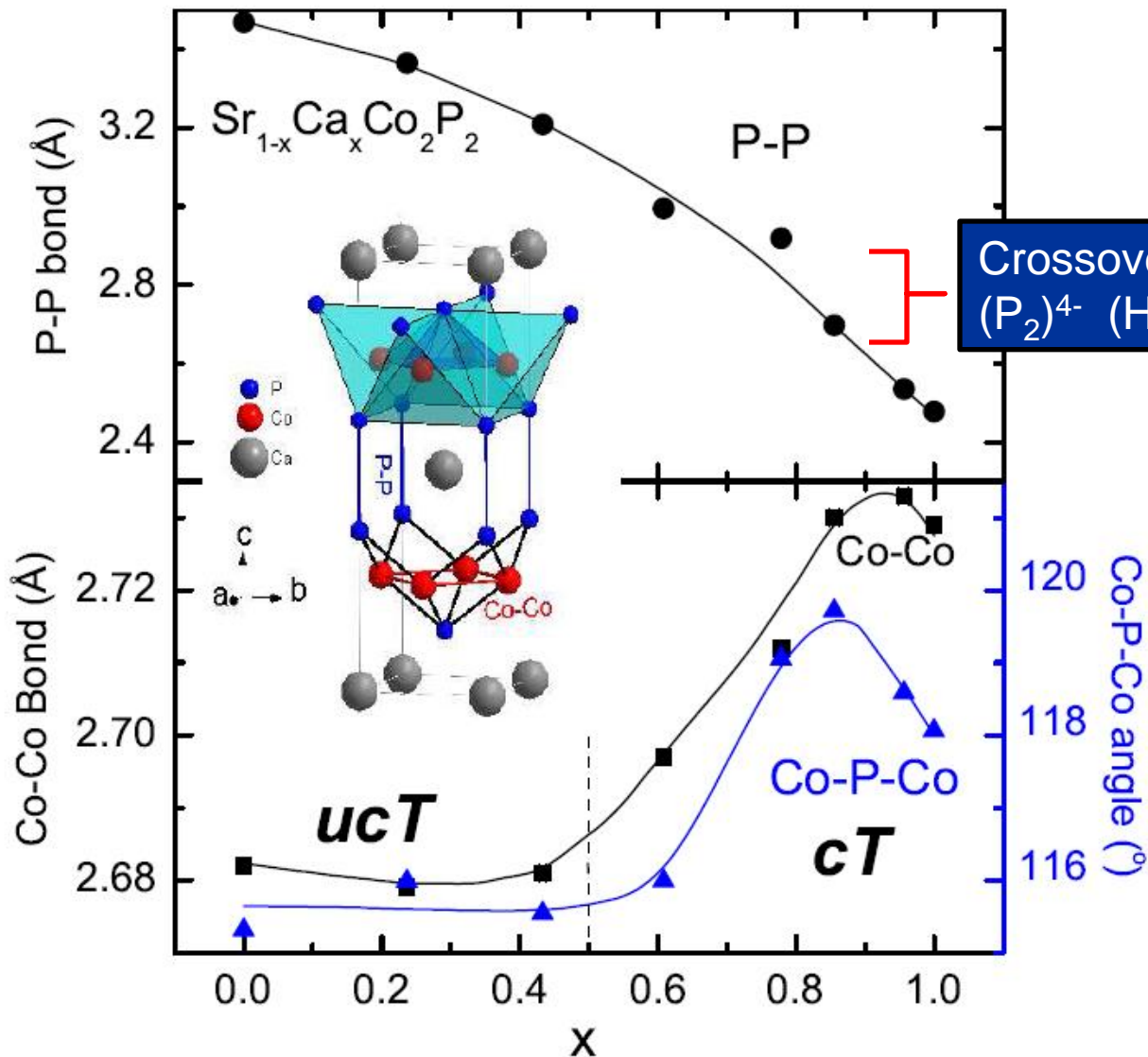
But the $Co_2P_2$ layer responds nonlinearly

In-layer bond angle changes. Co-P bond length does not

# The magnetic properties change dramatically across the series:
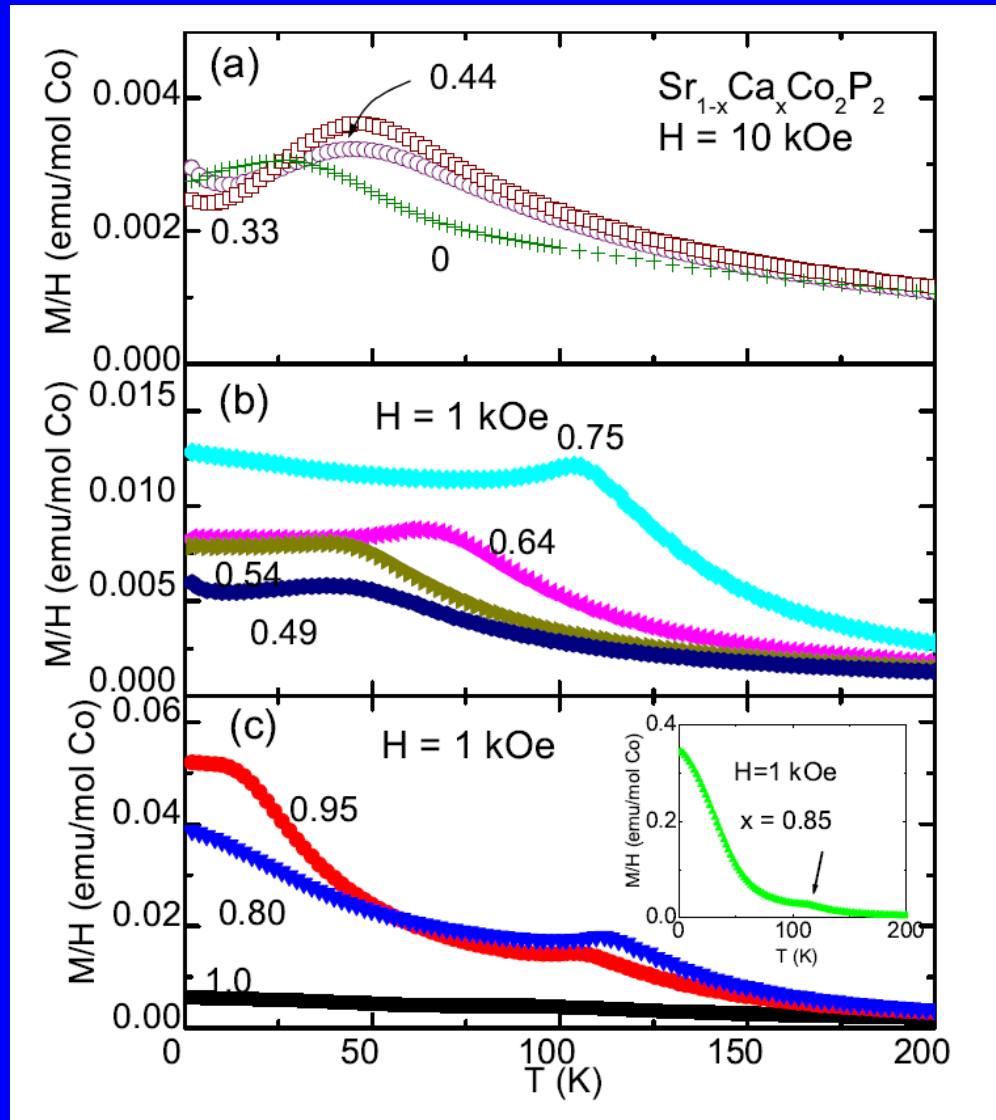


SrCo$_2$P$_2$ is paramagnetic

in between there is
a ferromagnet

CaCo$_2$P$_2$ is antiferromagnetic

# Summary of the electronic properties



Θ  strength of near neighbor magnetic interactions

μ magnetic moment per Co

χ magnetic susceptibility

γ ~effective mass of charge carriers
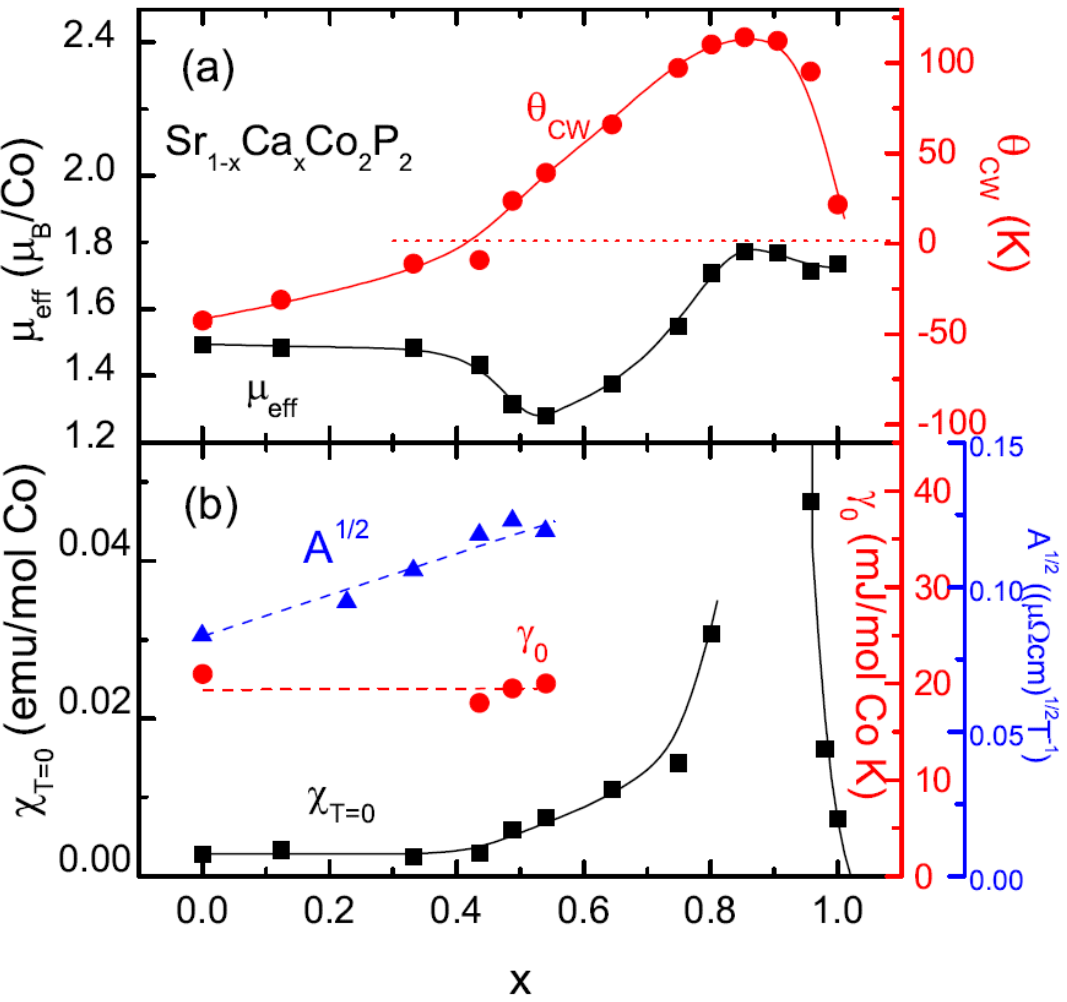
They follow the lattice collapse
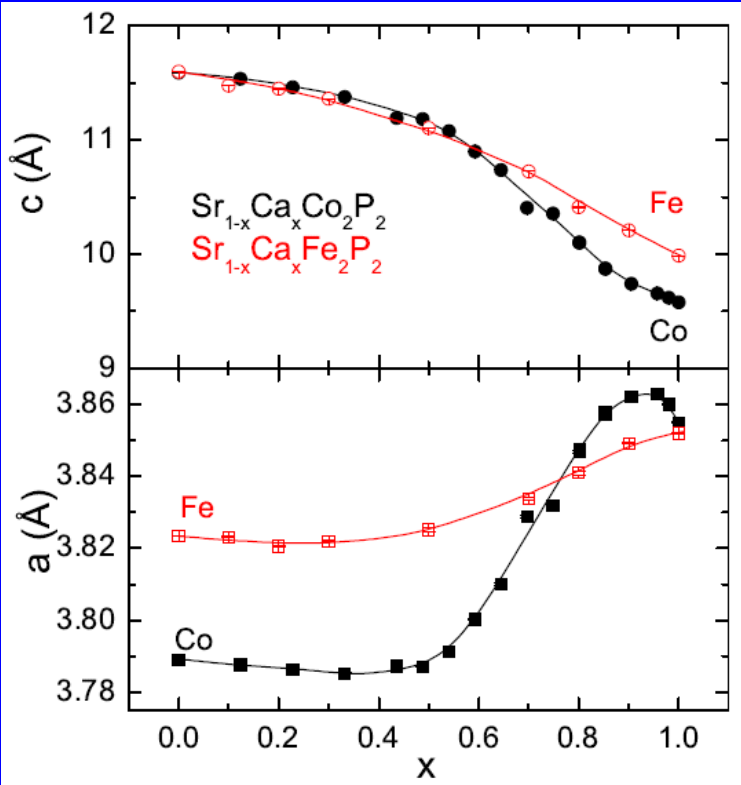
# Ca for Sr in $Sr_{1-x}Ca_xCo_2P_2$ Should be an isoelectronic substitution
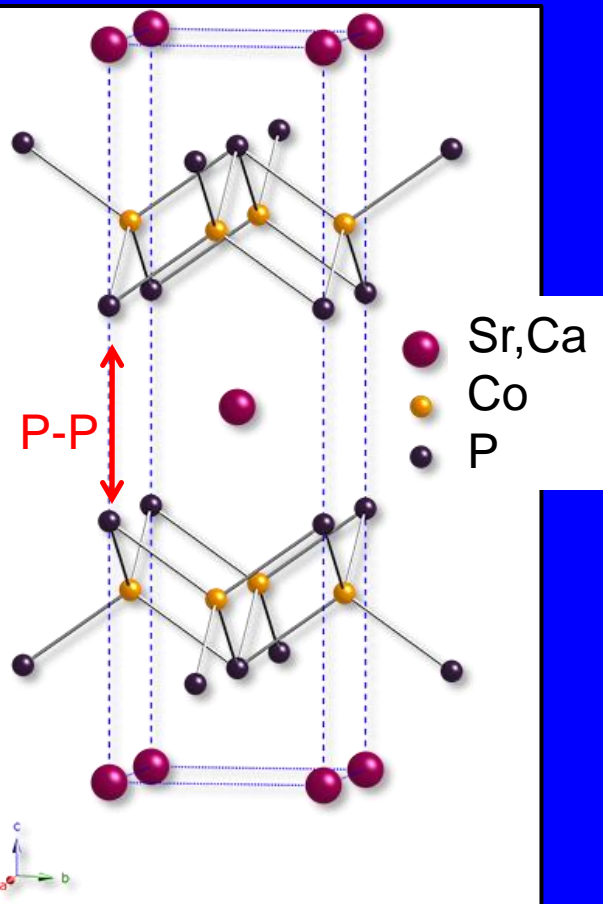
But is a rare (unique?) example of electronic doping through titrating an X-X bond through chemical pressure – Creating the dimer decreases the effective oxidation state of the P and thus the $d$-band filling



P-P

Sr,Ca
Co
P



$Sr_{1-x}Ca_xCo_2P_2$

$P_2^{4-}$

$cT$

$P_2^{3-}$   $ucT$

T (K)

100

50

0

NFFL   ?   AFM   FM   AFM

0.0   0.2   0.4   0.6   0.8   1.0

x
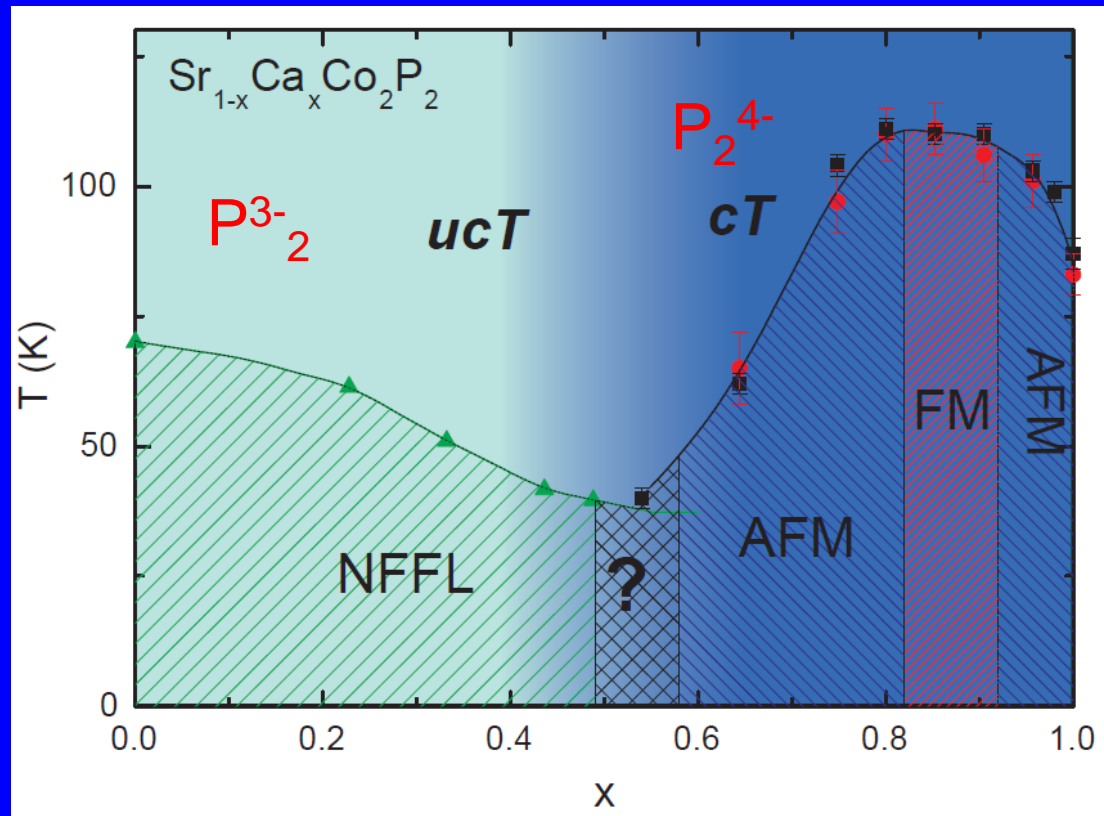
*cT, ucT* = collapsed, uncollapsed tetragonal; NFFL nearly ferromagnetic Fermi Liquid
AFM, FM = antiferromagnet, ferromagnet

Lets look a little deeper into the bonding picture for P-based ThCr$_2$Si$_2$ type compounds:
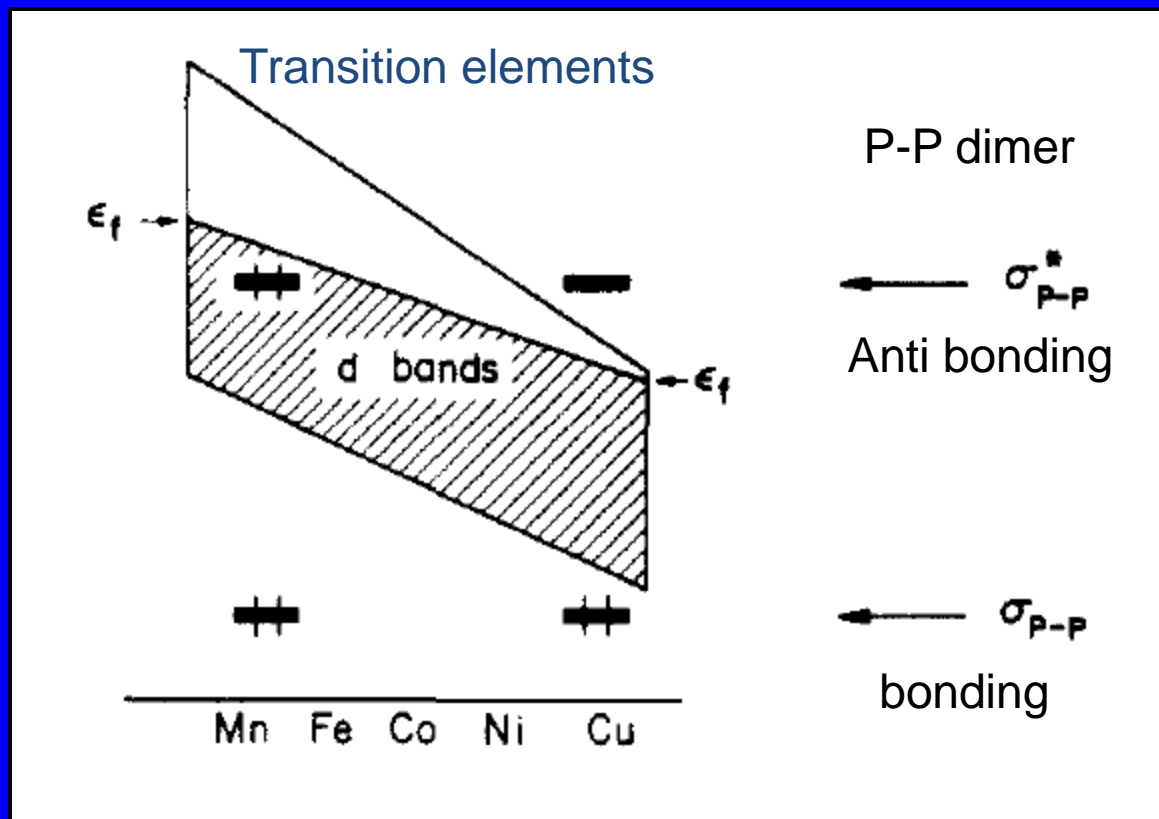


Bonding and antibonding states of the P-P dimer straddle the *d*-band manifold, which changes in energy and filling across the 3*d* series

From the original Hoffman and Zheng paper J. Phys. Chem. 1985

$Sr_{1-x}Ca_xCo_2P_2$ shows dramatic changes in P-P bonding induced by changing the distance between $Co_2P_2$ layers. Something should also happen when you cross the 3*d* series with everything else held constant
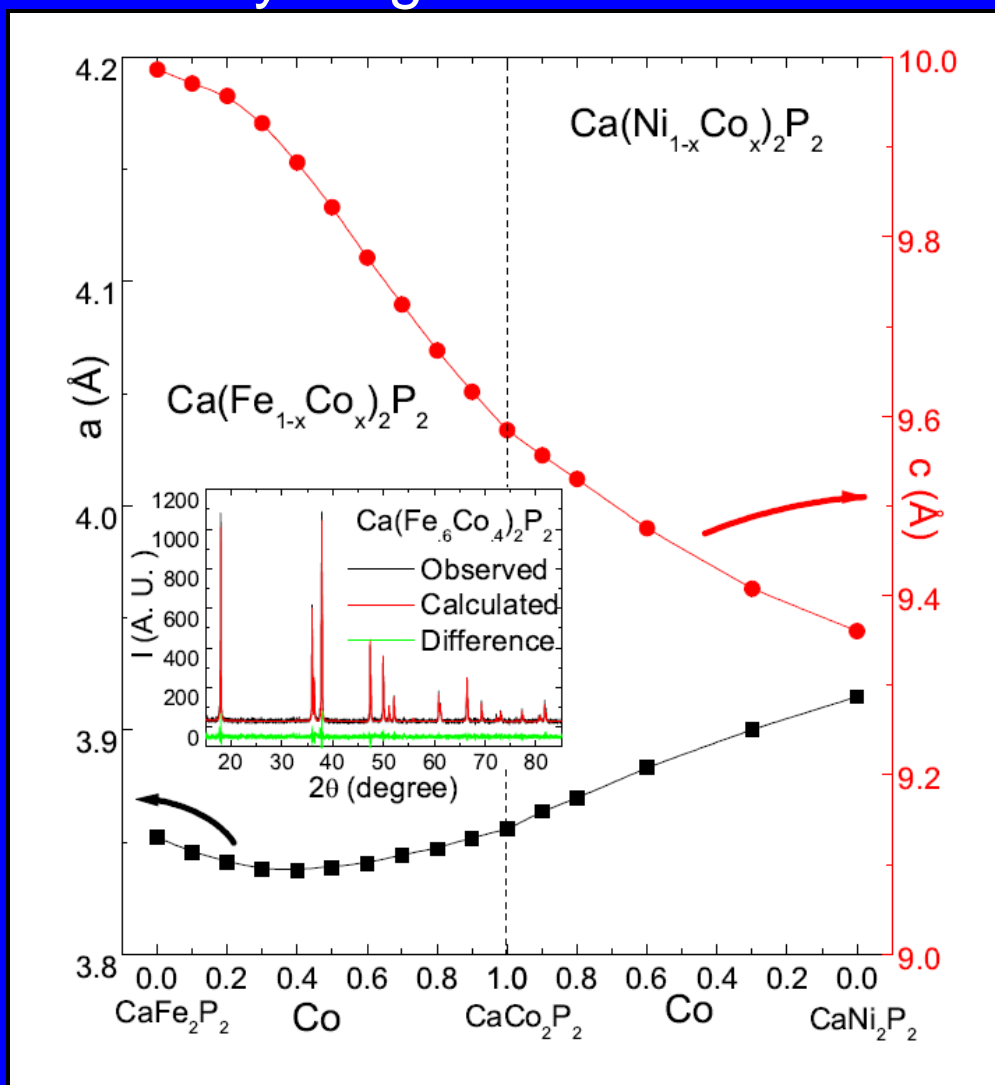


Consider $CaM_2P_2$

Test the Hoffman Picture on going from Fe to Co to Ni

In a simple picture the size of the ions decreases so unit cell parameters should decrease. They don't.

Can you see where the P-P antibonding band begins to empty?
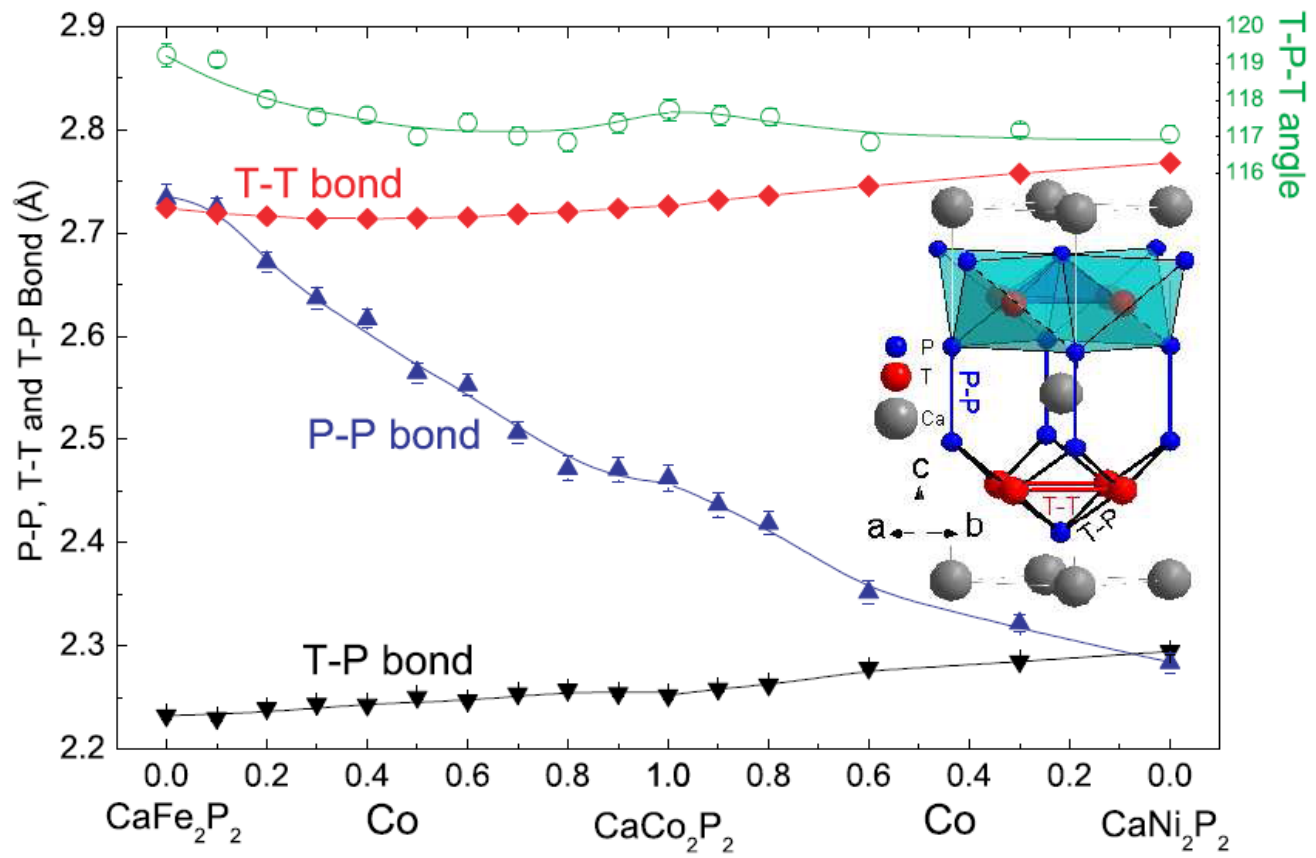
Variation of internal Parameters across the series

By far, the primary change on crossing From Fe to Co to Ni

is the bond strength in the P-P dimer!

The picture works –
The antibonding band becomes more empty as you cross the 3*d* series, so the P-P bond strengthens
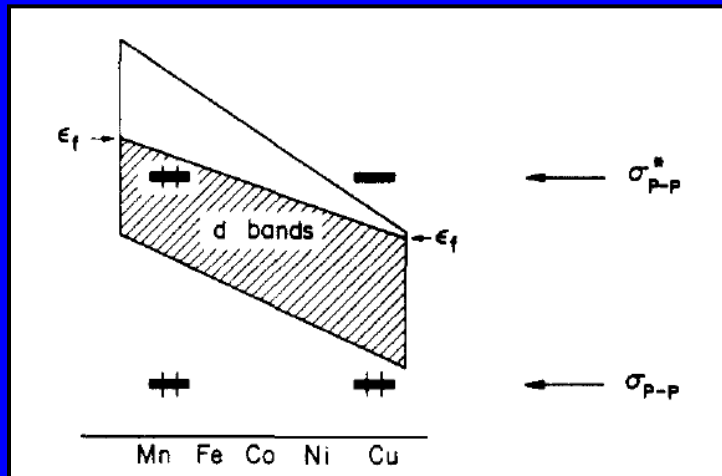
There is a corresponding change in properties.

# So… what drives this electronic phase diagram?
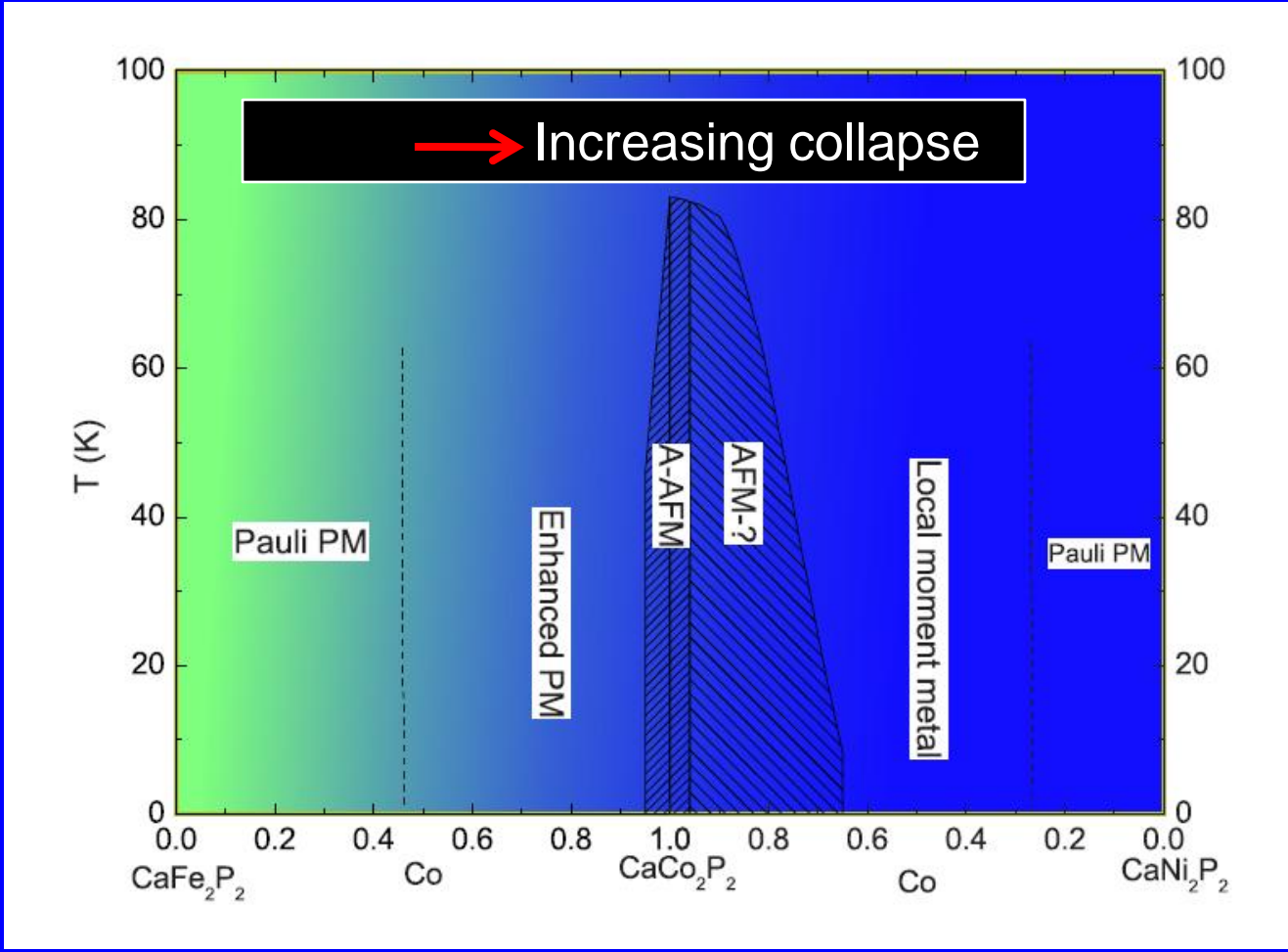


The usual picture is that a rigid-band-like
*d*-band filling
should rule

But for these materials, changing the effective charge of the P-P dimer is the primary effect of changing transition metals from Fe to Co to Ni.

This system straddles the boundary between
the physics and chemistry views of electrons in solids .

# How far can you take this?

Ge has similar orbital energies to P, but is minus one electron - thus the dimer antibonding band is more frequently empty and germanides have strong Ge-Ge bonding

so $SrCo_2Ge_2$ is strongly collapsed but $SrCo_2P_2$ is uncollapsed

The $SrCo_2(Ge_{1-x}P_x)_2$ solid solution undergoes a cT to ucT transition

The structural phenomenology Is somewhat different
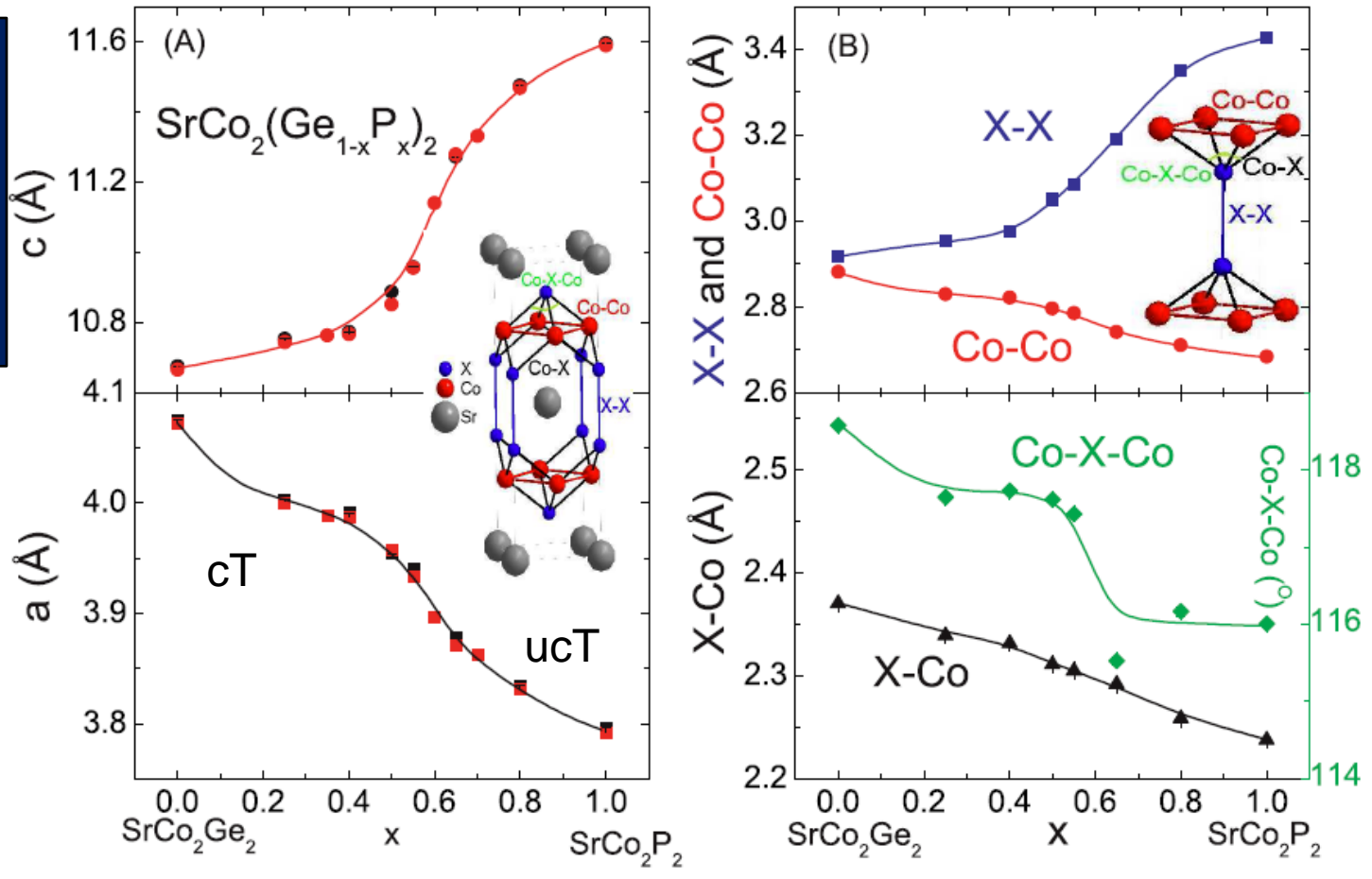
# Neither SrCo$_2$Ge$_2$ nor SrCo$_2$P$_2$ is magnetic

## But in the middle of their solid solution - Ferromagnetism appears
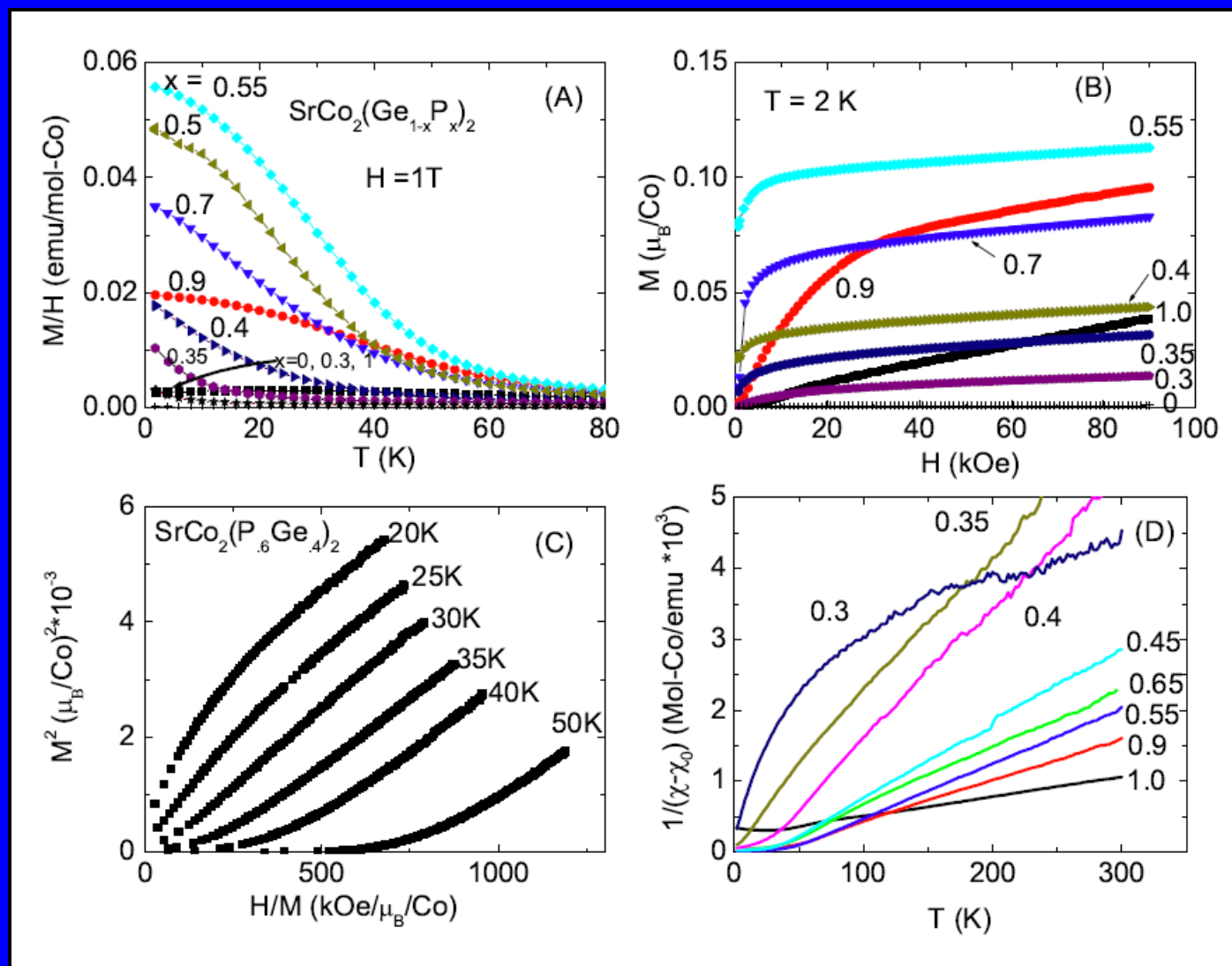
But the Tc for compositions where Ferromagnetism first appears

is very close to absolute zero
and the specific heat shows exotic behavior

x = 0.35
is a
Quantum
Critical
Point
(QCP)
Very rare!

i.e. mixing two vegetables together can sometimes give you caviar instead of guacamole.

This is a dimer-breaking induced quantum critical point.

The only one of its kind.
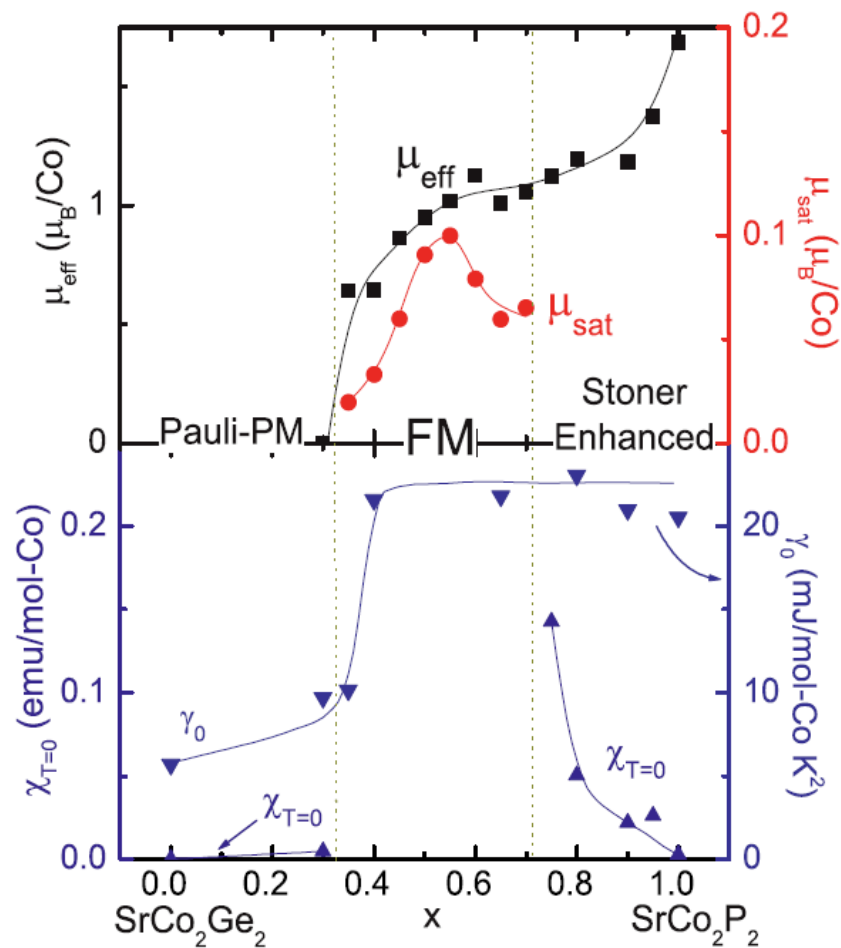
# Topological Insulators
## a new electronic state of matter



Confining electrons to 2D often leads to dramatic effects

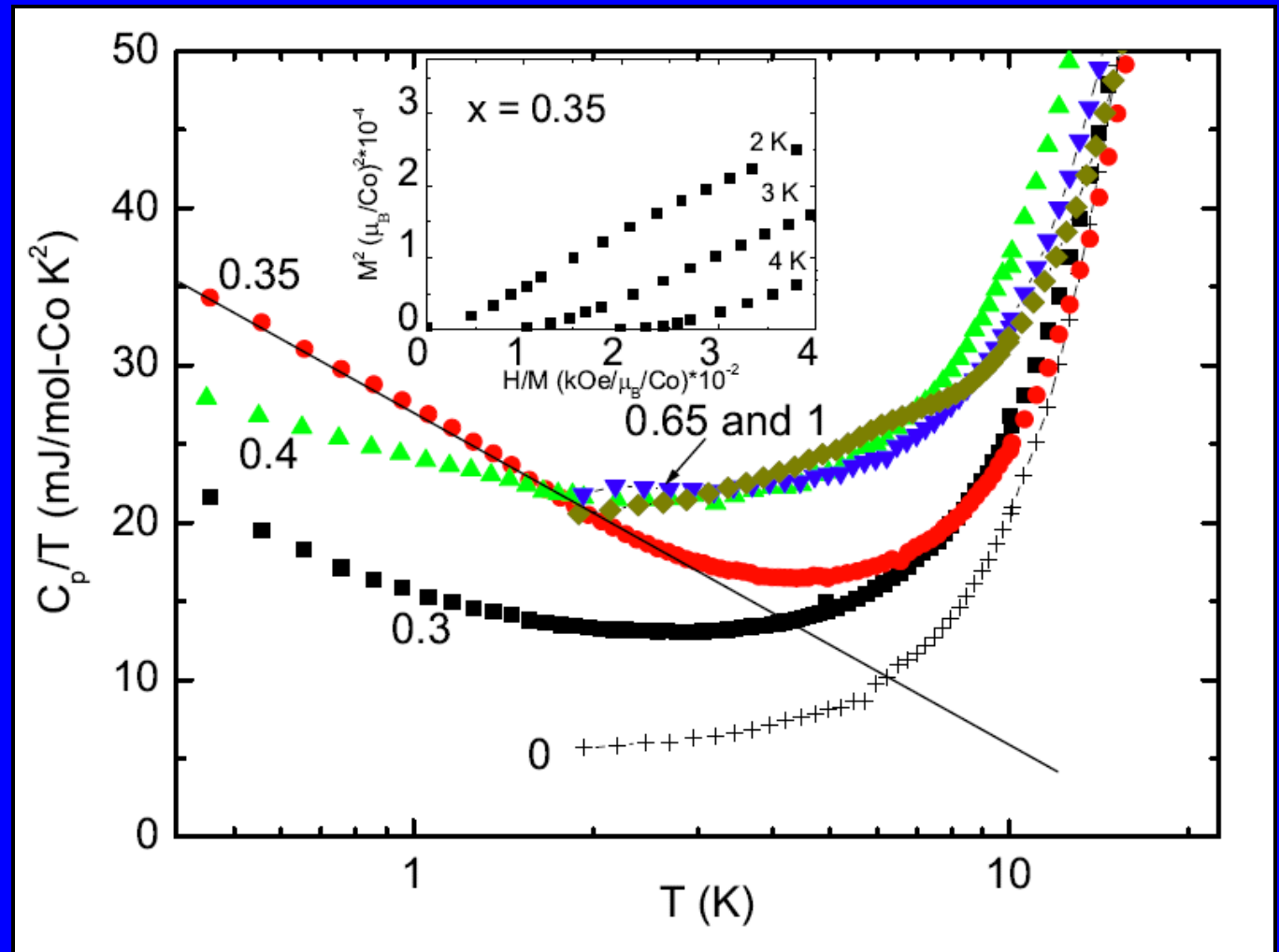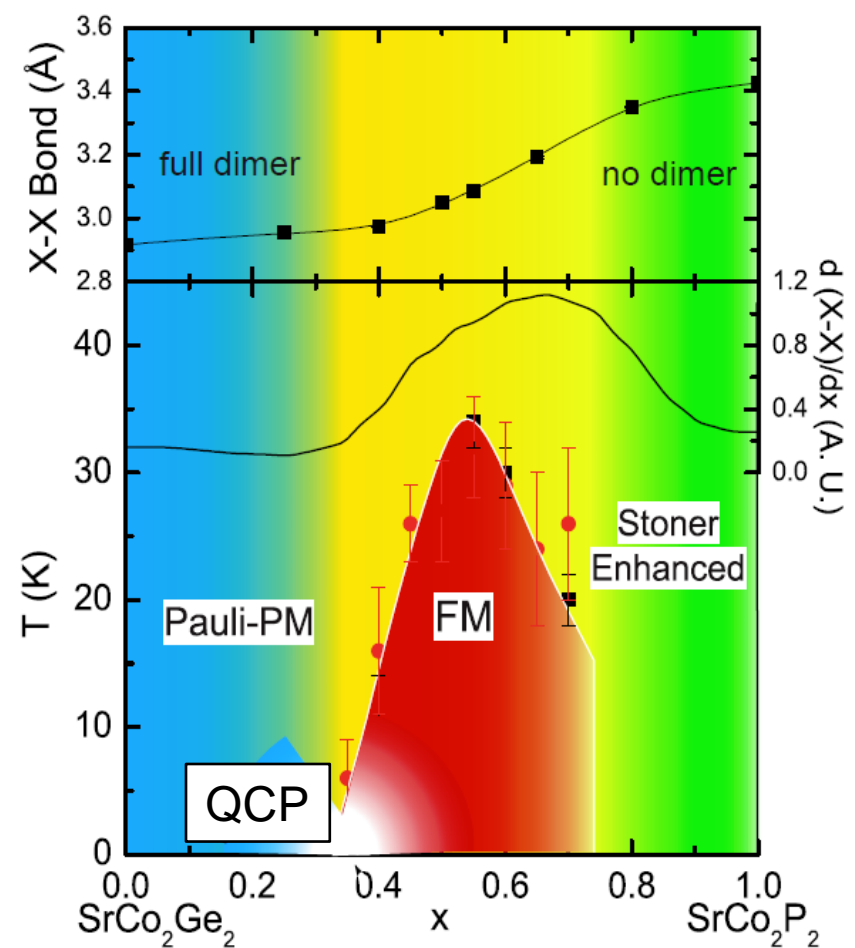e.g. charge density waves and superconductivity in bulk materials

Truly exotic "quantum effects"  like fractional electron charge
had only been seen in artificial materials:
i.e. III – V (In,Ga)(As,P) heterostructures several atomic layers thick

Bulk materials were never 2D enough to show these most exotic effects, but…

Enter graphene – bulk material that can be  shaved in the lab
into very thin layers a few atoms thick
– exotic physics appears

Inspired, theorists predict an exotic state for electrons
on the surface of specific bulk crystals with strong spin orbit coupling (SOC)

The SOC (absent in graphene) opens a band gap
and acts as an effective magnetic field

A  very rare case of a *prediction* of a *specific* new effect in a *specific* material

Some of the predictions:

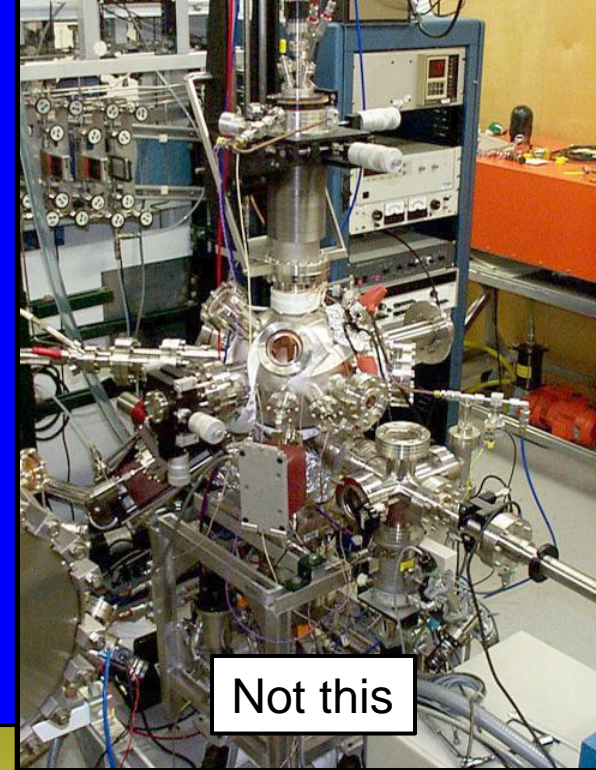E goes as $k$, not $k^2$, i.e. states are photon like!  (Mass ~ $d^2E/dk^2$ ( =0 ))

Electronic states on the surface are chiral –
Spin direction and electron momentum are coupled

States are immune to scattering by impurities – "protected"

Princeton Group: M.Z. Hasan   ARPES,
R. Cava and Y.S. Hor, Materials,
A.  Yazdani STM, N.P. Ong  Transport,
NSF MRSEC Program

Made with standard furnaces

Not this

Bi and Sb are both semimetals –

near $Bi_{0.9}Sb_{0.1}$ a band gap opens as energies of *s* and *p* derived orbitals invert
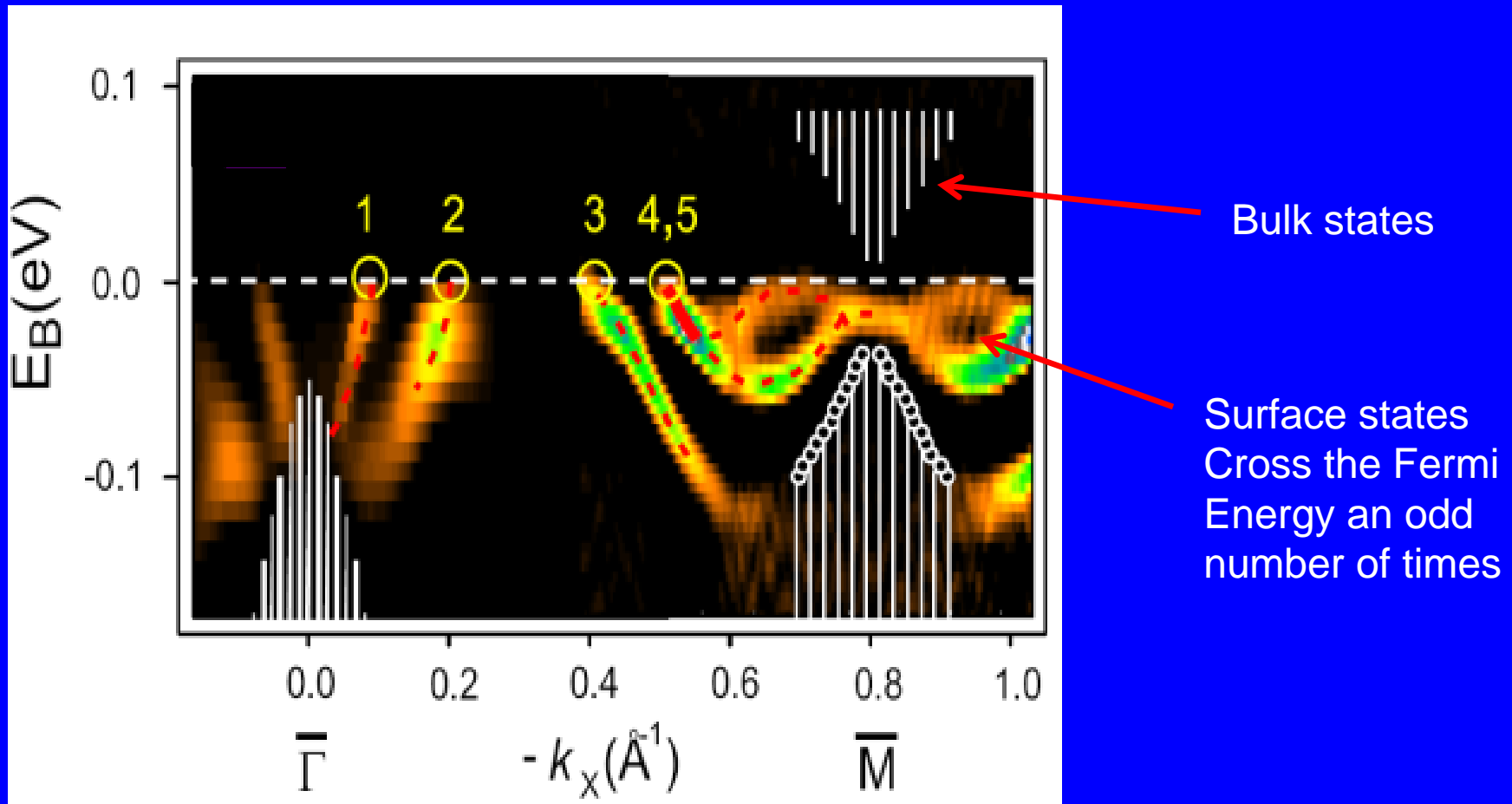
This is the material in the Kane, Mele, Fu prediction

You are looking at topological surface states

– they exist at room temperature in air.

Single Crystal of $Bi_{0.9}Sb_{0.1}$

Our initial work –
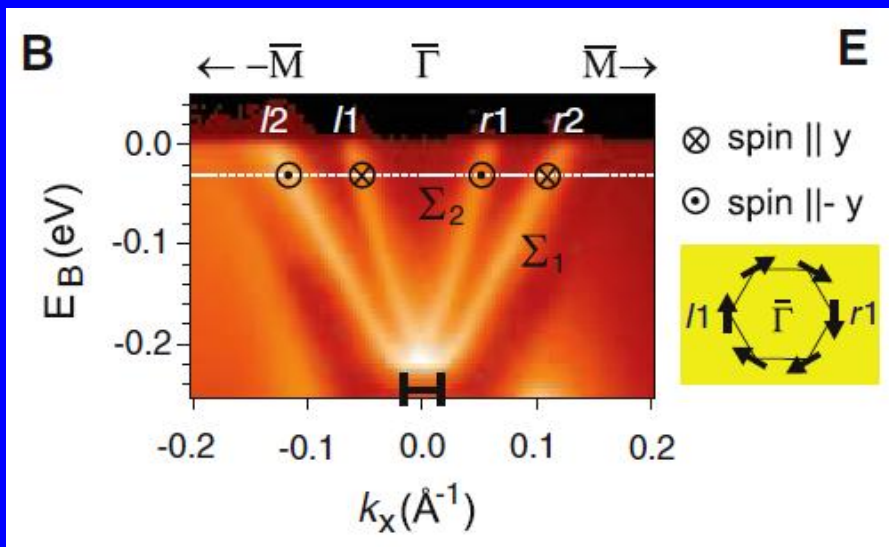Angle Resolved PhotoEmission Spectroscopy
discovery of topological surface states on $Bi_{0.9}Sb_{0.1}$



Bulk states

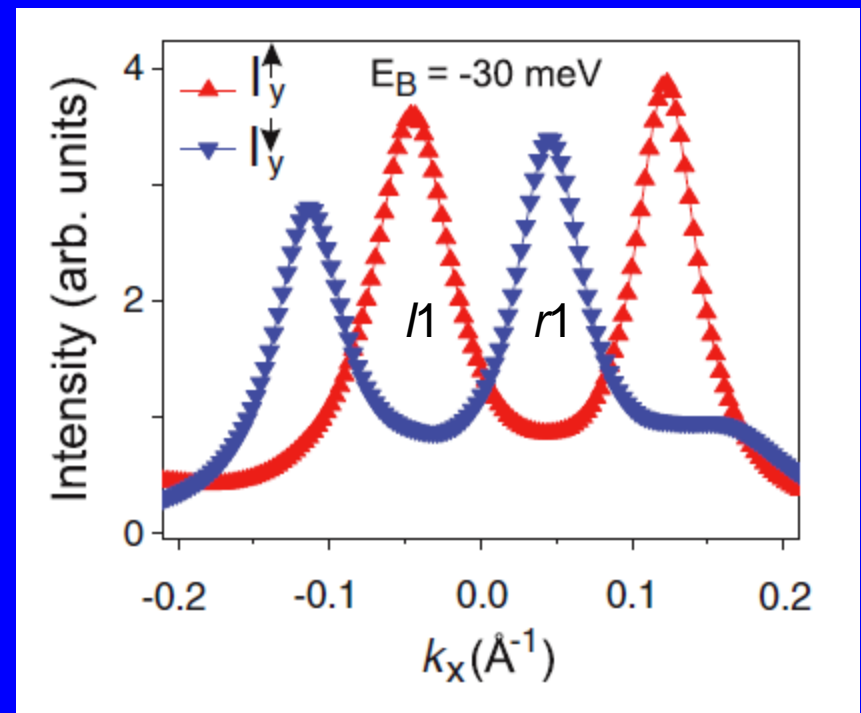Surface states
Cross the Fermi
Energy an odd
number of times

# The Spin chirality of the surface states is one of their novel characteristics:

Hasan used spin selective ARPES to demonstrate the chirality:

Detectors only see one spin direction:



The surface states near the gamma point on the elemental Sb 001 surface
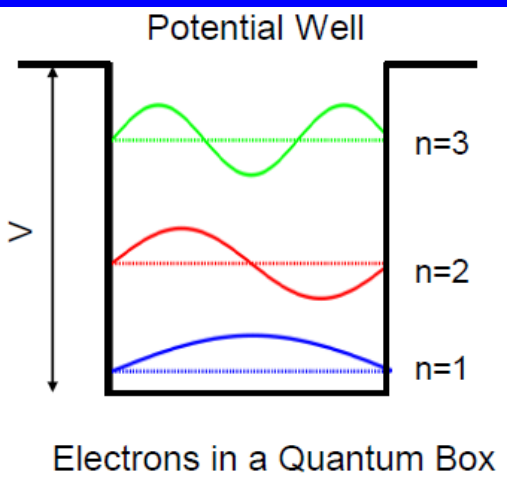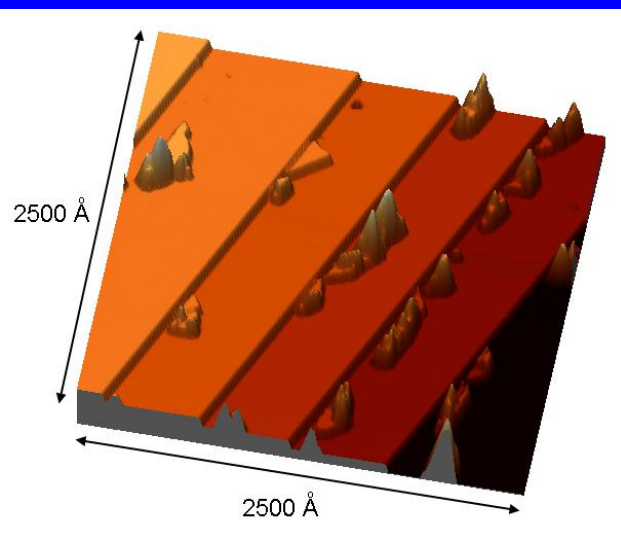
States are spin polarized!

# What about the quantization of a quasiparticle in the topological surface states?   -  i.e. what are the E vs. *k* relations?

We can use a "particle in a box" characterization to find out

Electron Confinement between step edges



Potential Well

$n=3$

$n=2$

$n=1$

Electrons in a Quantum Box



390Å   440Å   700Å

Energy (meV)

150
75
0
-75
-150
-225

390   440   700

Terrace Width (Å)

0 pS   500 pS



2500 Å

2500 Å
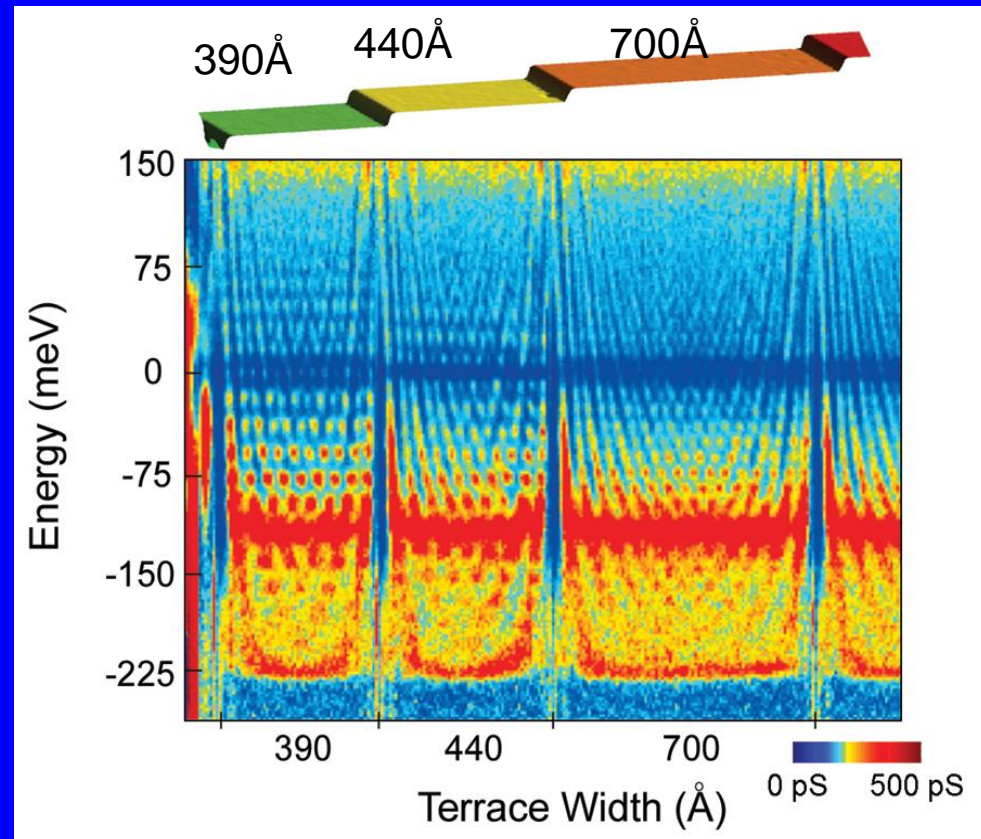
Sb (001) surface

Yazdani group

# Quantization rules and back scattering



$E_{14}$

$E_1$

0    390

Distance (Å)
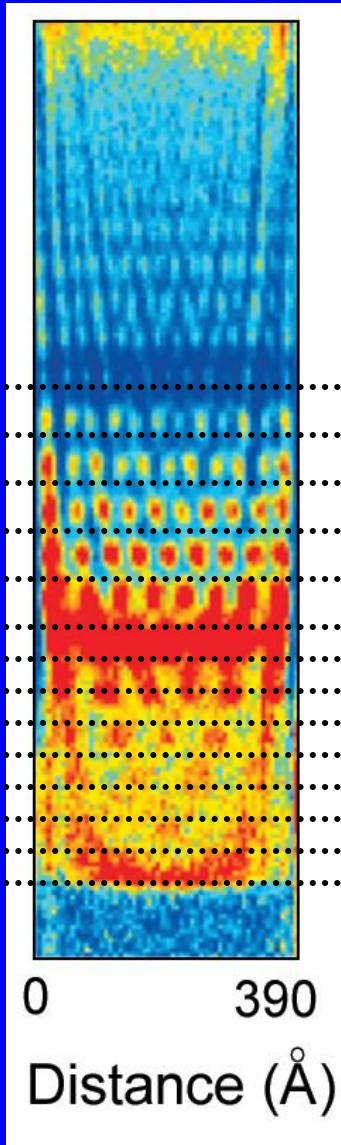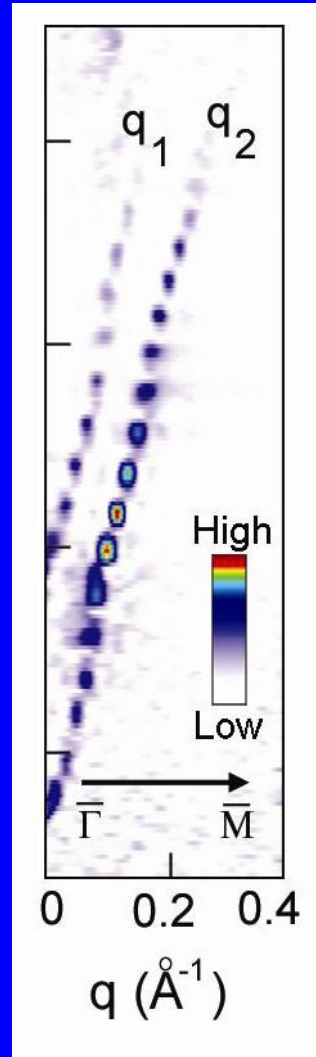
Energy dispersion of the surface states ~ n not $n^2$



$q_1$    $q_2$

High

Low

$\overline{\Gamma}$    $\overline{M}$

0    0.2    0.4

q (Å$^{-1}$)

Fermi surface of surface States including spins:



$q_1$

$\overline{K}$

$\overline{\Gamma}$

$\overline{M}$

$q_2$
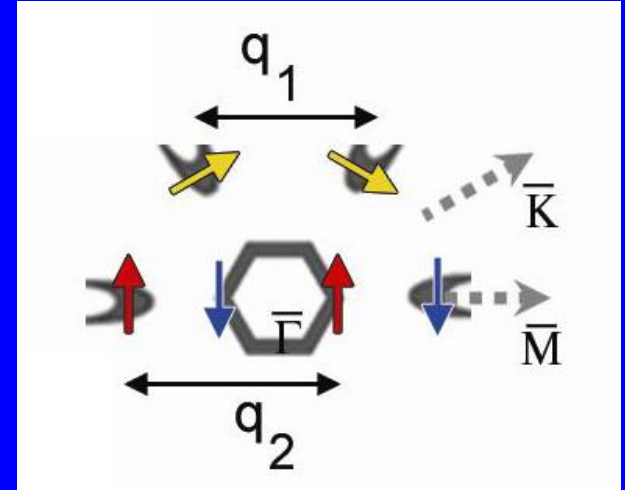
Due to the chirality, +q cant scatter to –q
e.g. when it hits the step edge or a defect.

therefore enhanced surface conduction.
Computer interconnects people are interested!

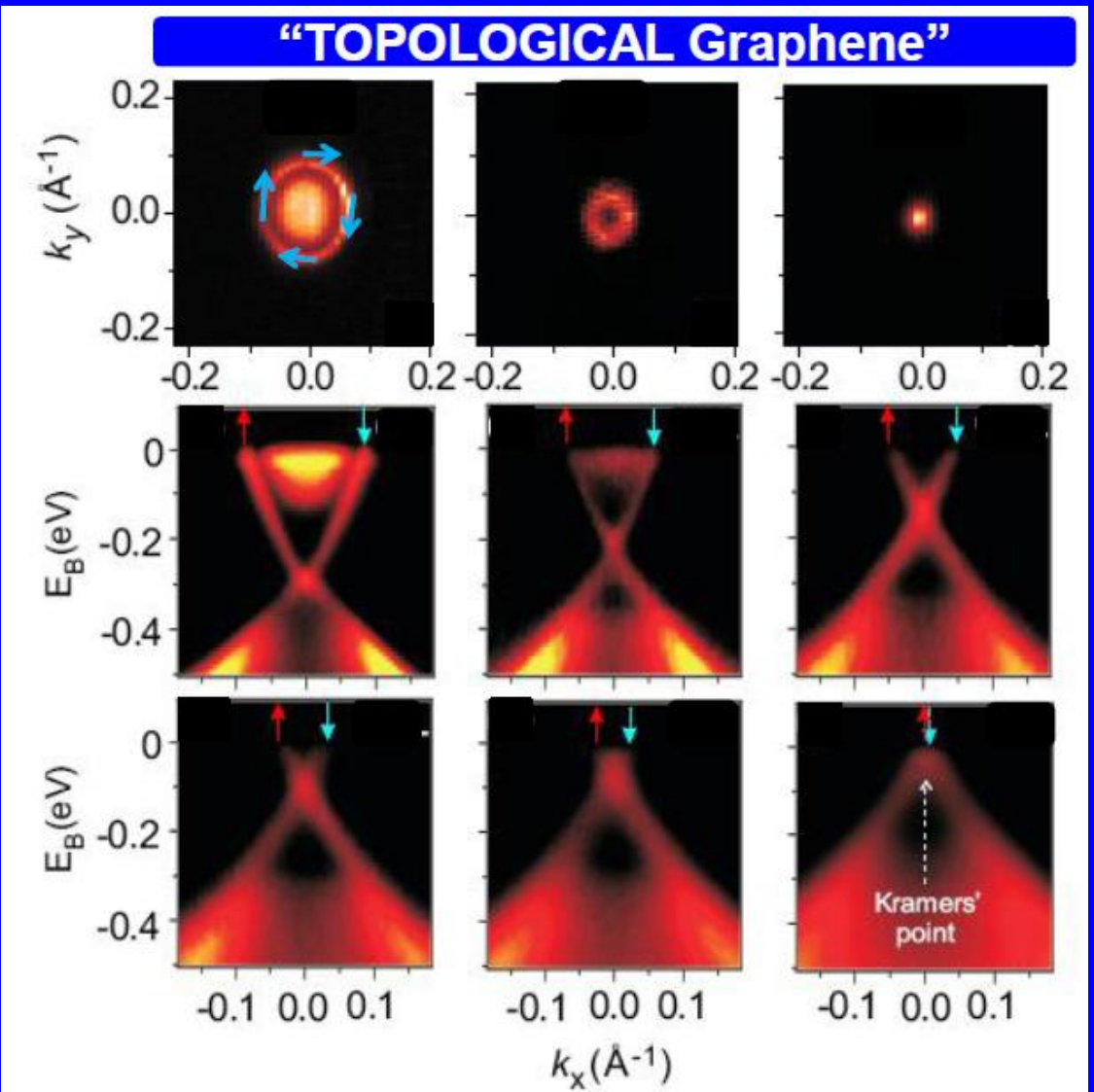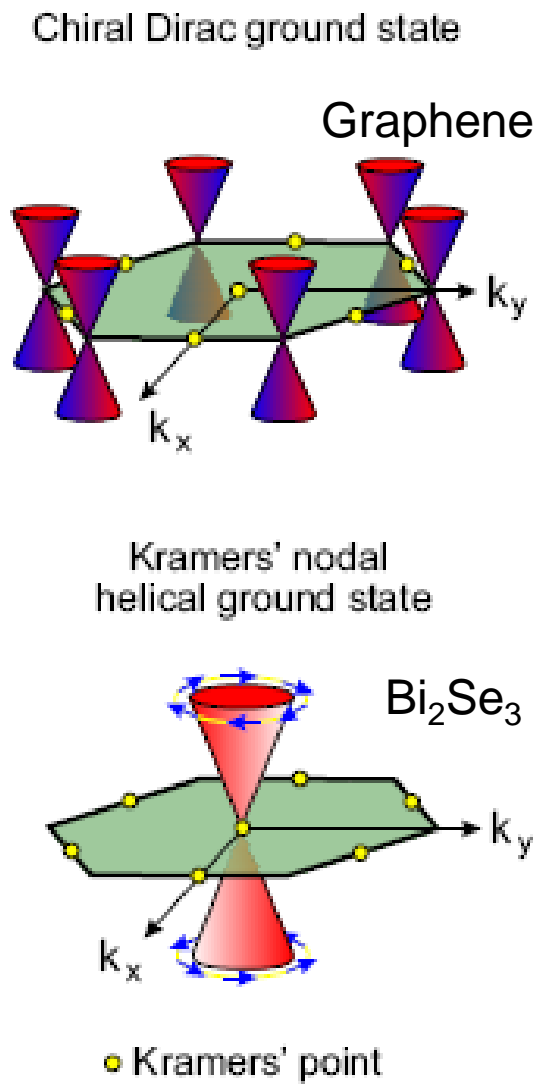# Bi$_2$Se$_3$ - I dreamed up a topological insulator that had not been predicted –heavy, small band gap, cleavable, same 2D symmetry as Bi

Bi$_2$Se$_3$ (001) plane surface ARPES



Chiral Dirac ground state

Graphene

Kramers' nodal helical ground state

Bi$_2$Se$_3$

• Kramers' point



"TOPOLOGICAL Graphene"

But how can you measure the transport properties of electrons in surface states on a bulk crystal? We need bulk insulating behavior so the surface states will dominate the transport - $Bi_2Se_3$ had never been made n-type or with a low carrier concentration

Defect chemistry is the key, the example of $Bi_2Se_3$:

For $Bi_2Se_3$ the major defects are charged Se vacancies:

$$Se_{Se} \rightarrow V_{Se}^{\bullet\bullet} + Se(g) + 2e'$$
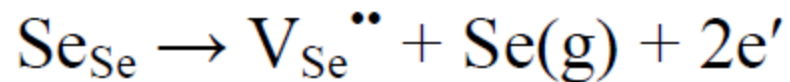
Defects typically enough to yield n-type carriers $10^{19} - 10^{20}$ cm$^{-3}$

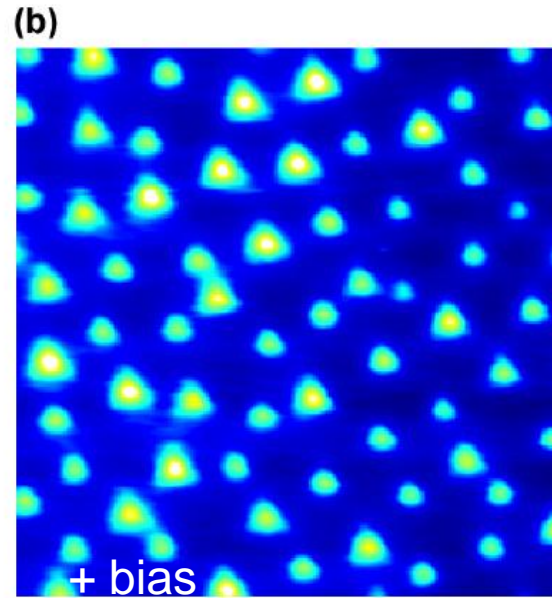Unlike for $Bi_2Te_3$, Pb and Sn dopants are ambipolar. They do not create enough p-type carriers to compensate the electrons in $Bi_2Se_3$
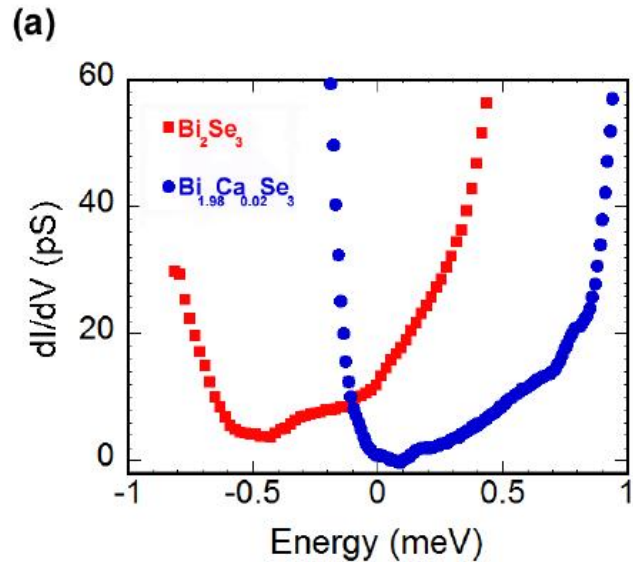
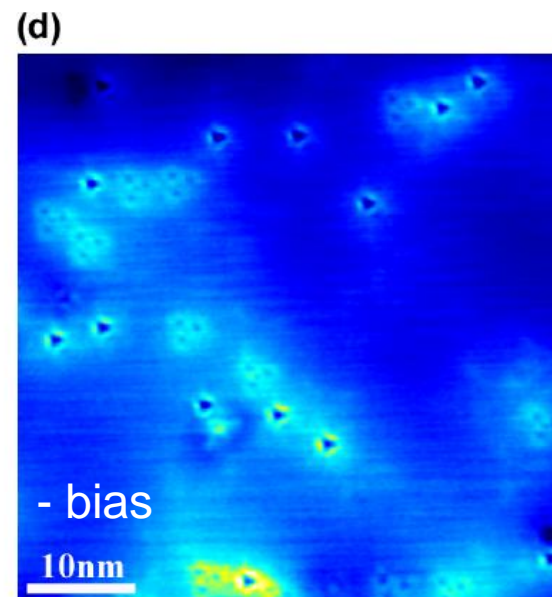An electronically unambiguous substitution was therefore needed:

$$2Ca \xrightarrow{Bi_2Se_3} 2Ca_{Bi}' + 2h^{\bullet}$$
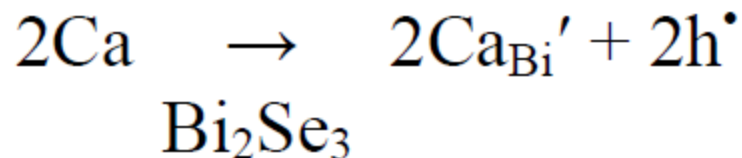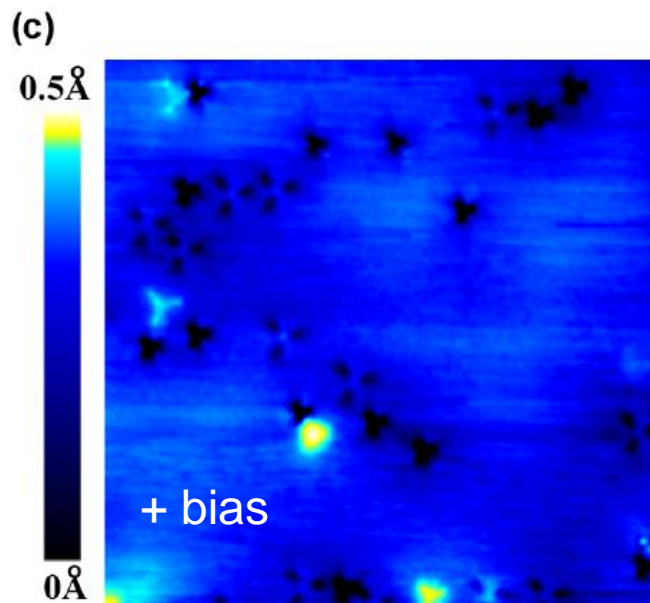
Ca-doped Bi$_2$Se$_3$ grows very nice crystals:

# STM characterization of the gap and defects



(a)

(b)
+ bias

Undoped $Bi_2Se_3$
Charged Se vacancies are seen

(c)
+ bias

(d)
- bias
10nm

Ca-doped $Bi_2Se_3$
Charged Ca substitutions

( + Se vacancy concentration significantly decreased)
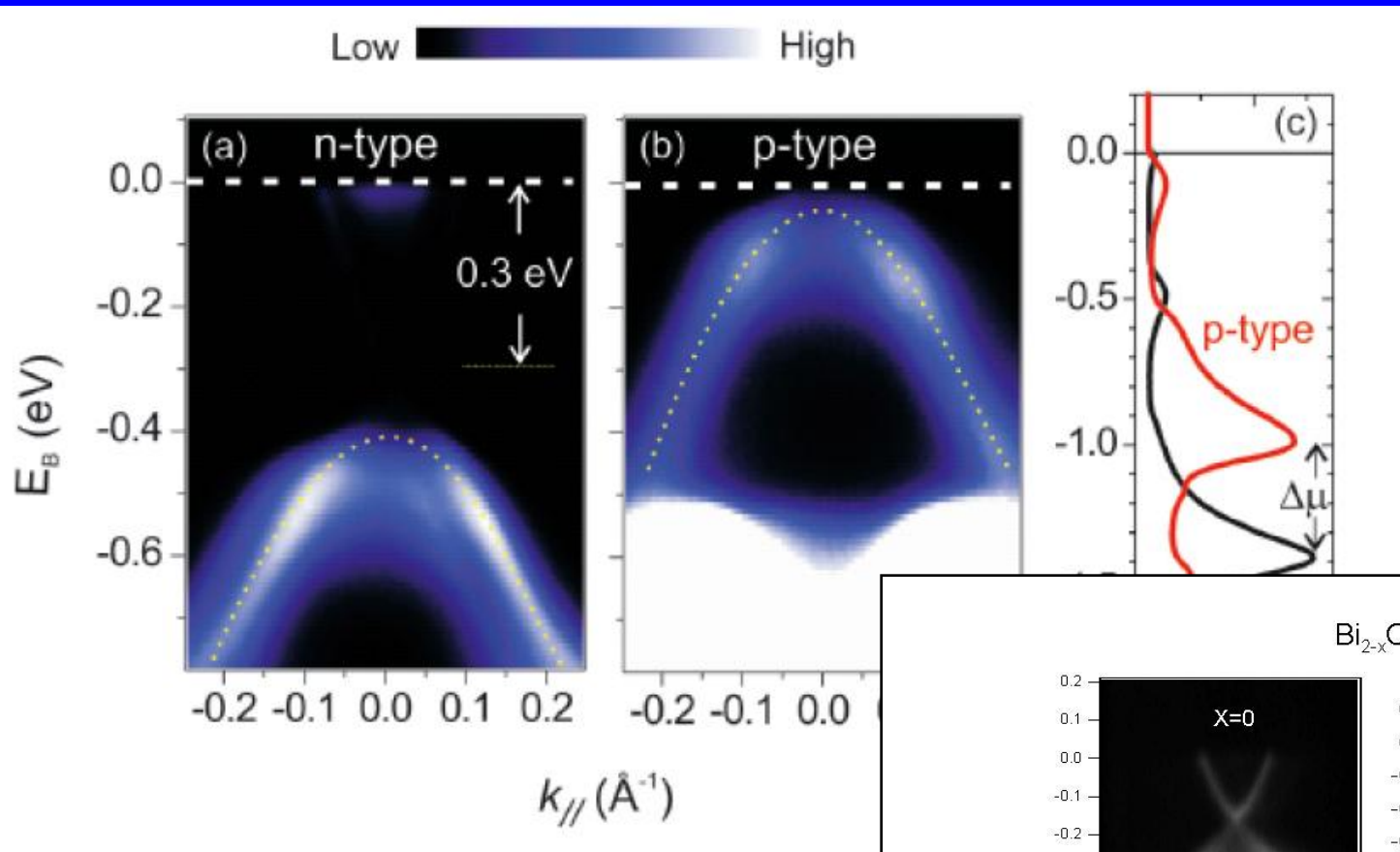
ARPES shows the evolution on doping
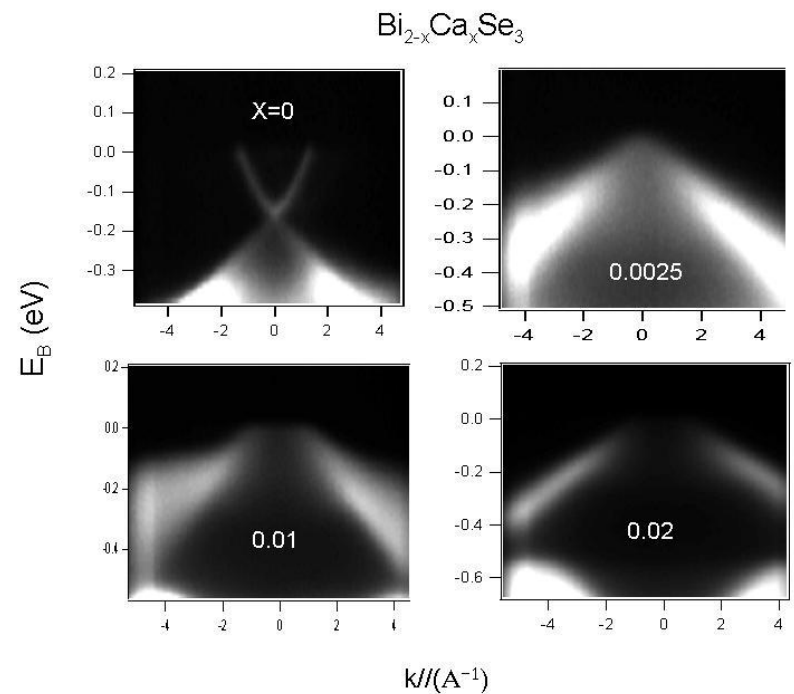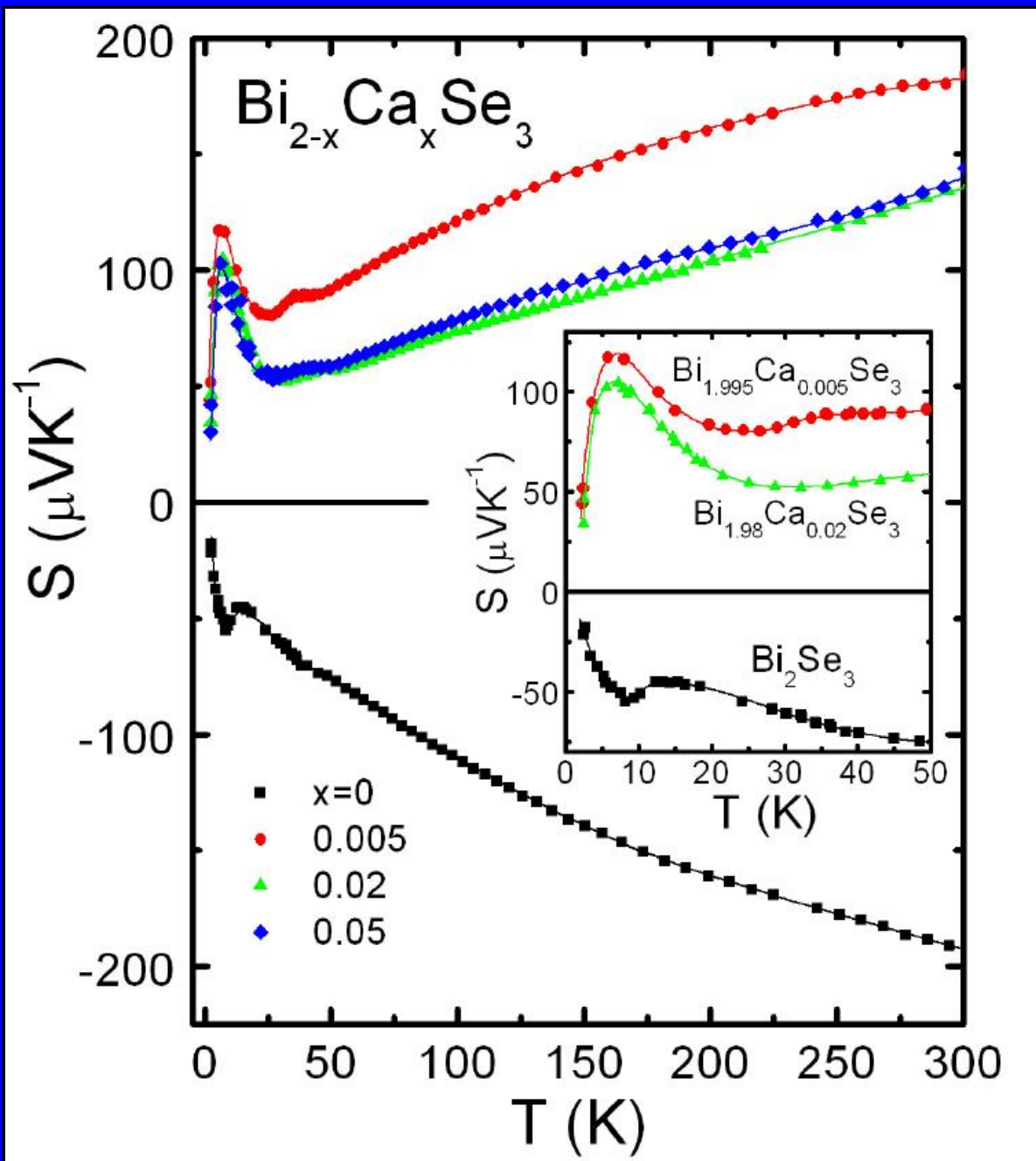
Seebeck coefficients are excellent.

Dramatic peak in
S, > 100 µVK$^{-1}$
at 7 K
in p-type material!

Very reminiscent of the low T peak in doped elemental Bi
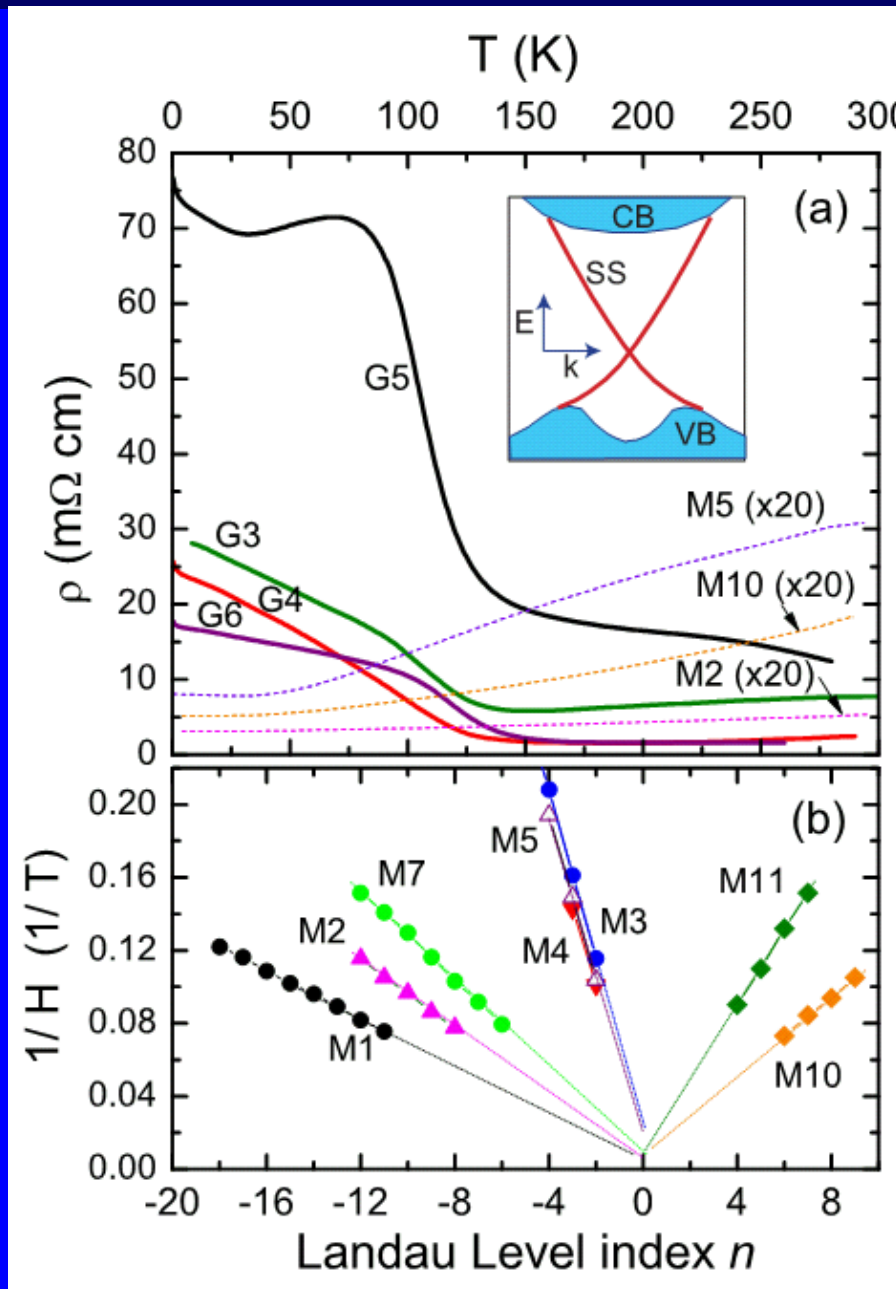
Onset of non-metallic behavior ~ 130 K

SdH oscillations seen in both n-type and p-type samples

Non-metallic samples show no discernable SdH

# With the high resistivity bulk crystals of $Bi_2Se_3$ :

2D surface states are seen in magnetoresistance

– Giant conductance fluctuations

Zooming in:



Conductance fluctuations of giant amplitude (200-500 X too large) Implies electron state coherence over long distances - much too long for bulk states.

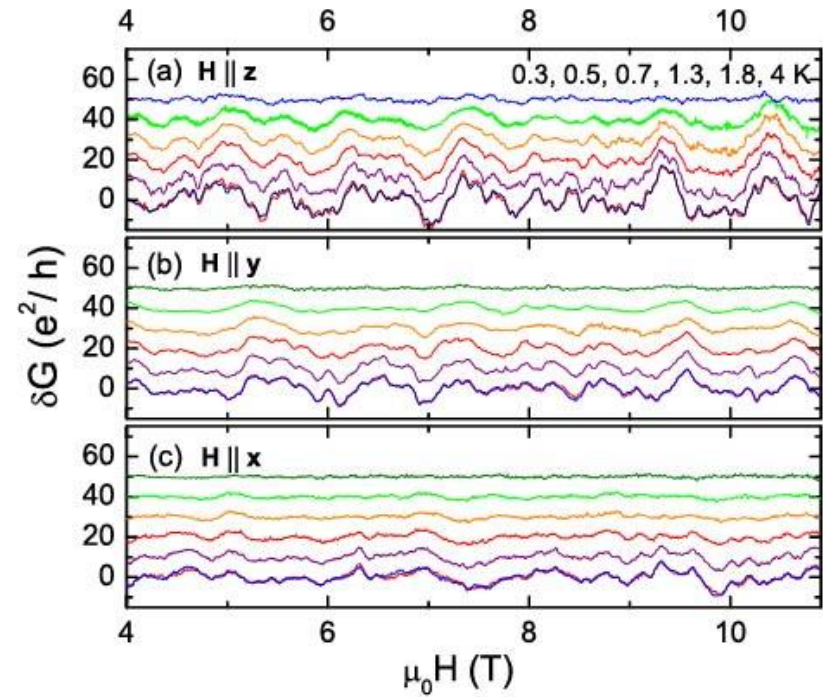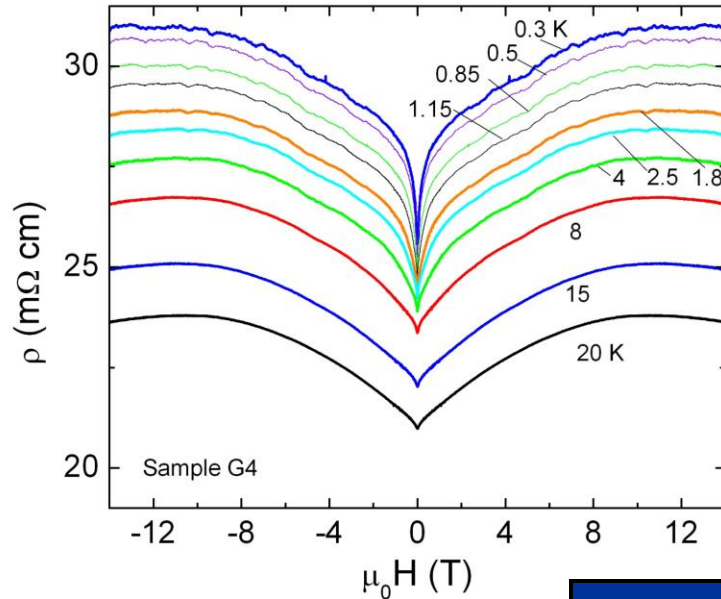Proposals to detect Majorana Fermions (chargeless particles obeying Fermi statistics) involve a device with a superconductor in proximity to a topological insulator
Physicists asked us for a superconductor to use.

It would have to be chemically inert with respect to $Bi_2Se_3$ or $Bi_{1-x}Sb_x$ to build a device.

Doping of those compounds to make a superconductor seemed best.

Doped $Bi_{1-x}Sb_x$ didn't work, but…

Copper intercalated $Bi_2Se_3$ single crystals superconduct at about 3.5 K
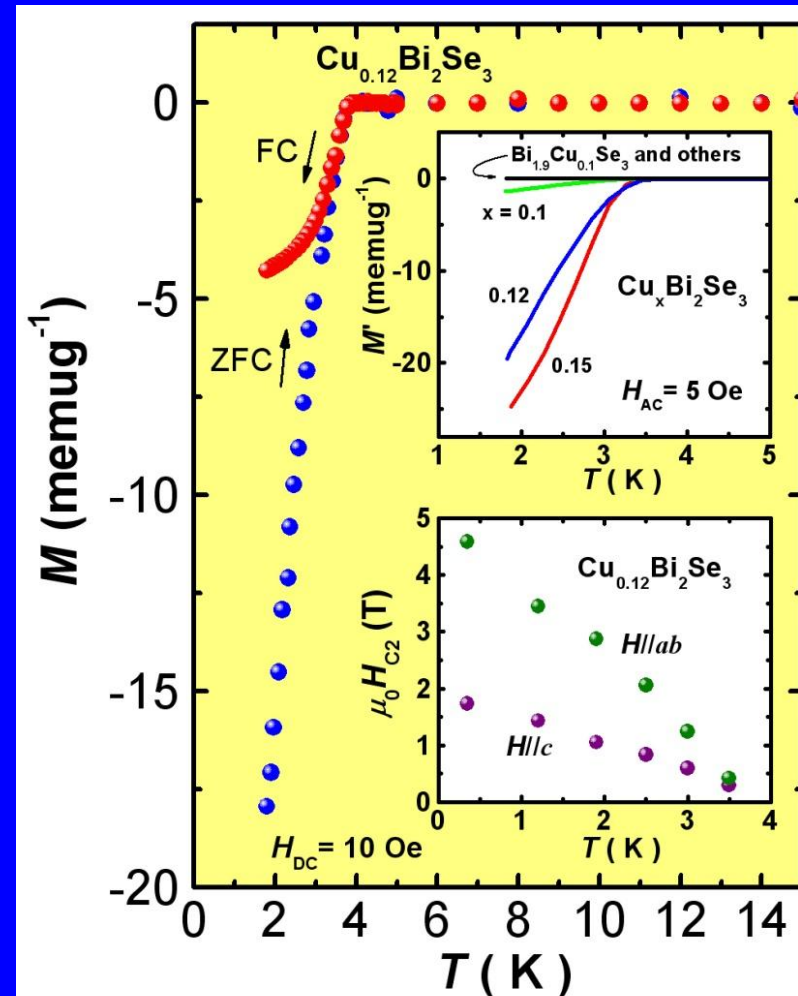
The interactions of the topological surface states with magnetic moments are expected to be novel.
Physicists asked for a ferromagnetic topological insulator.

We developed ferromagnetism in single crystals of Mn-doped $Bi_2Te_3$
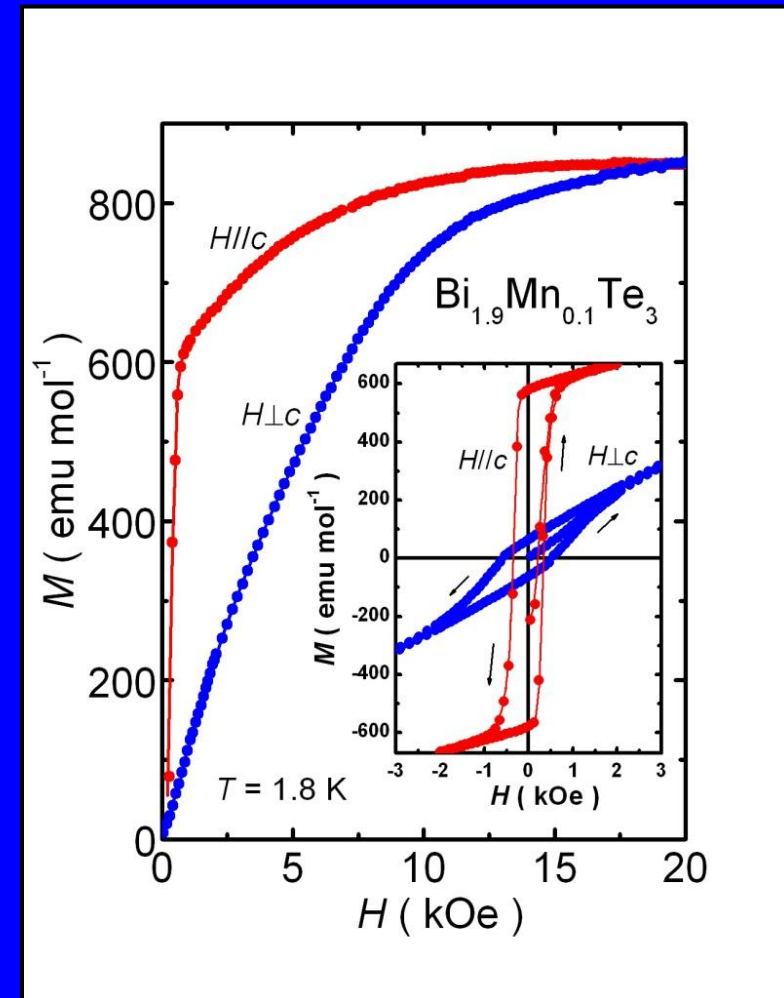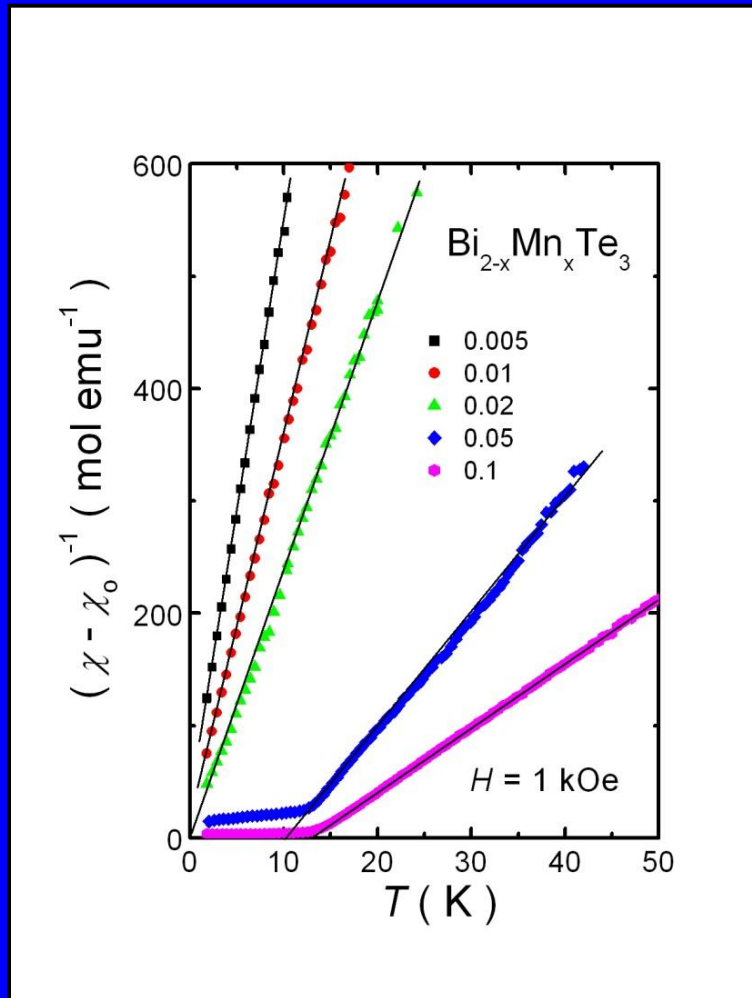
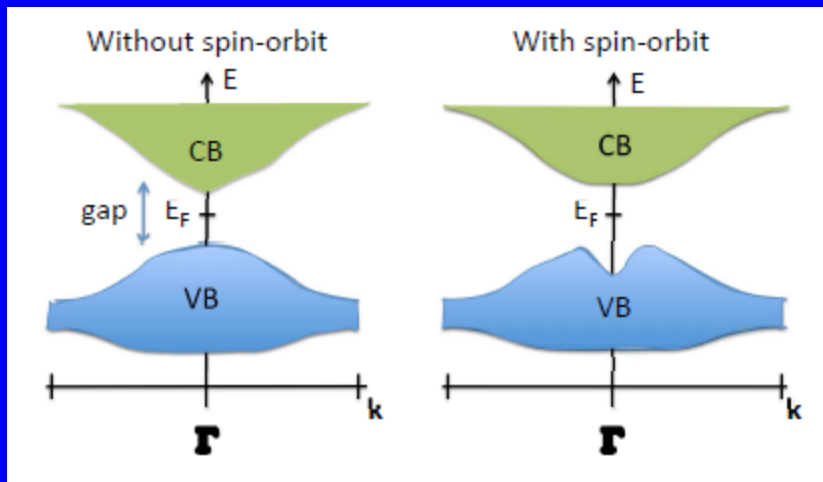# TIs inspire a materials theory first!     Posted 6 months ago

Band structures calculated automatically for 60,000 compounds in ICSD!
(for a restricted (most probable) set of electron wavevectors)

## The search for strong topological insulators.

M. Klintenberg[1, *]

[1] Department of Physics and Astronomy, Uppsala University,
(Dated: July 29, 2010)

Looked for this:



| Material | Spgrp | Struct. type | LDA band gap [eV] |
|---|---|---|---|
| $Ca_3PbO$ | P m -3 m | $CaTiO_3$ | 0.2 |
| $Sr_3PbO$ | P m -3 m | $CaTiO_3$ | 0.1 |
| $Ba_3PbO$ | P m -3 m | $CaTiO_3$ | 0.1 |
| $Yb_3PbO$ | P m -3 m | $CaTiO_3$ | 0.2 |
| $Ca_3SnO$ | P m -3 m | $CaTiO_3$ | 0.2 |
| $Sr_3SnO$ | P m -3 m | $CaTiO_3$ | 0.1 |
| $Yb_3SnO$ | P m -3 m | $CaTiO_3$ | 0.1 |
| GdPtSb | F -4 3 m | AlLiSi | 0.2 |
| $Bi_2SeTe_2$ | R -3 m H | $Bi_2Te_3$ | 0.3 |
| $Bi_2STe_2$ | R -3 m H | $Bi_2Te_3$ | 0.3 |
| $PbTl_4Te_3$ | I 4/m c m | $In_5Bi_3$ | 0.1 |
| $BiTl_9Te_6$ | I 4/m c m | $In_5Bi_3$ | 0.1 |
| $BiTlTe_2$ | R -3 m H | $NaCrS_2$ | $0.0^a$ |
| $SbTlTe_2$ | R -3 m H | $NaCrS_2$ | 0.2 |
| $Bi_2TeI$ | C 1 2/m 1 | $Bi_2TeI$ | 0.1 |
| $GeSb_4Te_7$ | P -3 m 1 | $AgBiSe_2$ | 0.2 |
| HgKSb | P 63/m m c | KZnAs | 0.2 |

(Out of 60,000, only 4 classes
not previously known.)

What do you think? Does this take the fun out of it or is it better?

# Conclusions

Complex new materials are being discovered whose properties challenge and advance condensed matter physics.

Consideration of structure and chemistry can help yield insights into those properties.

This talk has presented some examples.

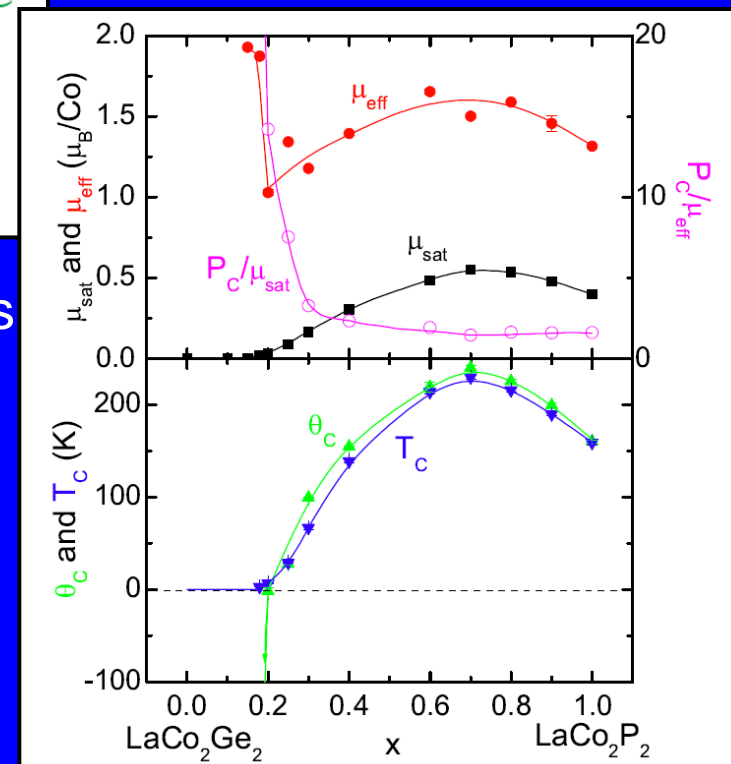# Only one lanthanide case shows a cT to ucT transiton
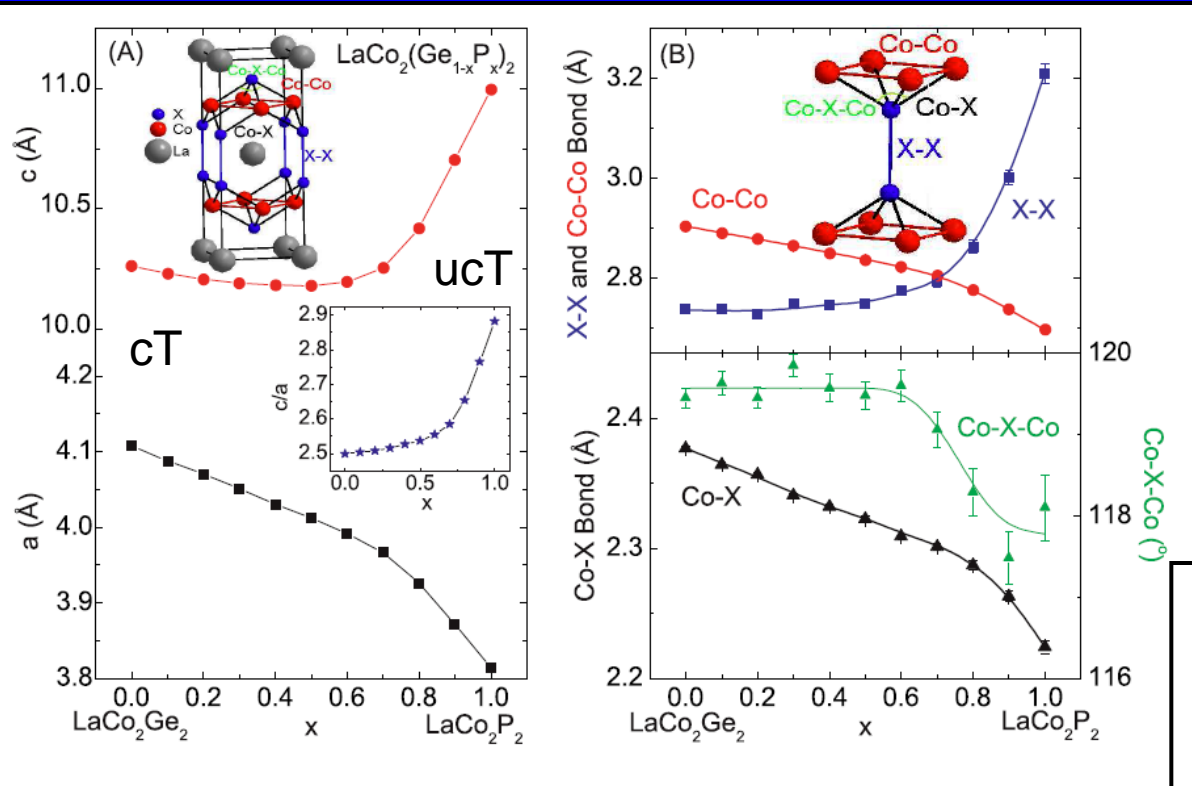


The P electrons first fill the Co derived 3$d$ bands then start breaking up the X-X dimer at high x

$LaCo_2Ge_2$ paramagnet

$LaCo_2P_2$ ferromagnet
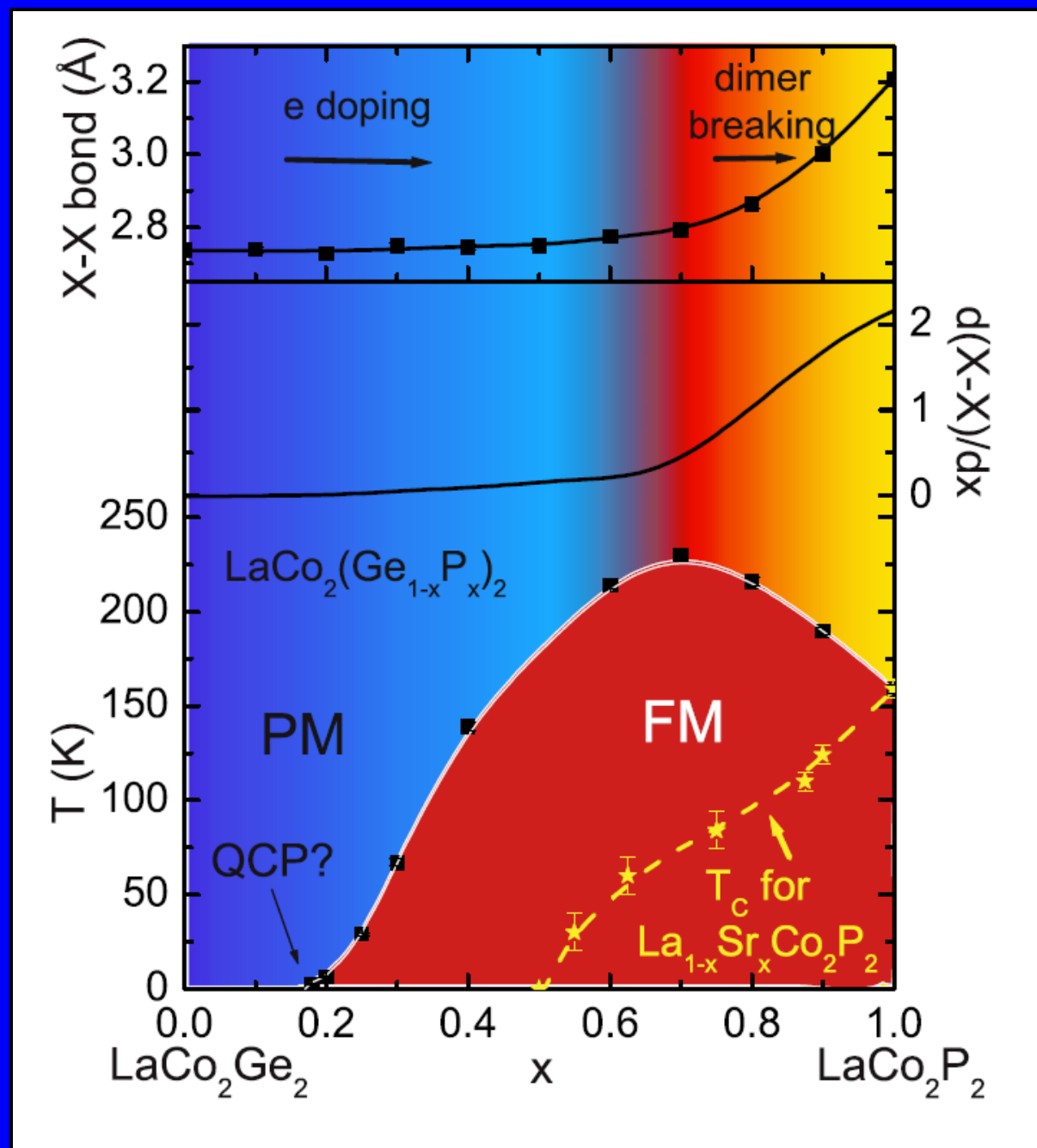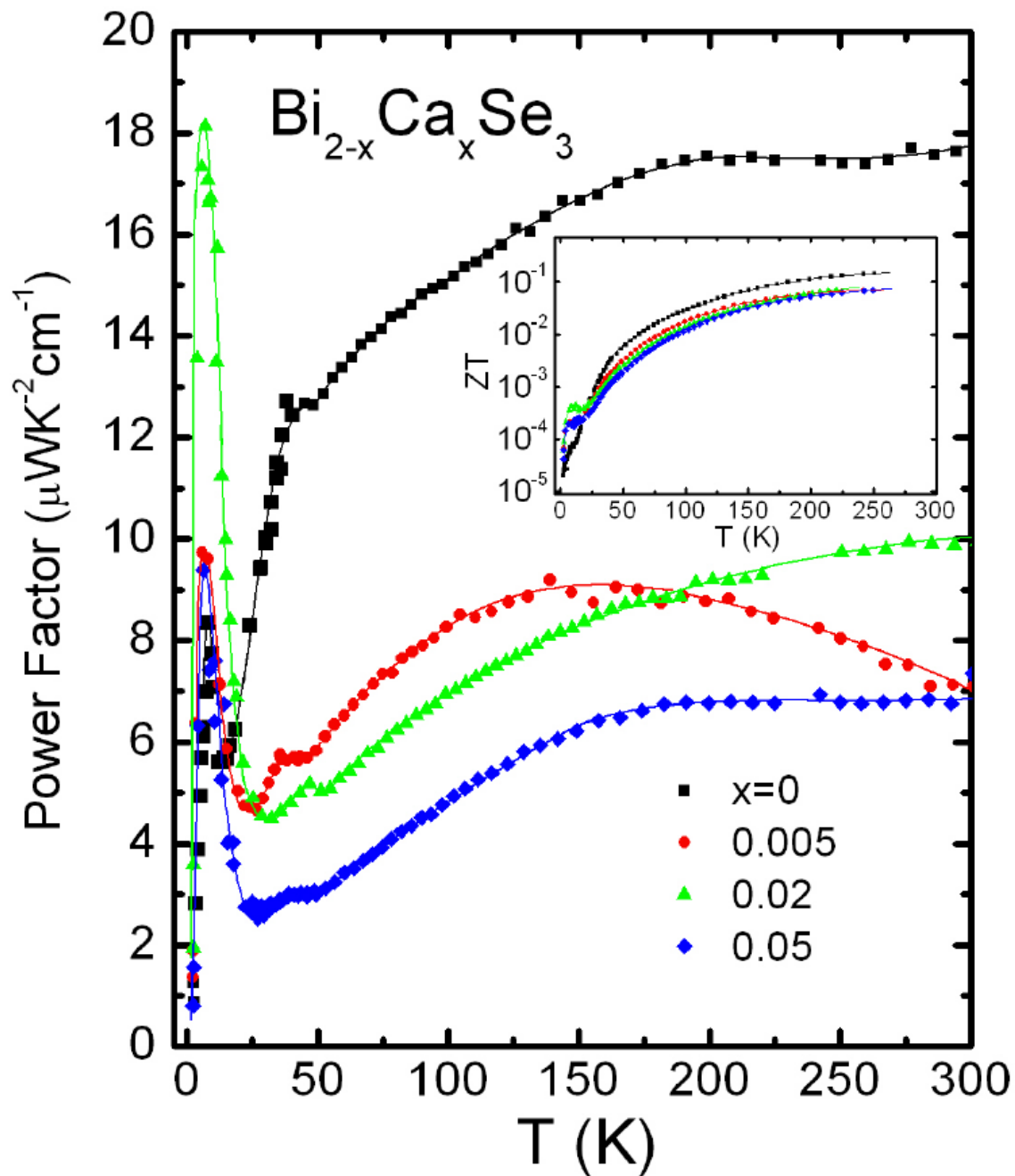
The crossover is not simple

an electron count
Induced
transition to
ferromagnetism

with a decrease
in Tc when the
dimer begins to
break up.

Ge doping of
$LaCo_2P_2$ is
not simple.
Compare to the
Isoelectronic
case
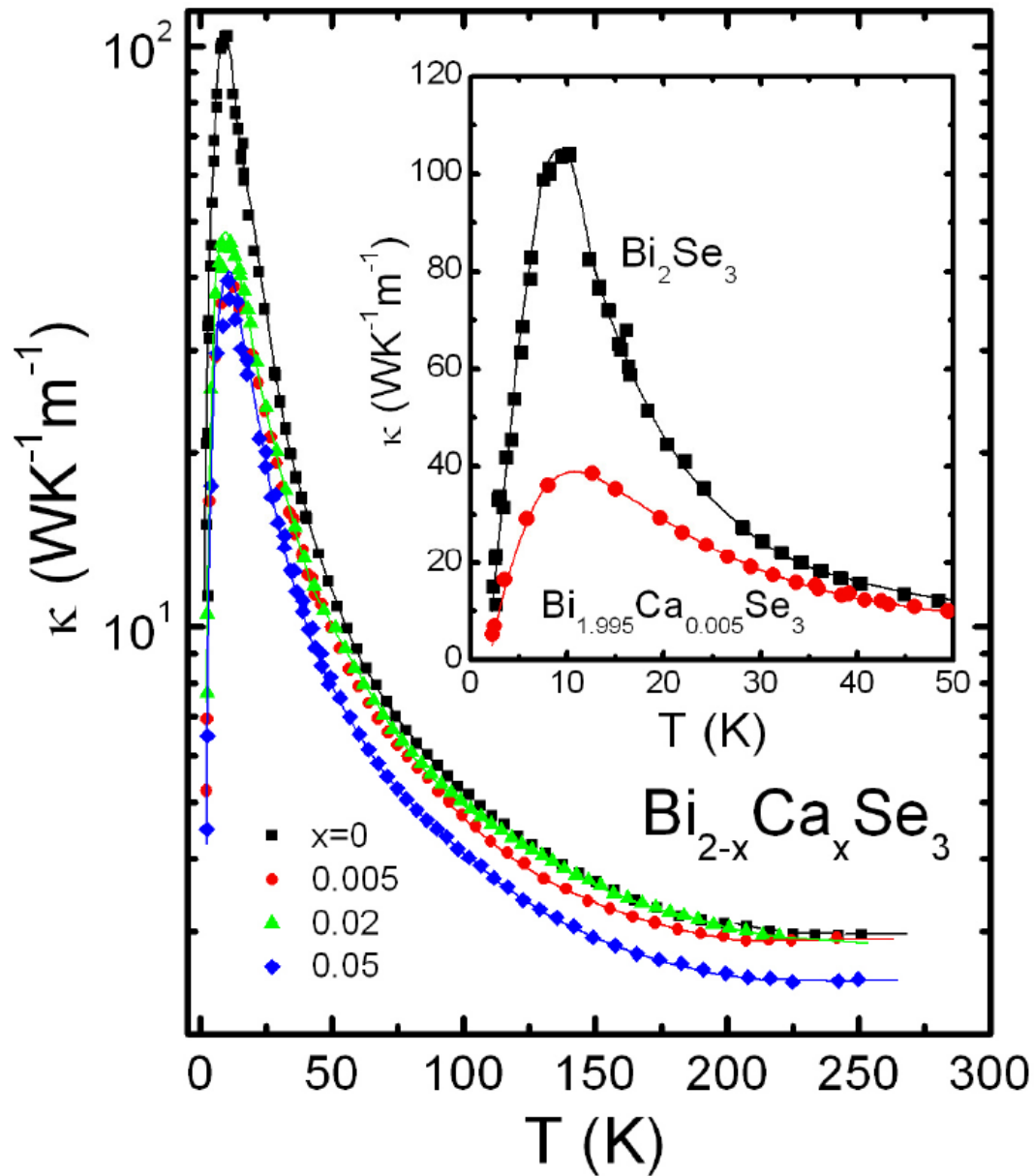$La_{1-x}Sr_xCo_2P_2$
where there are
no dimers.

Possibly another
QCP

Anomalous very high
low temperature
power factor

Equivalent to high
temperature value

Thermal conductivities are very large

Can they be decreased?

# Brief Tutorial on bonding and antibonding bands and dimer formation:

Antibonding orbitals

$\sigma^*$

Add 6e  no dimer

Add 4e still have dimer

$\sigma$

Bonding orbitals

isolated

dimerized

$P^{3-}_2$

$(P_2)^{4-}$

P – P separation tells you what you have