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
Earlier Iron superconductors:
- \( \text{U}_6\text{Fe} \) \( (T_c = 3.9 \text{ K}) \), 1958
- \( \text{Th}_7\text{Fe}_3 \) \( (T_c = 1.9 \text{ K}) \), 1961
- \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) \( (T_c = 6.1 \text{ K}) \), 1980
- \( \text{LaFe}_4\text{P}_{12} \) \( (T_c = 4.1 \text{ K}) \), 1981

But they are rare: magnetic states usually trump superconductivity.

Fe usually makes magnets. Max \( T_c \) near 55 K
The superconductors have layered crystal structures.

Unusual oxypnictides were first, then came ThCr$_2$Si$_2$-type phases.

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 (both sealed under vacuum)
- Polished Iron & Selenium Pieces
For the physics community:

- How does magnetism evolve into superconductivity?
- Is the superconductor itself exotic or conventional?
- Why is $T_c$ 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$_2$As$_2$ 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$_2$Si$_2$ structure:
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 \( \text{AM}_2\text{P}_2 \) phosphides are a special case:

If the large A atom is not large enough, you can get P-P bonding between the \( \text{M}_2\text{P}_2 \) layers.

In fact you can have \( \text{P}^{3-}_2 \) for large A atoms and \( (\text{P-P})^{4-} \) for small A atoms.
Brief Tutorial on bonding and antibonding bands and dimer formation:

Antibonding orbitals

σ*

Add 6e no dimer

Add 4e still have dimer

Bonding orbitals

isolated

P\(^{3-}\)_2

dimerized

(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$_2$P$_2$ compounds.

But no property implications until recently.

Then in 2009 CaFe$_2$As$_2$ 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

\[
\begin{align*}
\text{SrCo}_2\text{P}_2 & \quad \text{and} \quad \text{CaCo}_2\text{P}_2 \quad \text{are anomalous:} \\
\text{SrCo}_2\text{P}_2 & \quad a = 3.79 \quad c = 11.6 \\
\text{CaCo}_2\text{P}_2 & \quad a = 3.85 \quad c = 9.6 \\
\text{- The } a \text{ axis grows on going from Sr to Ca, and there is a large decrease in } c.
\end{align*}
\]

Does a non-bonded \( \text{P}^{3-} \) to bonded dimer \( \text{P}^{4-} \) transition occur in the \( \text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2 \) 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$_2$P$_2$ layer responds non-linearly.

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

- $\Theta$: strength of near neighbor magnetic interactions
- $\mu$: magnetic moment per Co
- $\chi$: magnetic susceptibility
- $\gamma$: $\sim$ effective mass of charge carriers

They follow the lattice collapse
Ca for Sr in $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$

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

c$T$, uc$T$ = 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:

Transition elements

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

Bonding and antibonding states of the P-P dimer straddle the $d$-band manifold, which changes in energy and filling across the $3d$ series.
Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ shows dramatic changes in P-P bonding induced by changing the distance between Co$_2$P$_2$ layers. Something should also happen when you cross the 3$d$ series with everything else held constant.

Consider CaM$_2$P$_2$

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?
By far, the primary change on crossing From Fe to Co to Ni is the bond strength in the P-P dimer!

Variation of internal Parameters across the series

The picture works – The antibonding band becomes more empty as you cross the 3d 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$_2$Ge$_2$** is strongly collapsed but **SrCo$_2$P$_2$** 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
da 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! ($\text{Mass} \sim \frac{d^2E}{dk^2} (=0)$)
- 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
Bi and Sb are both semimetals – near $\text{Bi}_{0.9}\text{Sb}_{0.1}$ 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 $\text{Bi}_{0.9}\text{Sb}_{0.1}$
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:

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

Sb (001) surface

Yazdani group
Quantization rules and back scattering

Due to the chirality, $+q$ cannot scatter to $-q$, e.g. when it hits the step edge or a defect.

Therefore enhanced surface conduction.

Computer interconnects people are interested!

Fermi surface of surface states including spins:

Energy dispersion of the surface states $\sim n$ not $n^2$
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

"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$_2$Se$_3$ had never been made n-type or with a low carrier concentration.

Defect chemistry is the key, the example of Bi$_2$Se$_3$: For Bi$_2$Se$_3$ the major defects are charged Se vacancies:

$$\text{Se}_\text{Se} \rightarrow V_{\text{Se}} + \text{Se(g)} + 2e'$$

Defects typically enough to yield n-type carriers $10^{19} - 10^{20}$ cm$^{-3}$

Unlike for Bi$_2$Te$_3$, Pb and Sn dopants are ambipolar. They do not create enough p-type carriers to compensate the electrons in Bi$_2$Se$_3$.

An electronically unambiguous substitution was therefore needed:

$$2\text{Ca} \rightarrow 2\text{Ca}_{\text{Bi}}' + 2h'$$

Bi$_2$Se$_3$
Ca-doped Bi$_2$Se$_3$ grows very nice crystals:
STM characterization of the gap and defects

Undoped Bi$_2$Se$_3$
Charged Se vacancies are seen

Ca-doped Bi$_2$Se$_3$
Charged Ca substitutions
(+ Se vacancy concentration significantly decreased)
ARPES shows the evolution on doping
Seebeck coefficients are excellent.

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

Very reminiscent of the low T peak in doped elemental Bi.
Transport measurements that probe surface states become possible

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$_2$Se$_3$:

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$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$Te$_3$. 
TIs inspire a materials theory first!  

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

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

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

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

LaCo₂Ge₂ paramagnet

LaCo₂P₂ 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$_2$P$_2$ is not simple. Compare to the Isoelectronic case La$_{1-x}$Sr$_x$Co$_2$P$_2$ 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

Bonding orbitals

Add 6e no dimer
Add 4e still have dimer

isolated $P^{3-}_2$ dimerized $(P_2)^{4-}$

$P - P$ separation tells you what you have