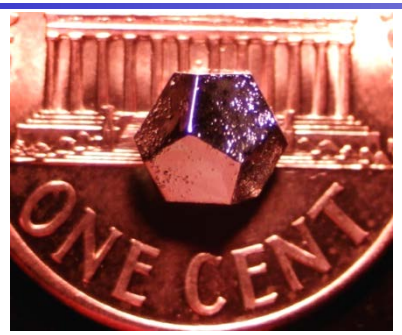

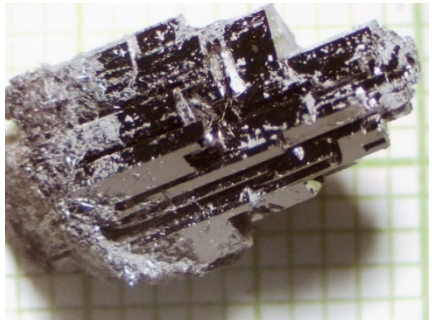
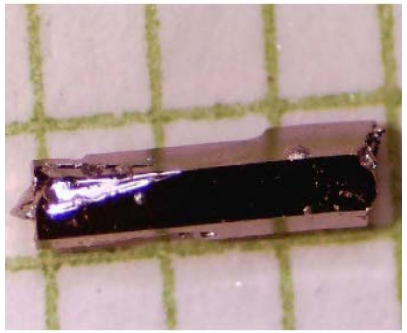

Synthesis as the heart of New Materials Physics

Paul C. Canfield
Senior Physicist, Ames Laboratory
Distinguished Professor, Department of Physics
Iowa State University

Braga Workshop
October 9, 2018

Let’s start with conclusions:

The design, discovery and growth of novel materials is the heart and soul of New Materials Physics.

Synthesis combined with broad characterization tools and an eclectic interest in novel states of matter is the wellspring from which the solution of humanity’s pressing problems will emerge.

Our charge it to refine and utilize this powerful tool as efficiently as possible and teach its multifaceted use to as many researchers as possible.

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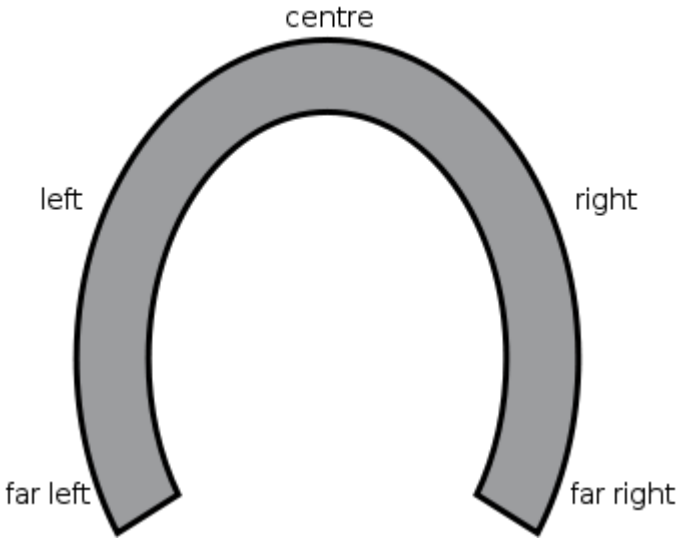
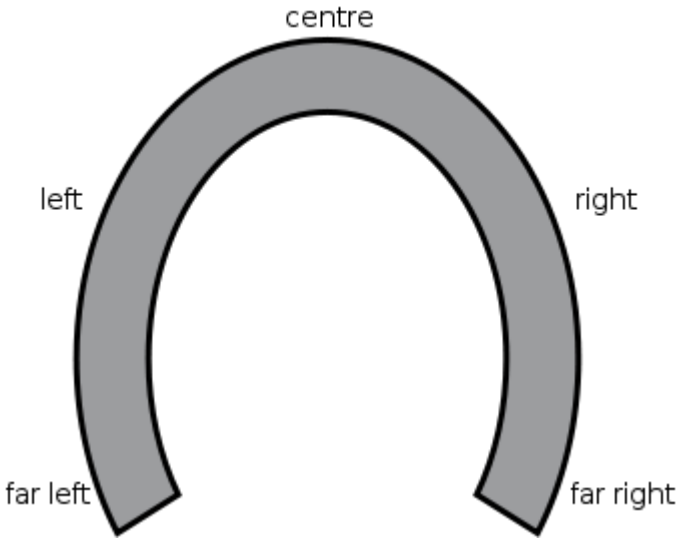
For luck, or for the iron, we can start with horseshoes....

Horseshoe Theory in Politics



The horseshoe theory in political science asserts that rather than the far left and the far right being at opposite and opposing ends of a linear political continuum, they in fact closely resemble one another, much like the ends of a horseshoe.

Horseshoe Theory in Politics



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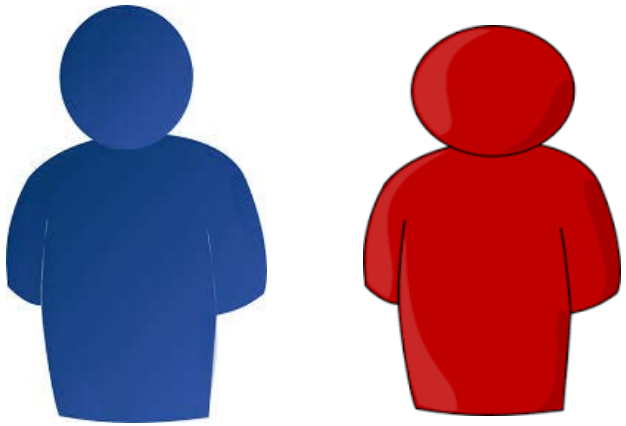
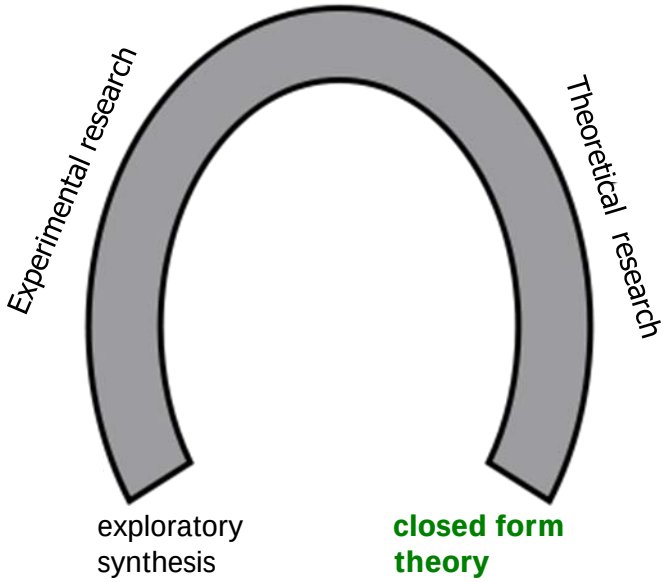


Insert you preferred examples here....You each have your own.

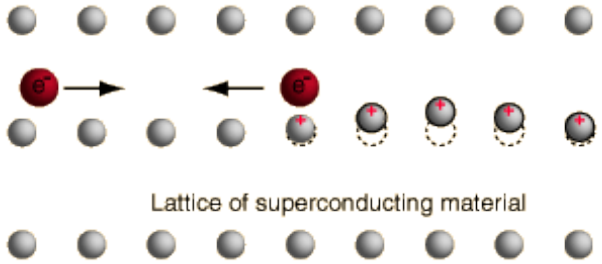
Horseshoe Theory of Physics



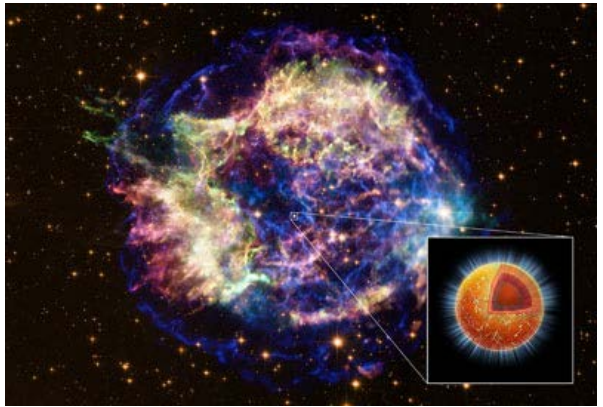
The extremes of the research spectra are actually much closer then one might appreciate. As most of us appreciate, theory can change the system of interest by just changing a pre-factor or coupling term. I am told that it is "trivial" to progress from lead to a neutron star to the quark-gluon plasma....

"Trivial"....

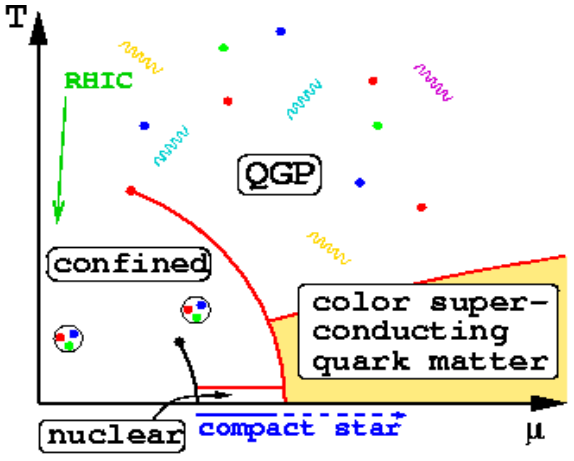
Electron-phonon superconductor



Inside neutron star



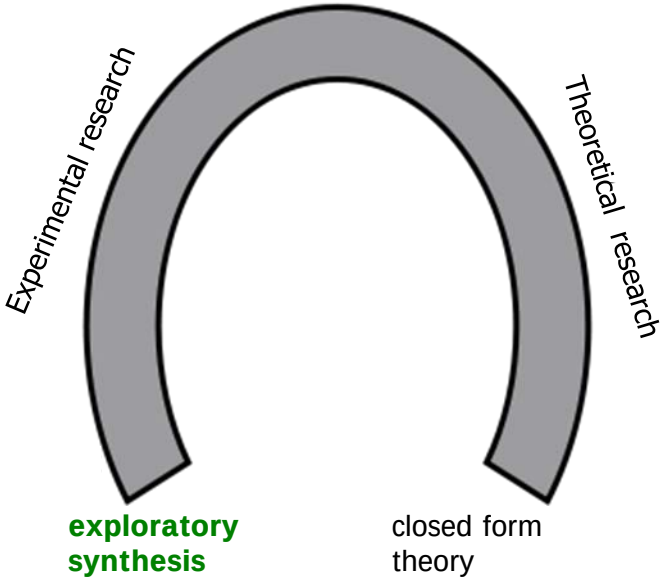
Quark-Gluon Plasma



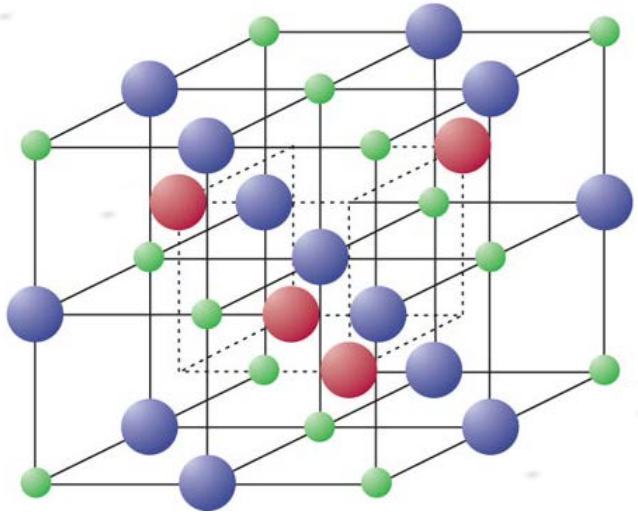
Horseshoe Theory of Physics

What's really *"trivial"* is...

By simply changing the elements on a simple, face-centered-cubic lattice the ground state of a compound can be varied profoundly.



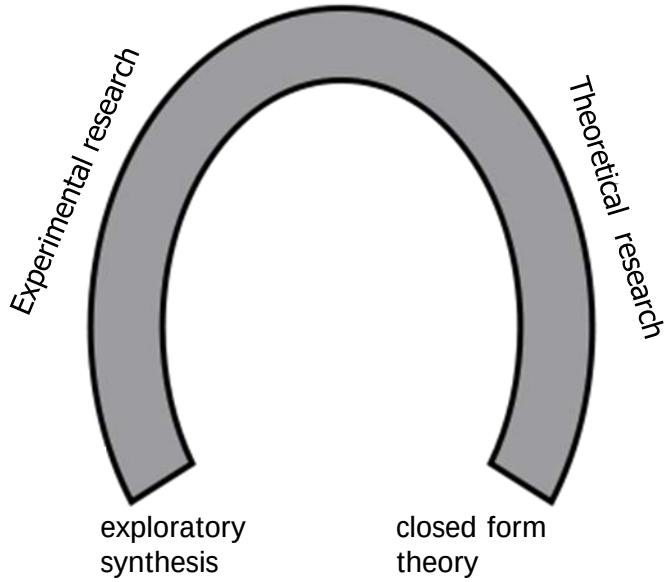
Half Heusler Structure



TiNiSn -- ~ 1 eV gap semiconductor
MnNiSb -- ~ 700 K Ferromagnet
YbPtBi -- Heaviest heavy Fermion
LaPtBi -- non-centrosymmetric superconductor
LuPtBi -- proposed topological insulator

Horses and Pygs

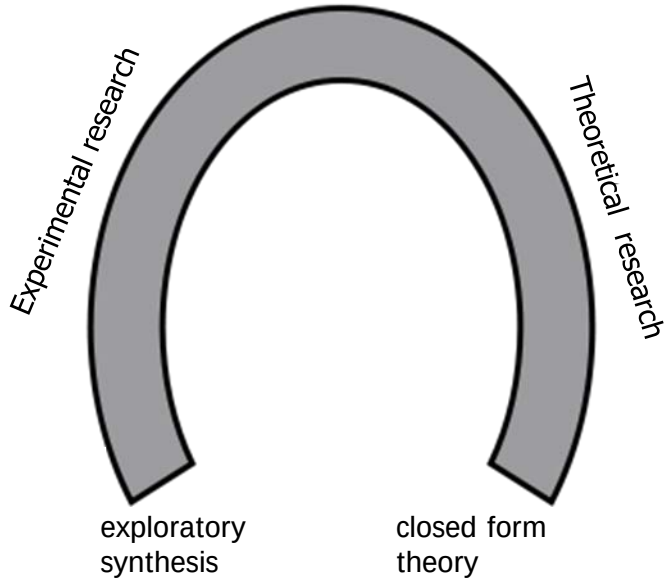
Pygmalion by Jean-Baptiste Regnault, 1786



The advantage of synthesis over closed form theory is that instead of just dreaming about how things might be....

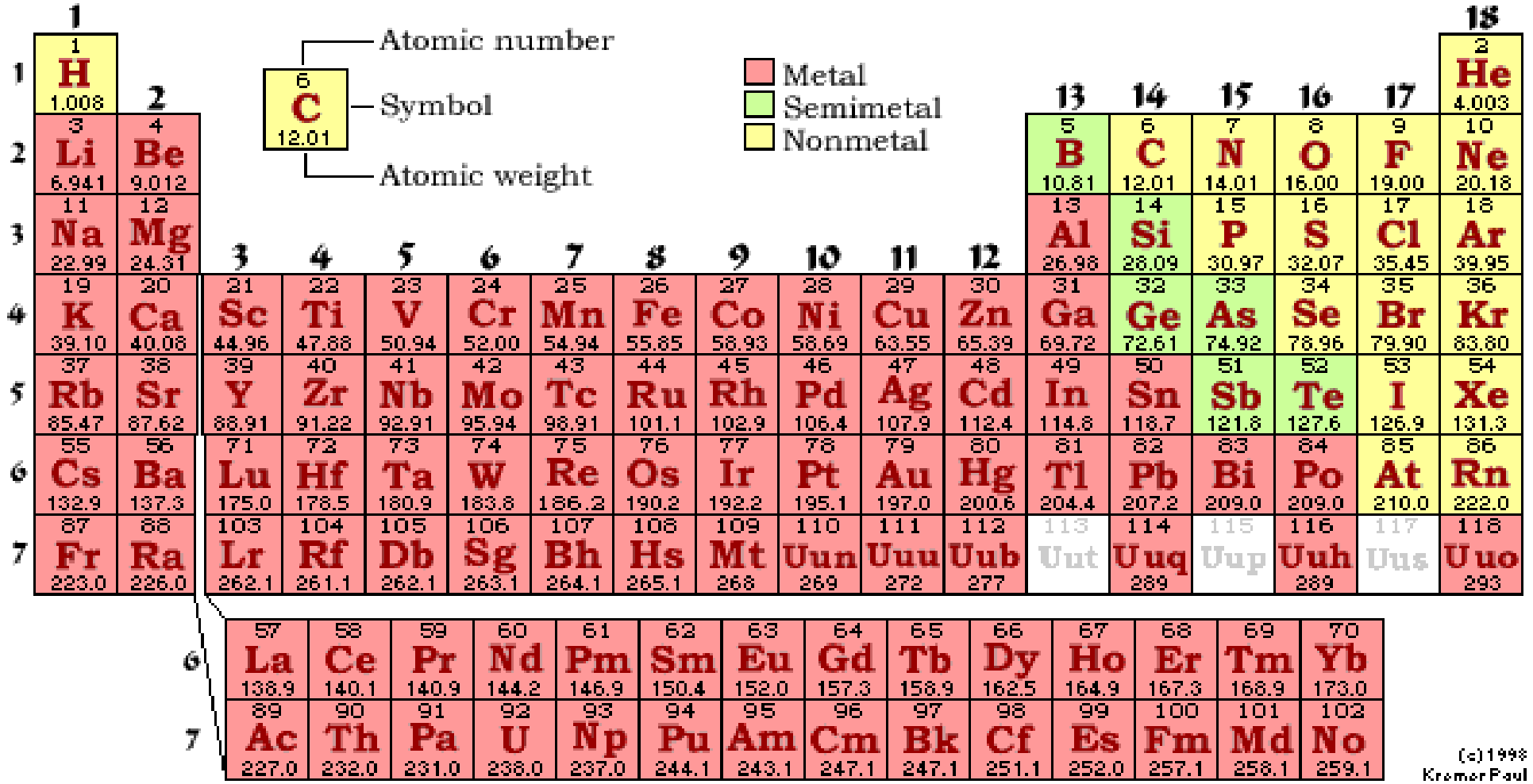
Horses and Pygs

Depiction of Ovid's narrative by Jean Raoux.



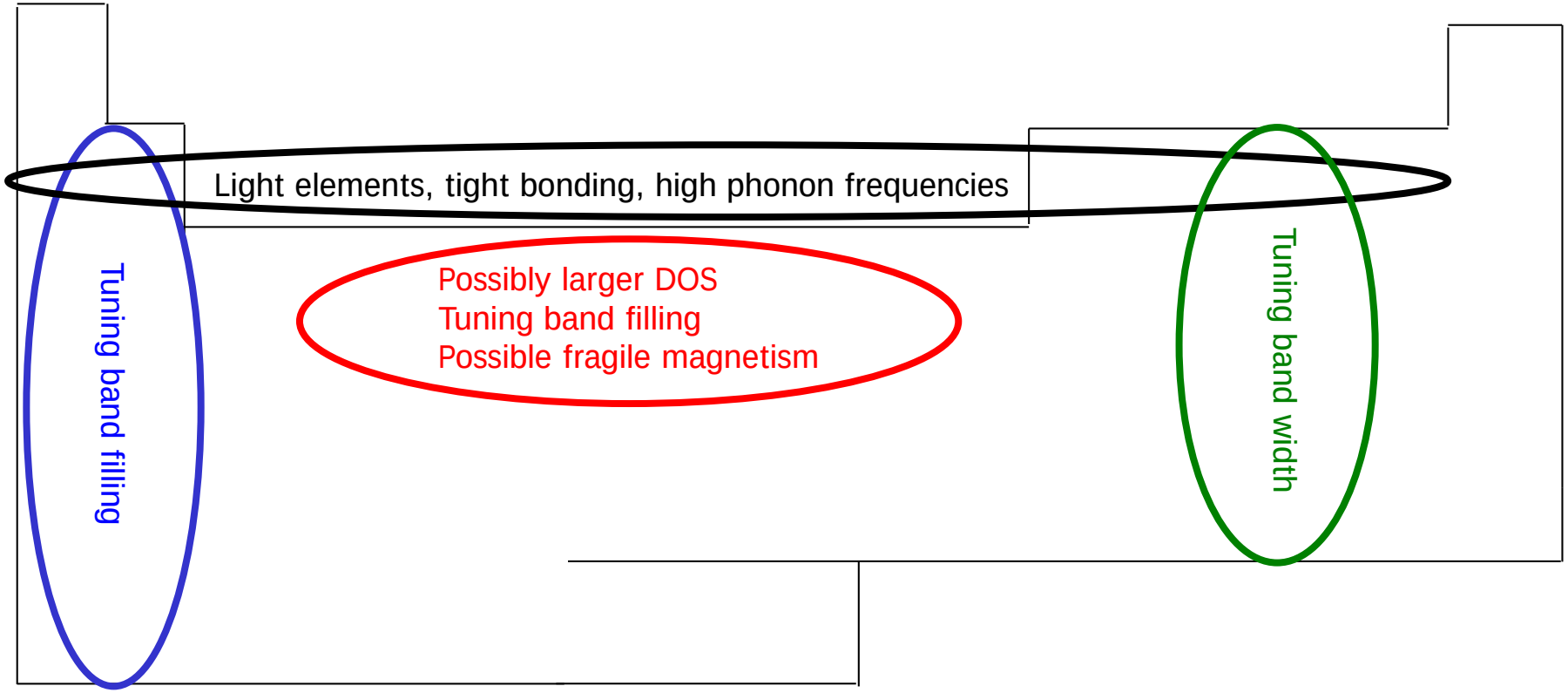
We actually can have our manipulations and ideas become physical reality.

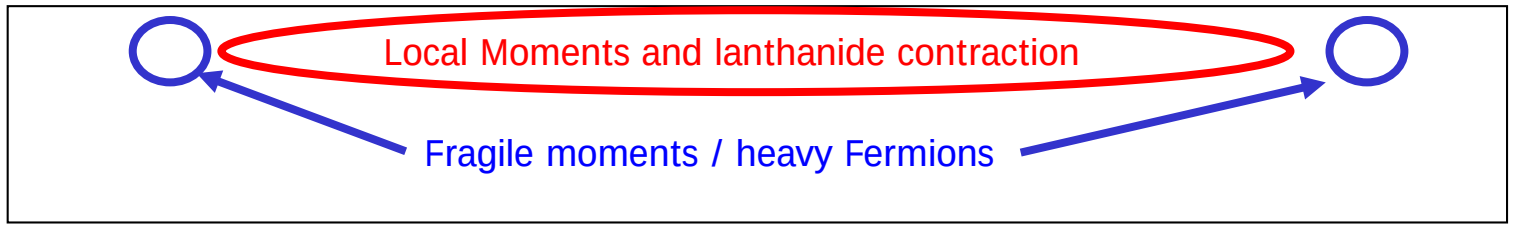
We try to project a Hamiltonian onto the periodic table.



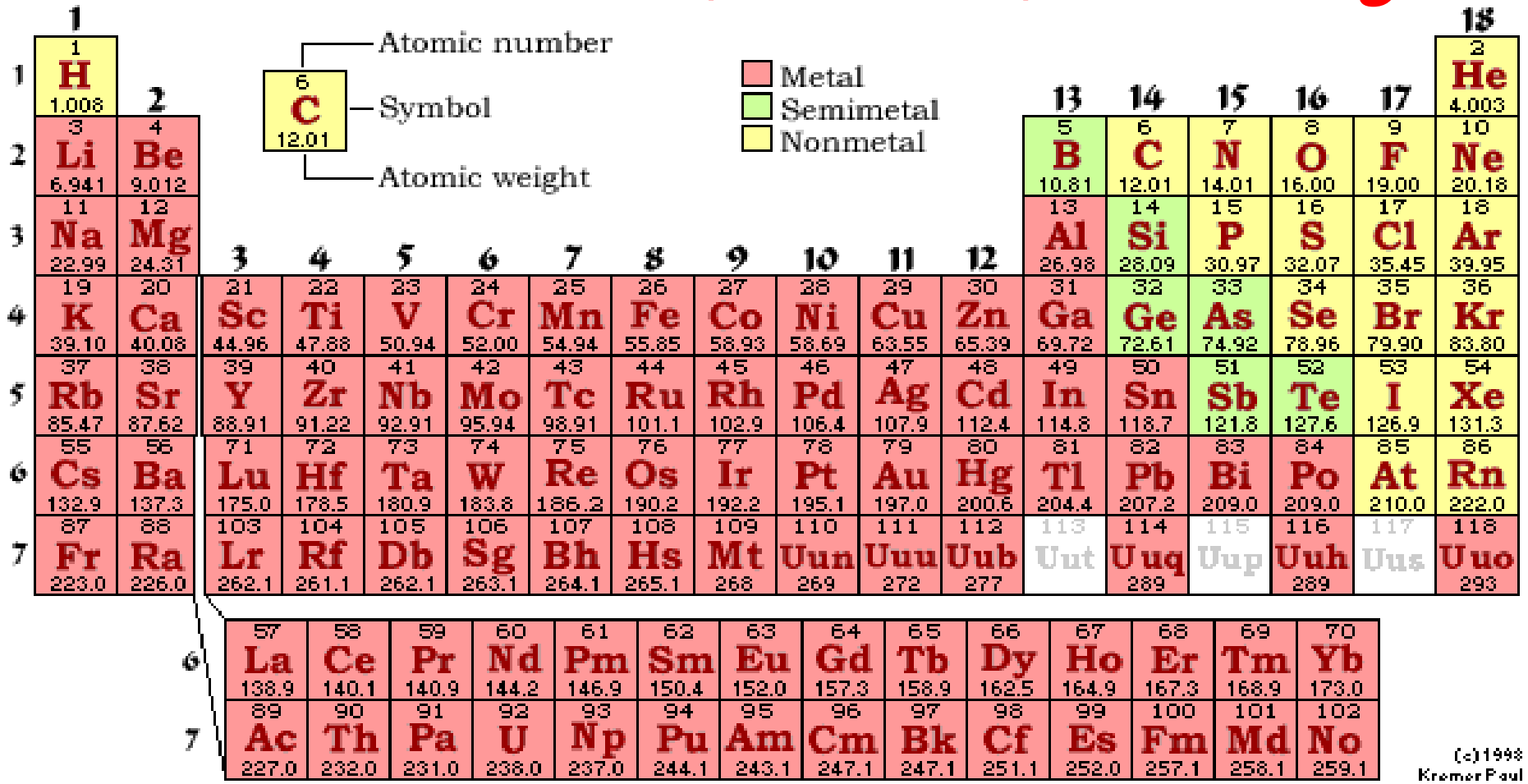
And then grow actual substances

For example, for superconductivity. Depending on type....





But the number of potential compounds is *huge!!*



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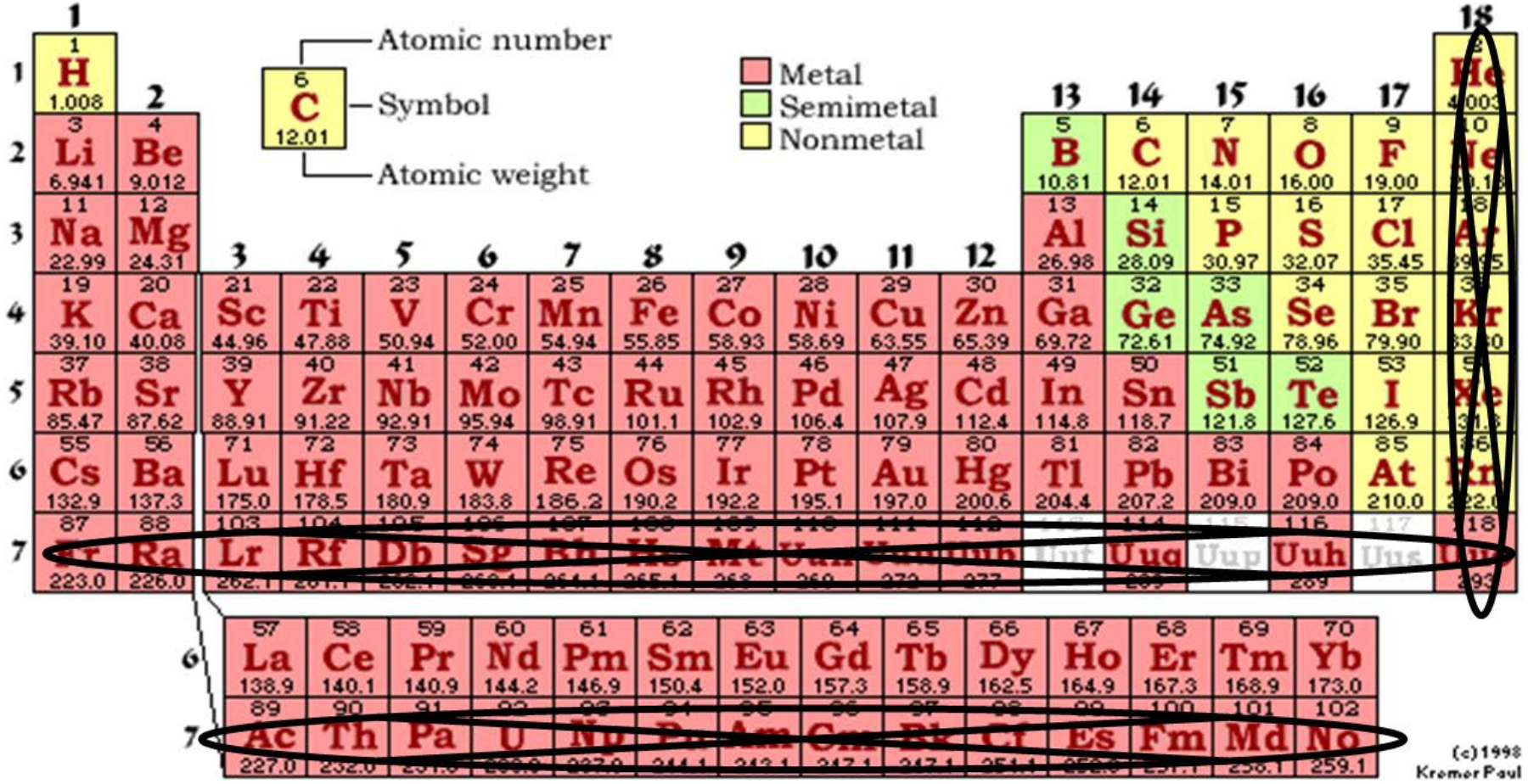
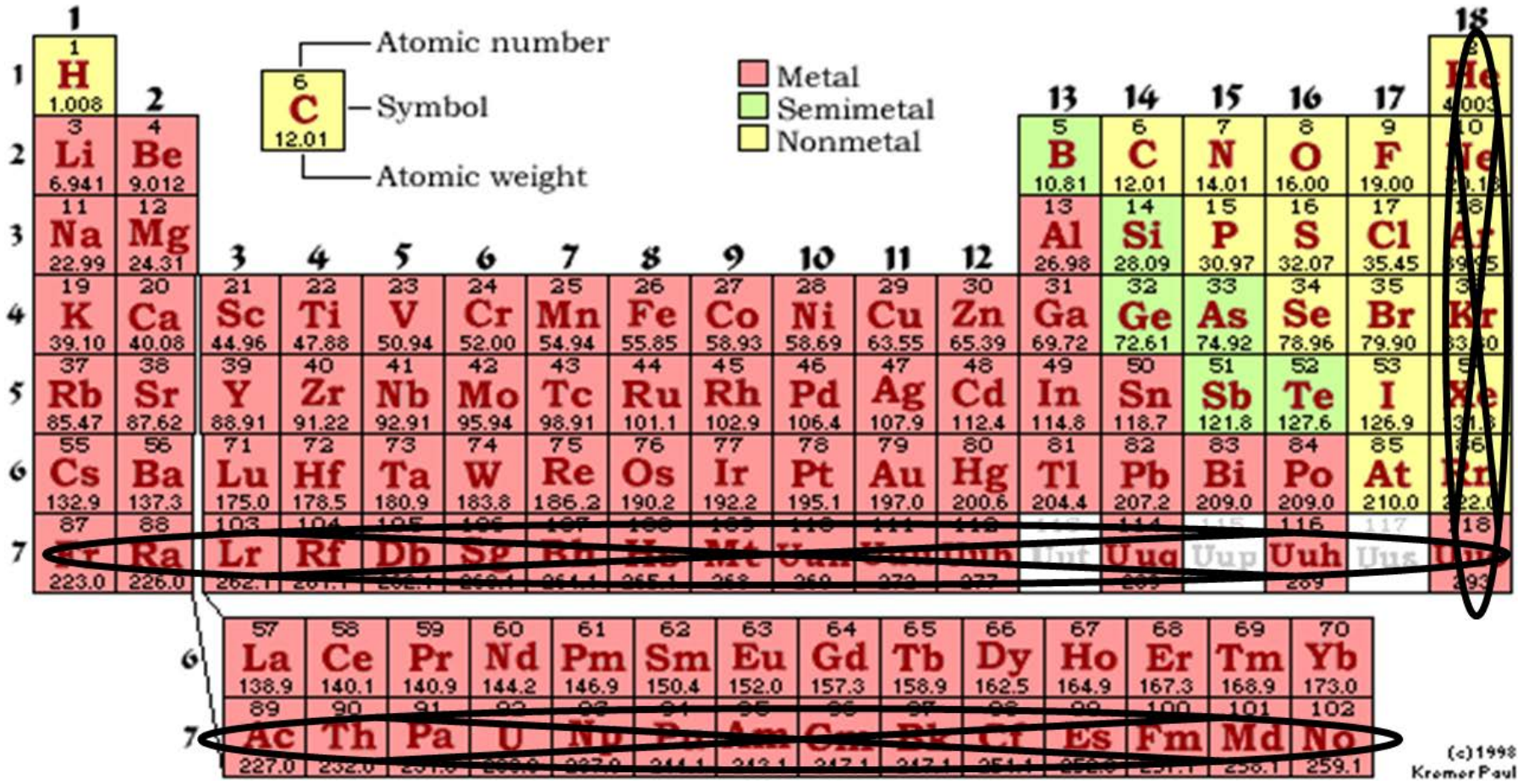


Even getting rid of noble gasses and most hot elements we have 80 elements to play with.

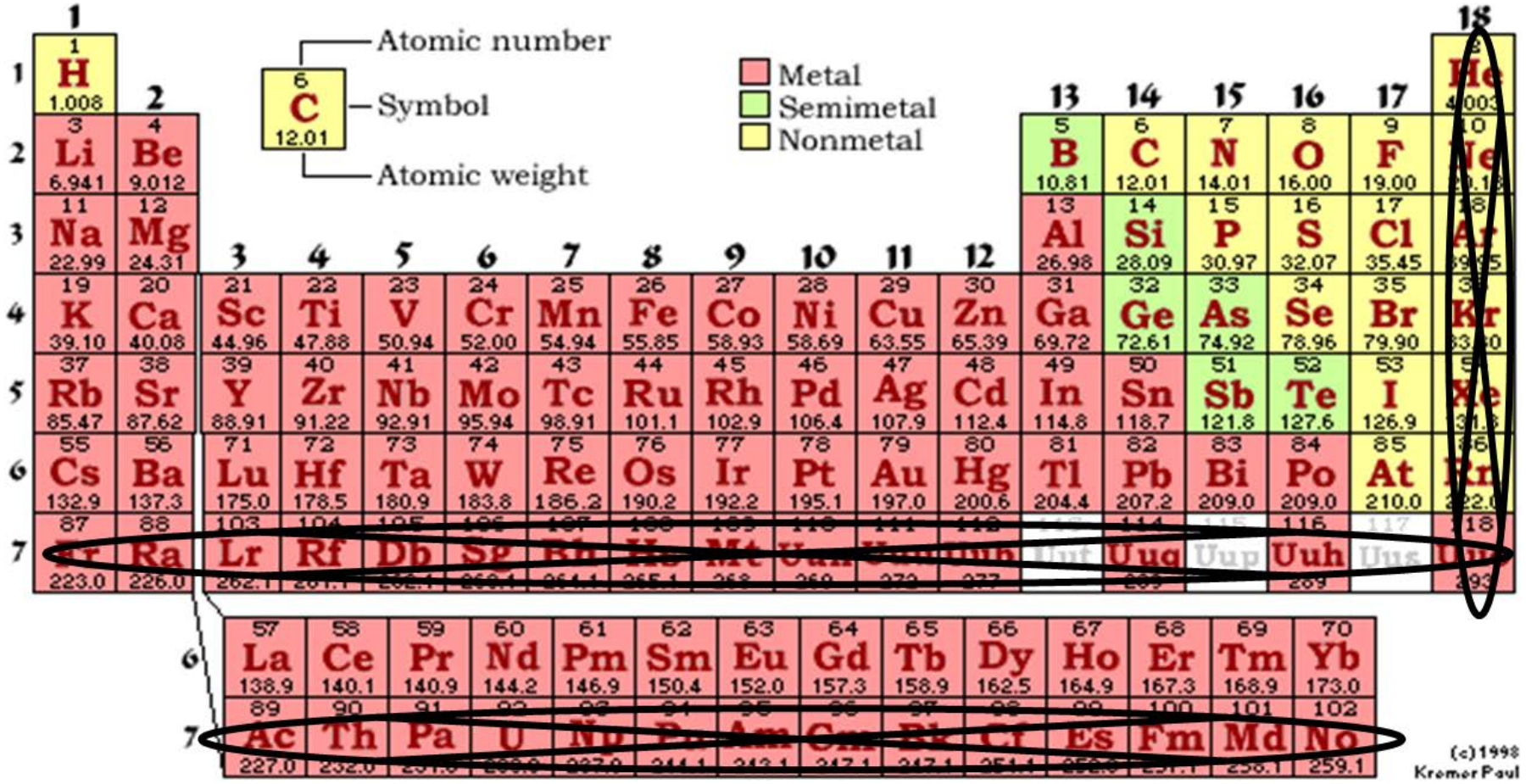
But the number of potential compounds is *huge!!*



Binary compounds: (80!/78!2!) x 3 ~ 10^4
Ternary compounds: (100!/97!3!) x 8 ~ 10^6

With quaternary and higher compounds, alloys, dopings, substitutions, etc.
There are millions – tens of millions of inorganic compounds.

But the number of potential compounds is *huge!!*



Binary compounds: (80!/78!2!) x 3 ~ 10^4

Ternary compounds: (100!/97!3!) x 8 ~ 10^6

The phase space is TOO BIG for blind combinatorials!!

How do we choose what sample to make?

In this talk, I want to give you an idea of how to...

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Coax the unicorn out of the forest

In this talk, I want to give you an idea of how to...

Coax the unicorn out of the forest

Encourage visions of sugar plums to dance through your head....

Or, if not “sugar plums” then other delightful things.

Or, if not “sugar plums” then other delightful things.

I *really* want to give you an idea of how to create ideas for new materials, and then make them manifest themselves.

For my own group, there are three basic motivations for making a growth:

Three ways we narrow the phase space.

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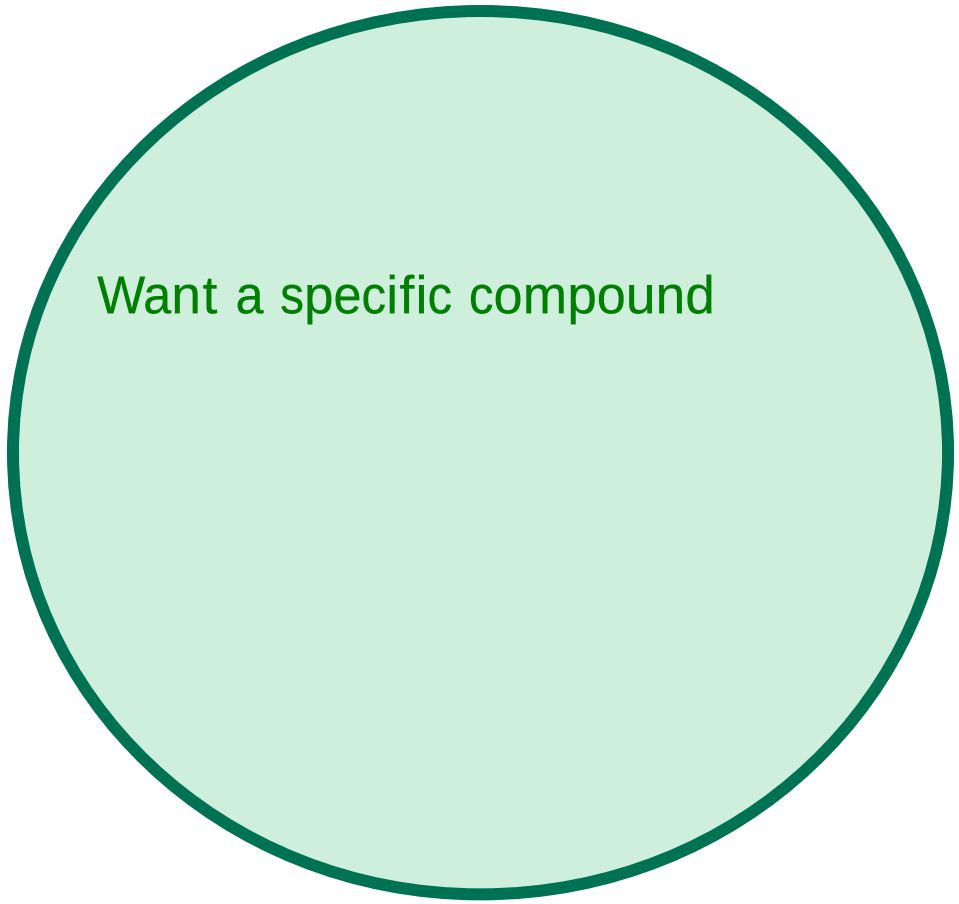
Three ways we narrow the phase space.



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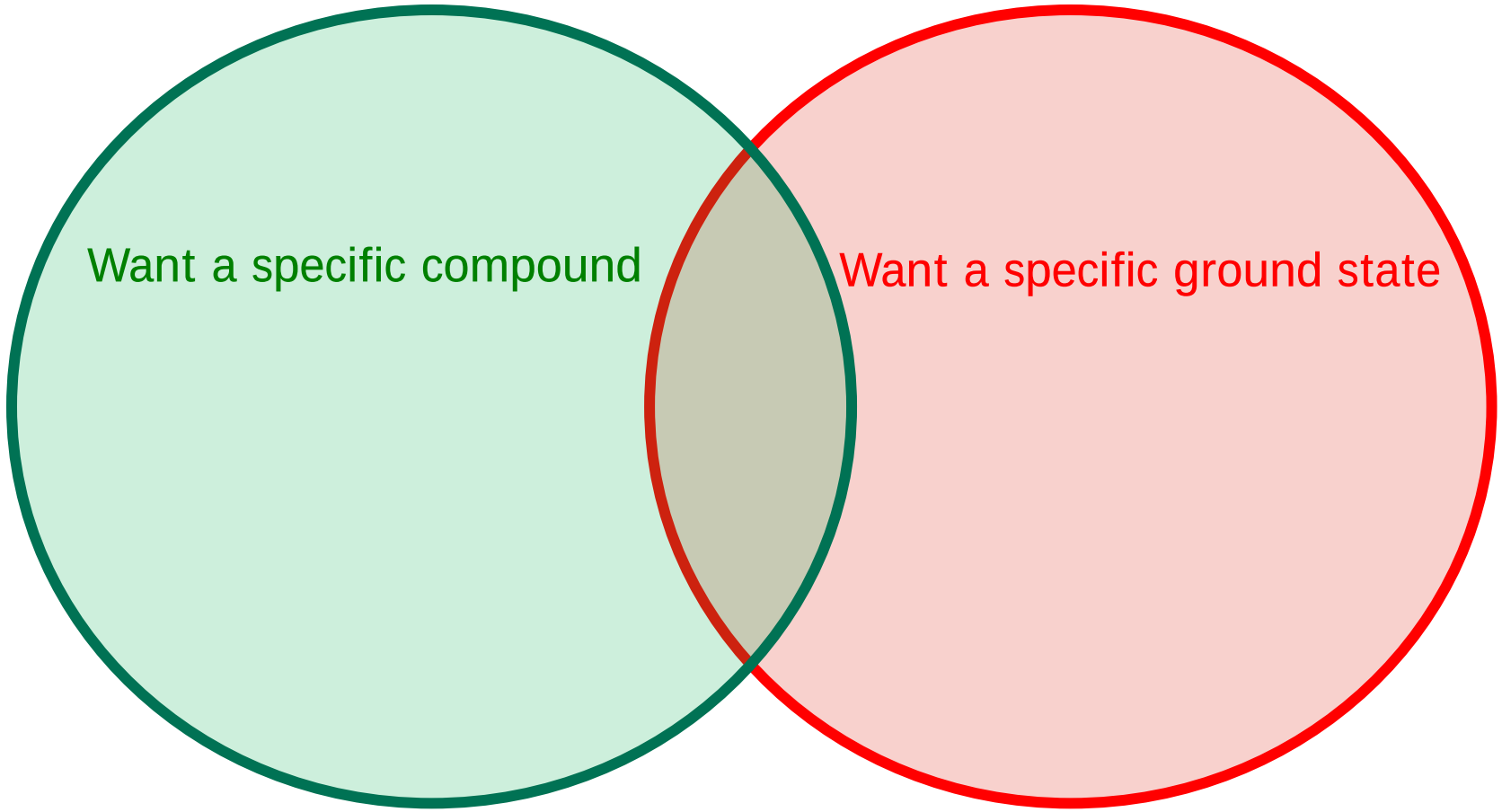

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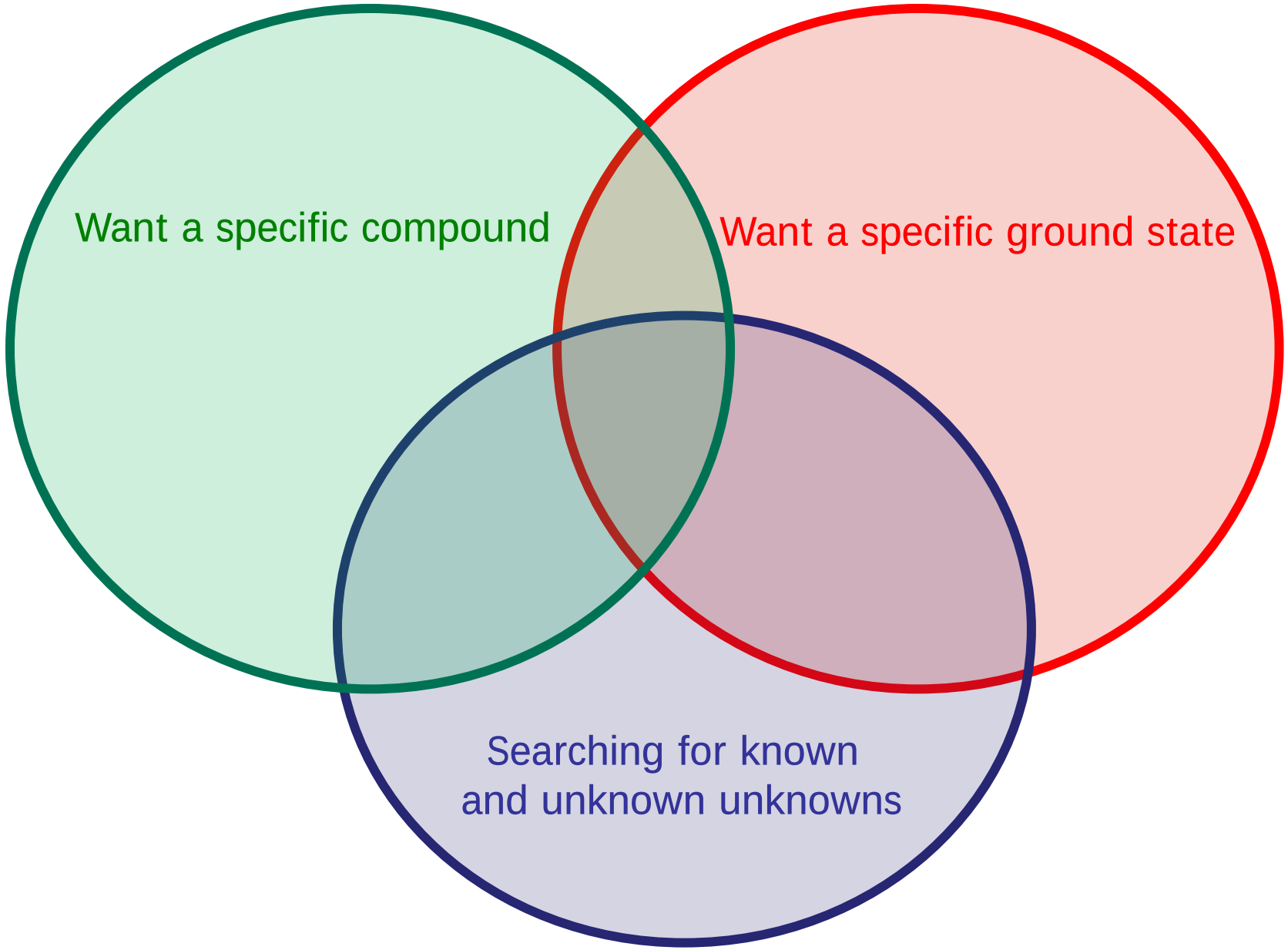

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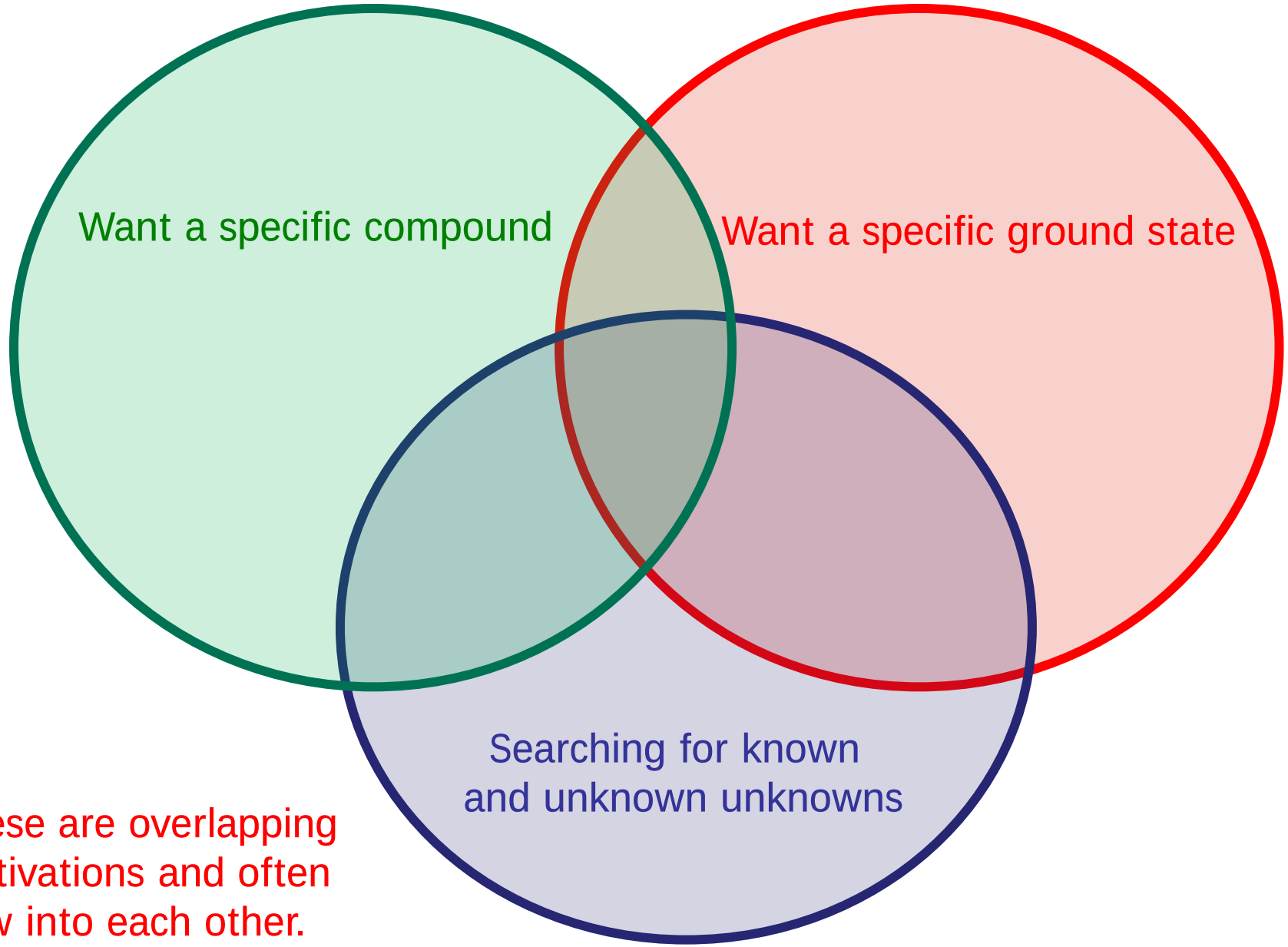

These are overlapping motivations and often flow into each other.

We can start with

Want a specific compound

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This greatly reduces phase space!

All possibilities become… .

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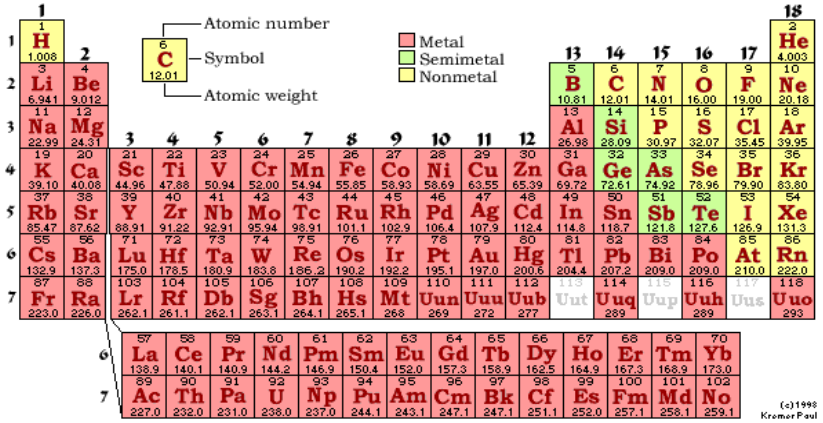

$= \delta(x, \bigcirc)$

A specific compound

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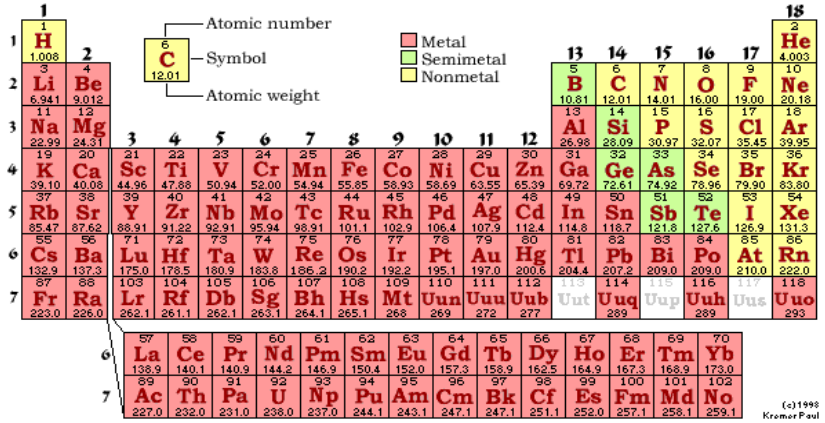


$= \delta(x, \bigcirc)$

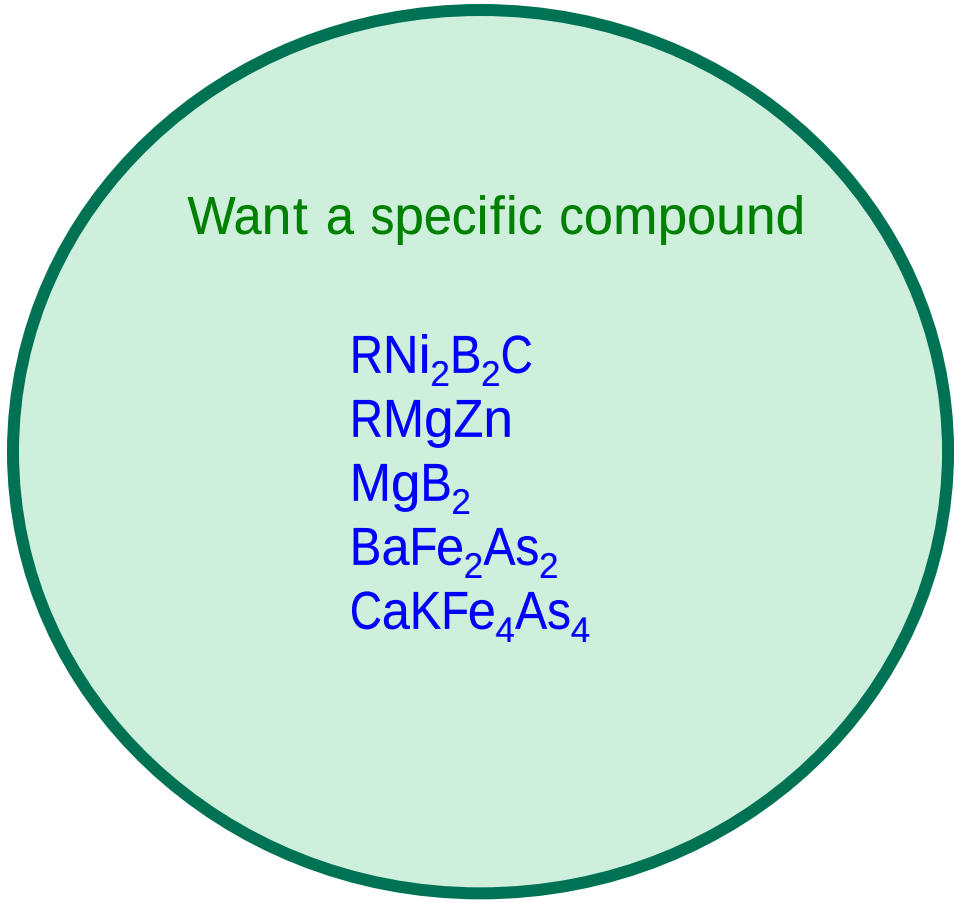
A specific compound*…that often is part of the birth of a new field*

Examples

Want a specific compound

RNi_2B_2C
RMgZn
MgB_2
$BaFe_2As_2$
$CaKFe_4As_4$

Examples



It is worth noting that in each of these cases the very strong desire to make the compound (so that we could get on with the measurement) led us to extend out growth techniques and capabilities.

In 1994 two related superconducting compounds were discovered:

YPd_2B_2C: $T_C \sim 23$ K

$LuNi_2B_2C$: $T_C \sim 17$ K

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Quaternary compound

Refractory compound

It is incongruently melting

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This is a tricky growth.

Quaternary compound

Refractory compound

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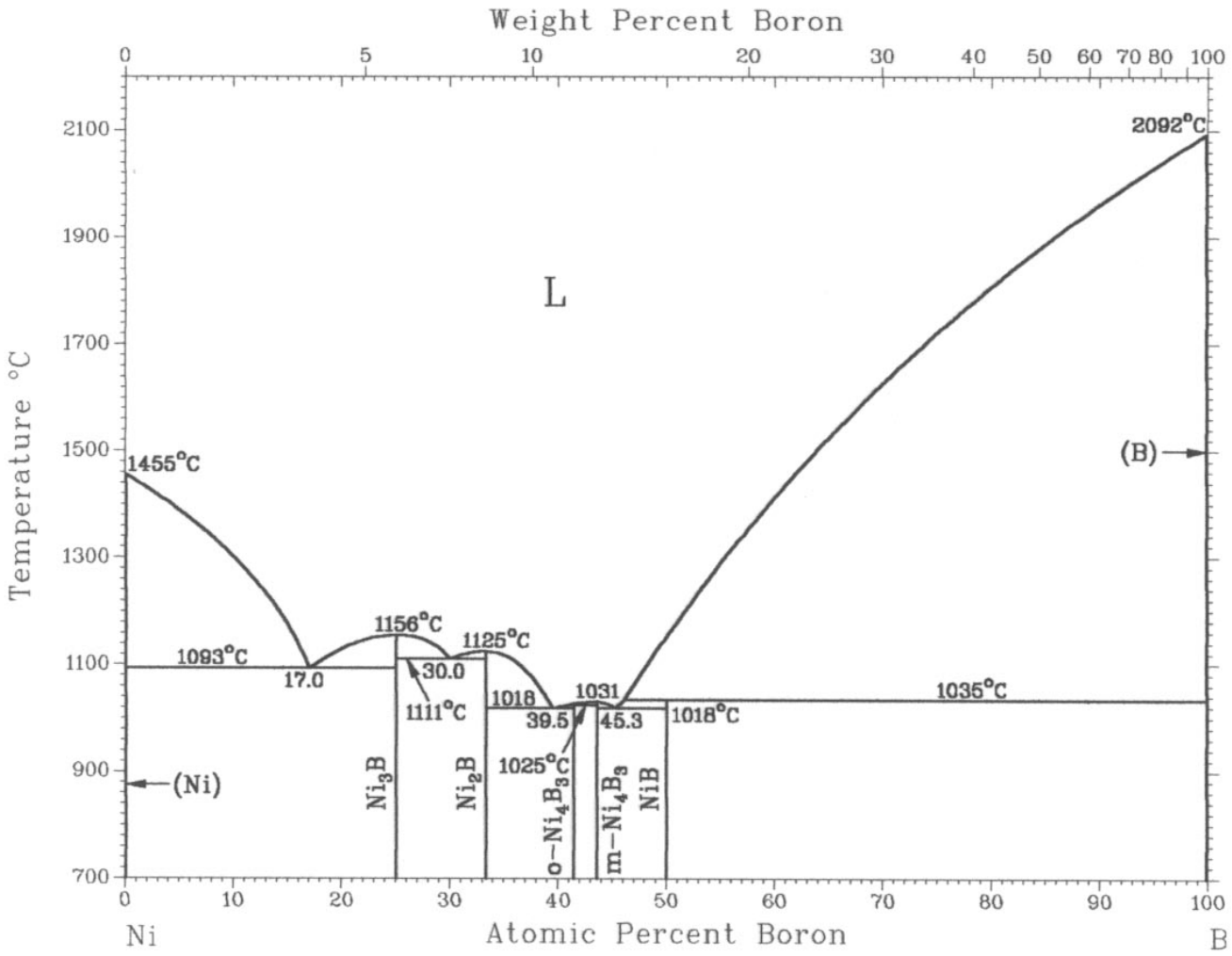
On the other hand, there is a nice eutectic in the B-Ni binary system....



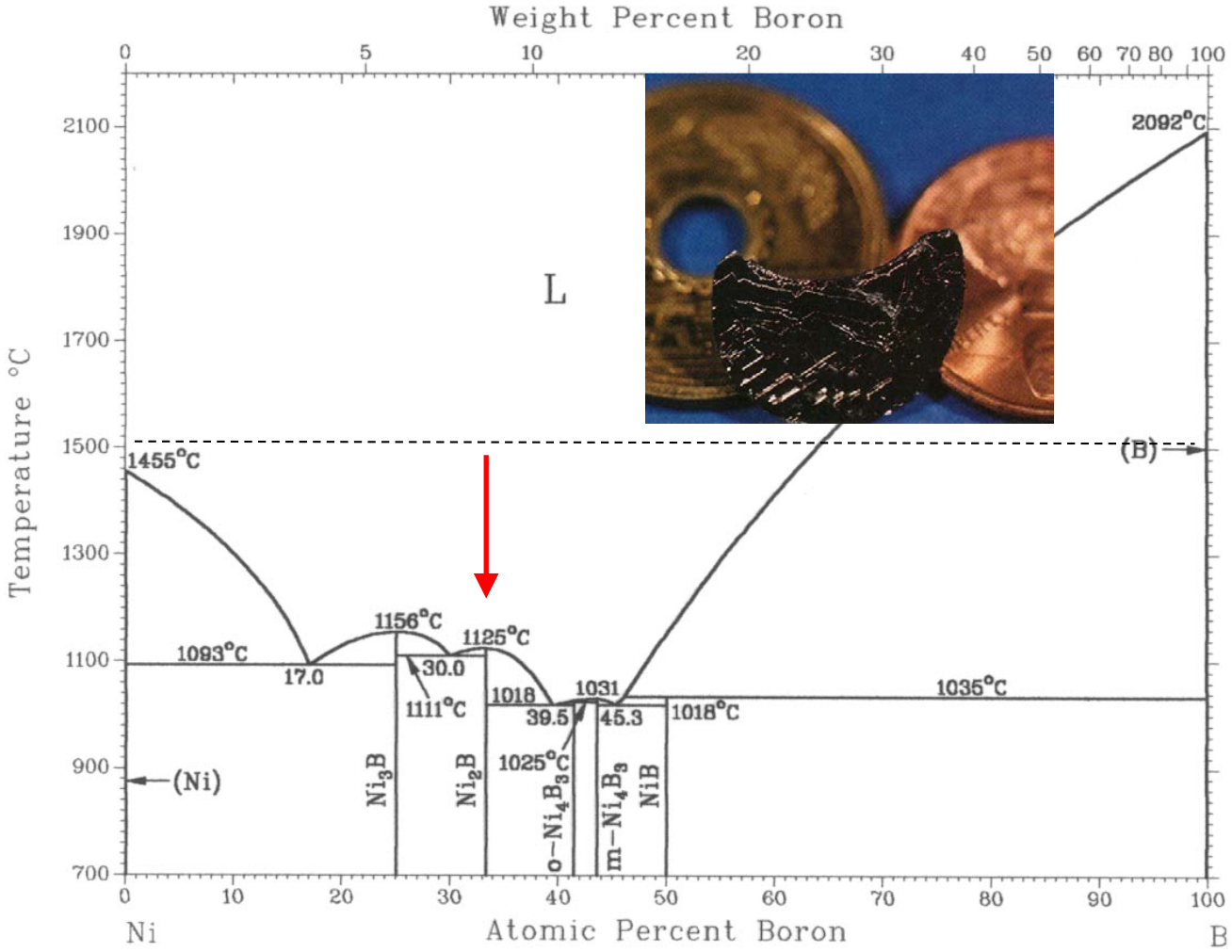
In 1994 two related superconducting compounds were discovered:

$LuNi_2B_2C$: T_C ~17 K

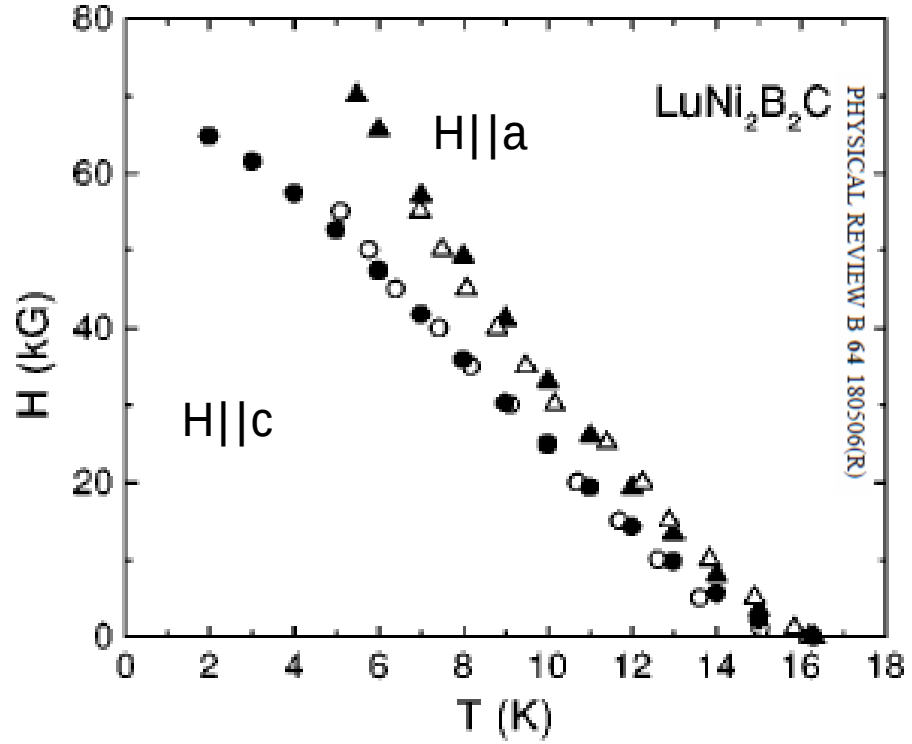
Want a specific compound

This is a tricky growth.

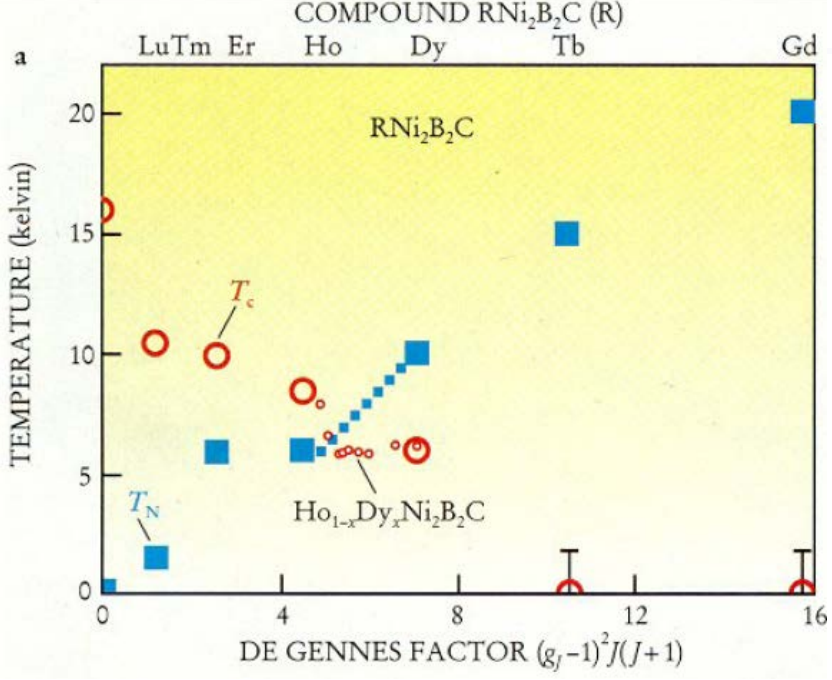
With a two step growth from 1500 C to 1200 C followed by a resealing in silica and a 1200 C decant, we could grow substantial single crystals.

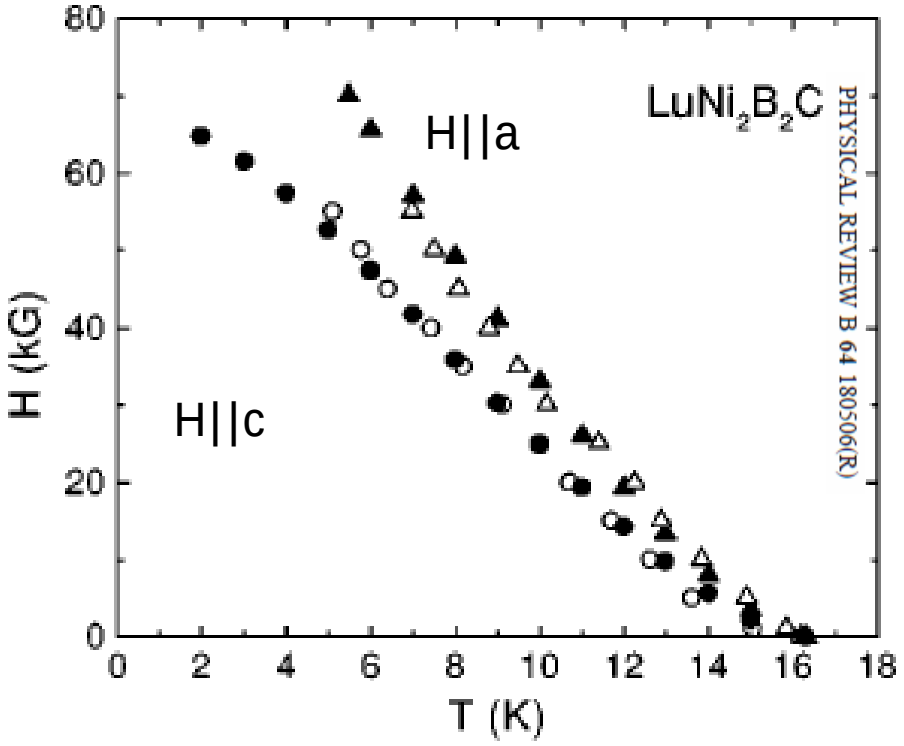


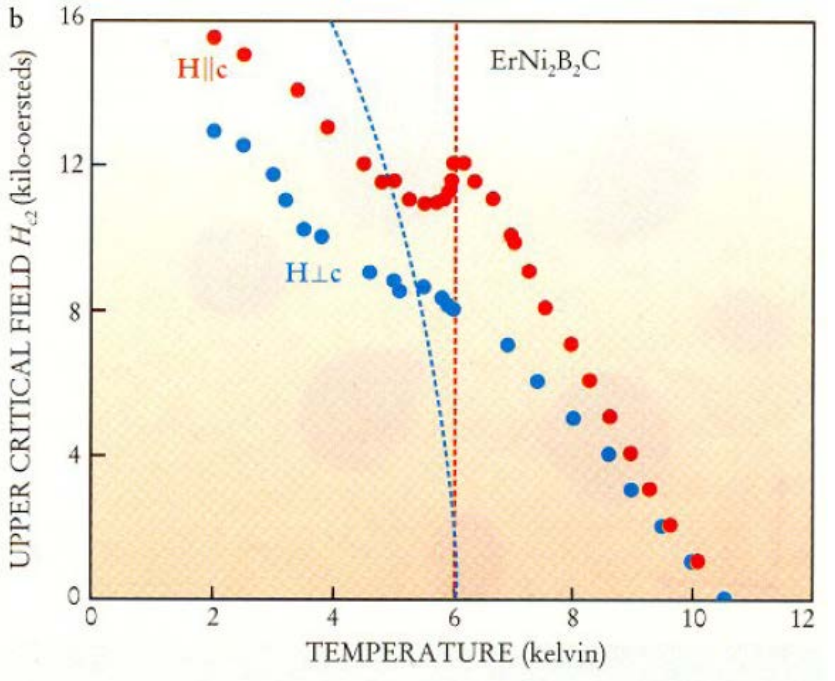
We could study $LuNi_2B_2C$

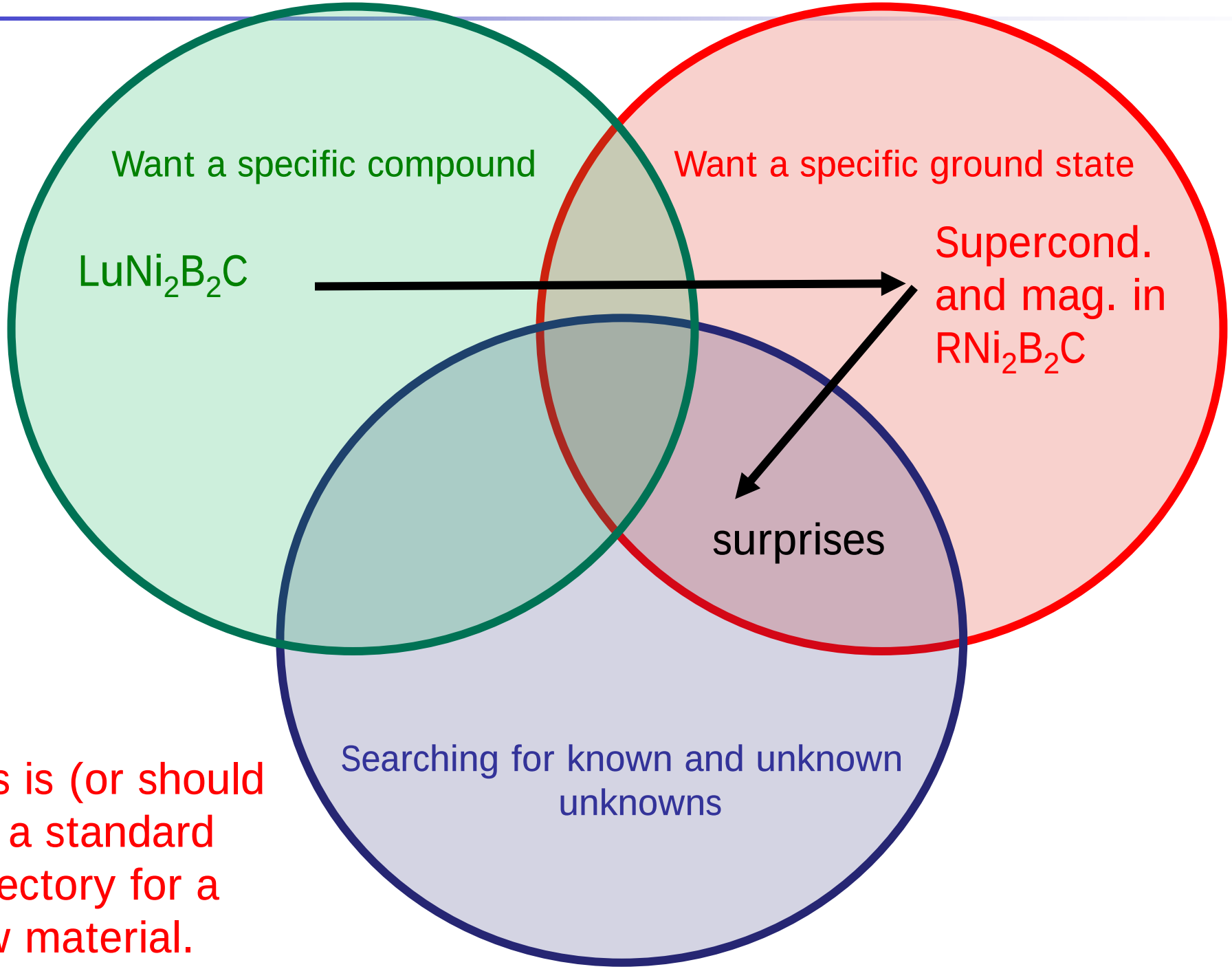


We could study $LuNi_2B_2C$ and then, with growth under control, study the interaction between superconductivity and local moment magnetism across the RNi_2B_2C series.



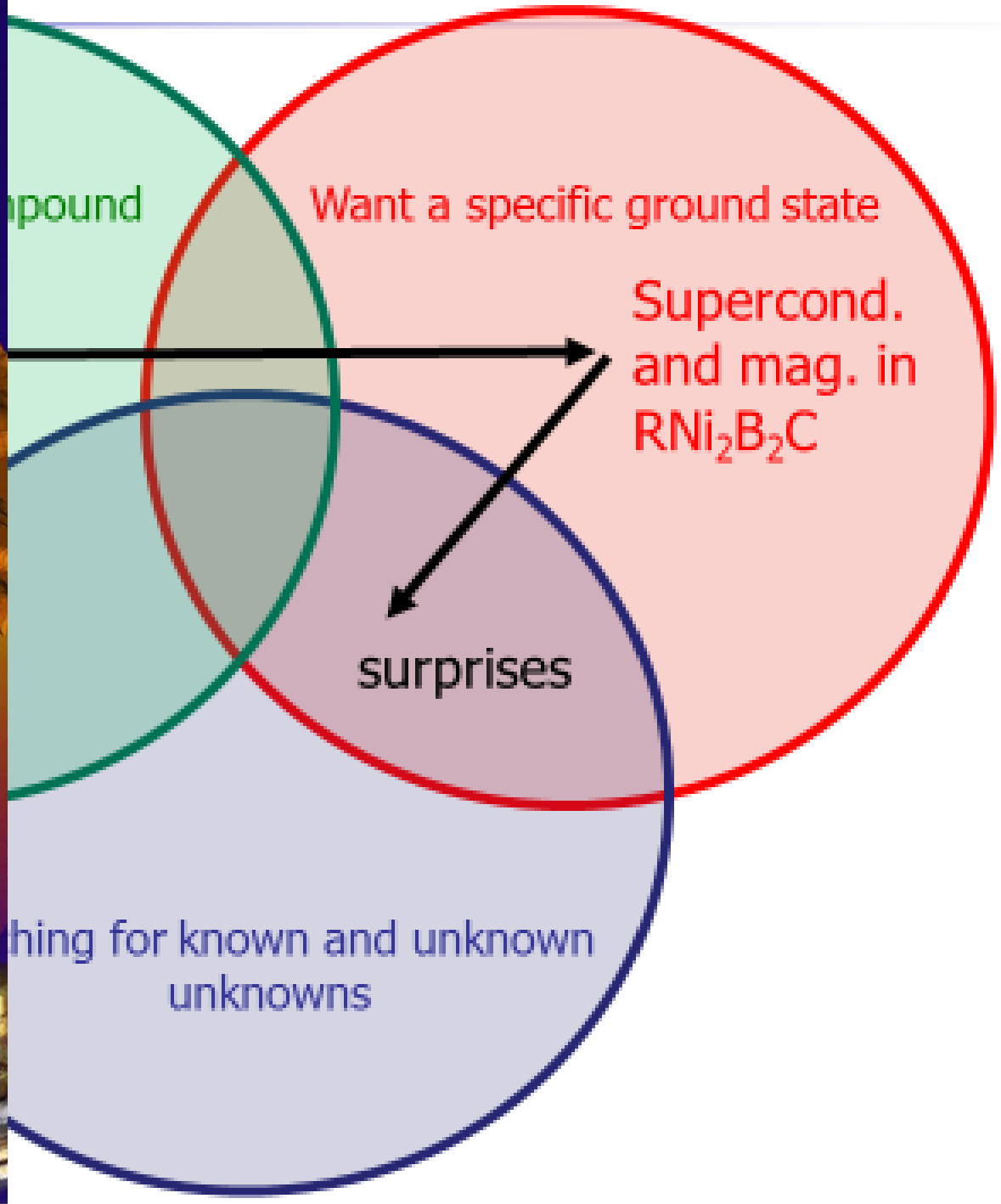






This is (or should be) a standard trajectory for a new material.

21 May 1998
International weekly journal of science
nature
$10.00
Magnetism in superconductors
Carbon cycle
Changing climate, shifting stocks?
Risk factor
p53 polymorphism and cervical cancer
Video games
Striatal dopamine release


pound
Want a specific ground state
Supercond. and mag. in RNi_2B_2C
surprises
hing for known and unknown unknowns

In 1997 we became interested in growing RMgZn quasicrystals (to study their magnetic properties).
All prior samples had been poly-grain and poly-phase.

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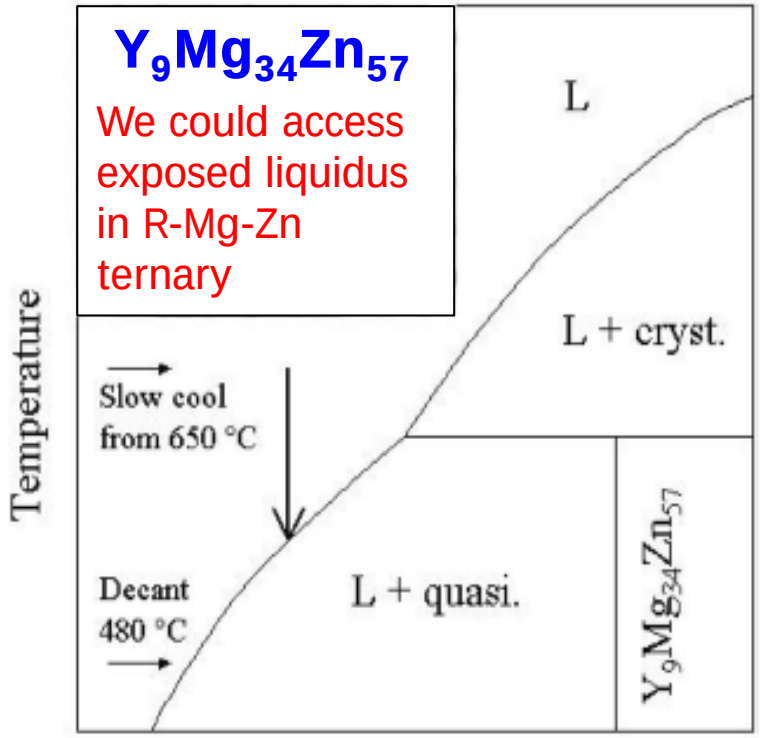

Journal of Alloys and Compounds 317–318 (2001) 443–447

Fig. 1. (a) Schematic pseudo-binary cut of the Y–Mg–Zn phase diagram approximately along the $Y_xMg_{60-3x}Zn_{40-2x}$ line (based on Ref. [2]). Vertical arrow represents initial melt with composition $Y_3Mg_{51}Zn_{46}$. Note: neither axis is to scale. Inset: photograph of HoMgZn single grain over mm scale.

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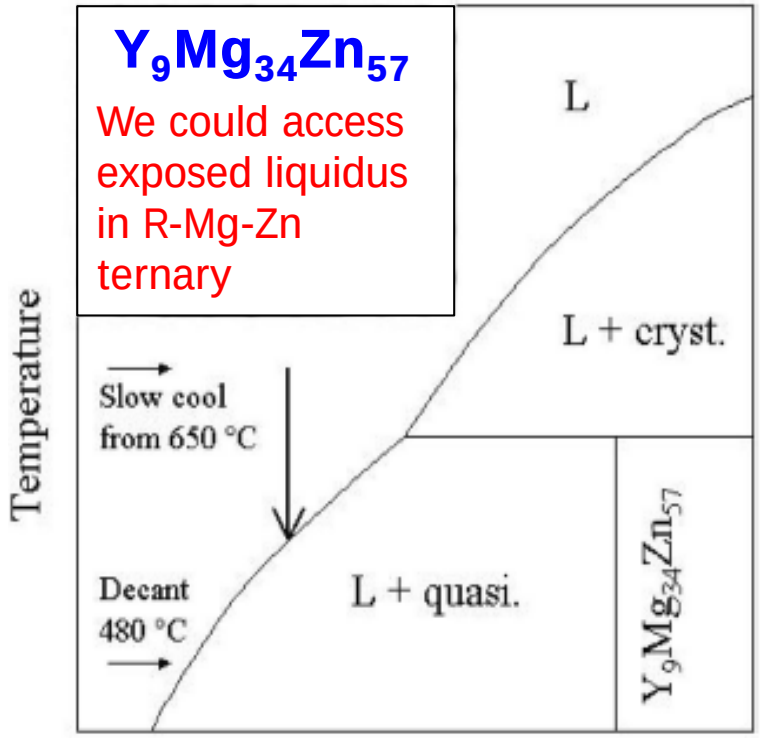

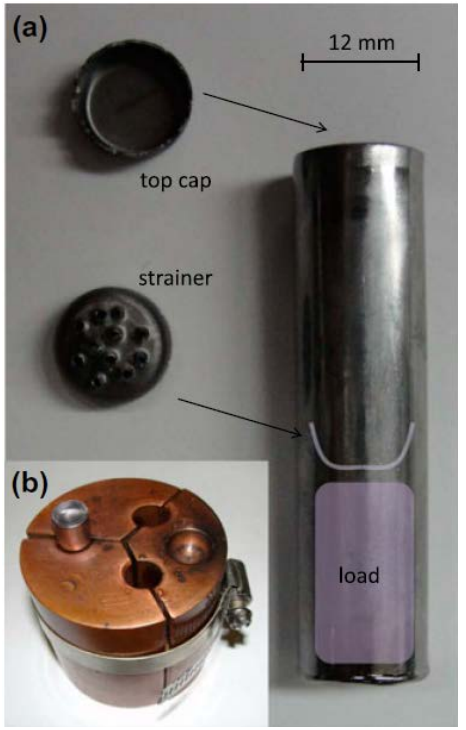

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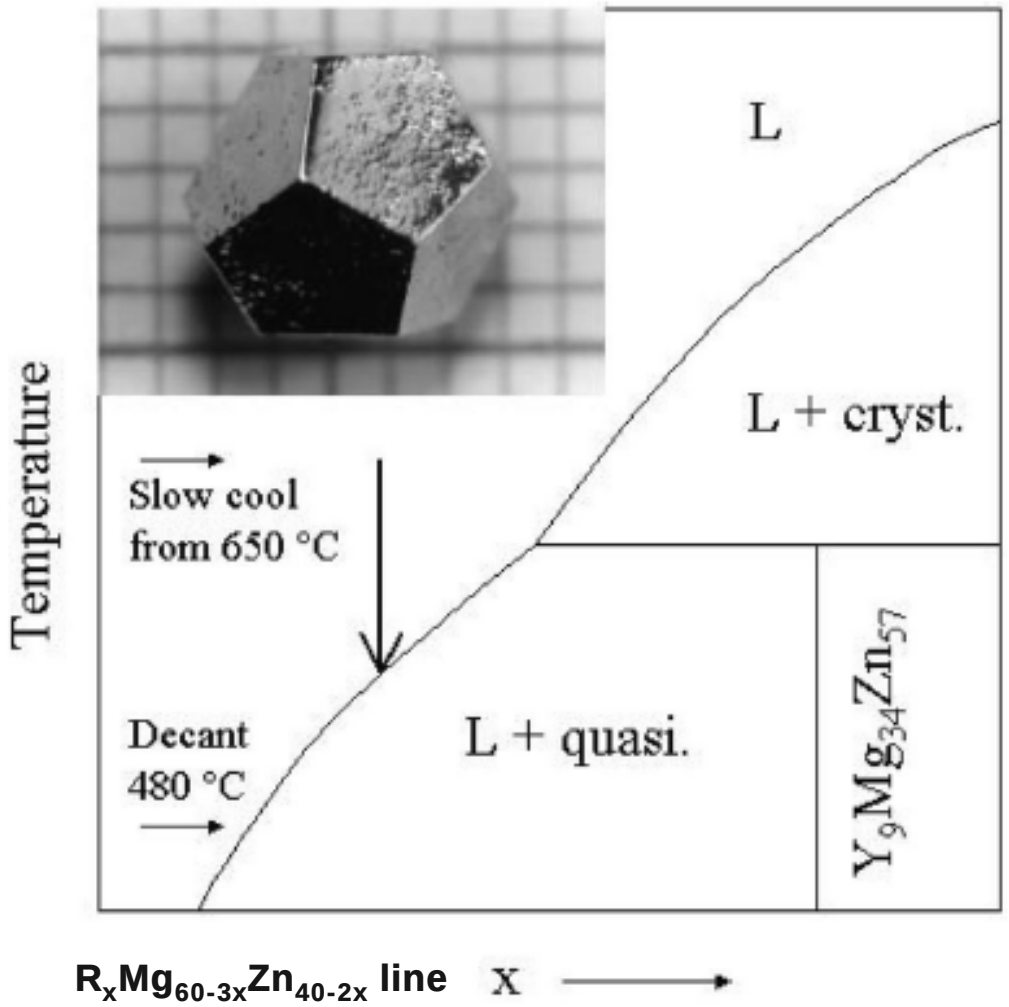
Since the growth was done out of a Mg rich solution we had to develop a Ta 3-cap crucible to hold the melt and still allow for decanting of the liquid *(due to extreme reactivity of Mg with Al_2O_3 and silica)*.

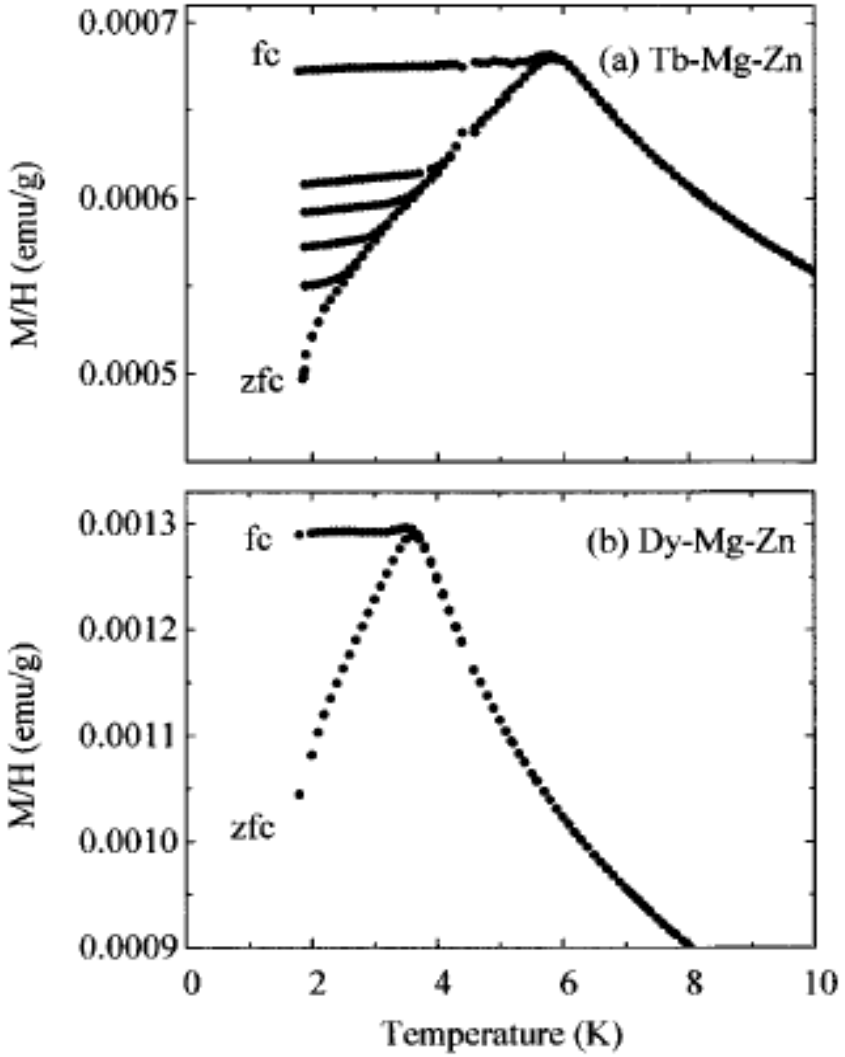
Solution grown single grain of $R_9Mg_{34}Zn_{57}$ revealing natural growth habit.

With samples like this we were able to clearly determine the intrinsic properties of this compounds.

$R_9Mg_{34}Zn_{57}$

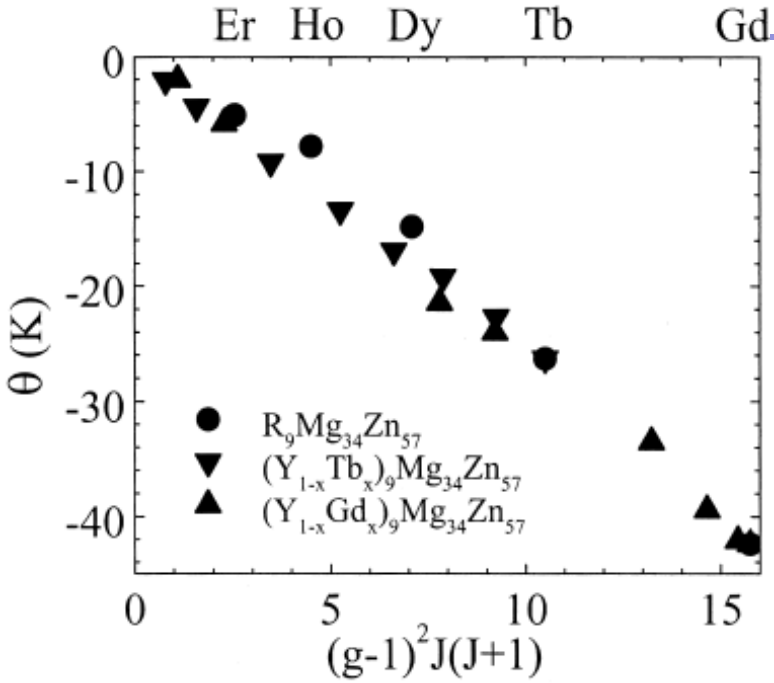
We were able to grow for R = Y, Gd – Er

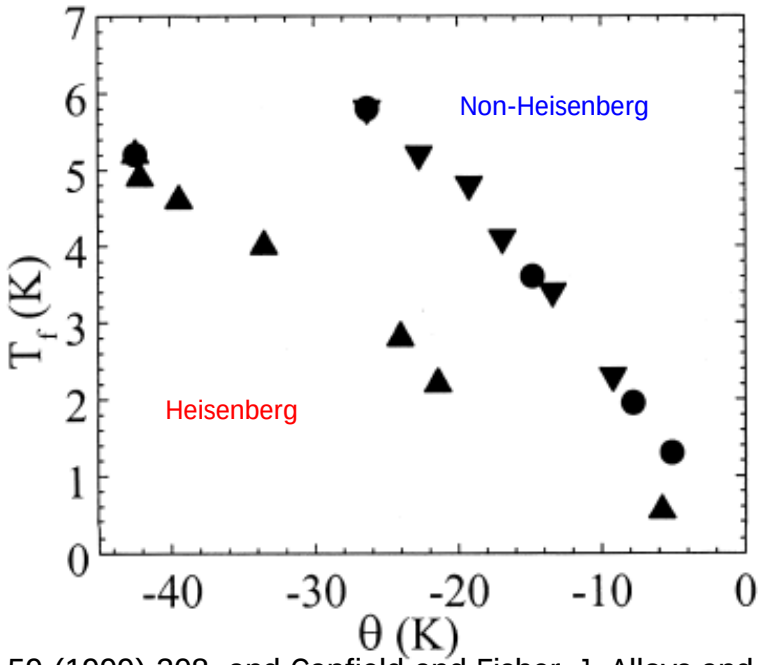




Fisher et al., PRB 59 (1999) 308, and Canfield and Fisher, J. Alloys and Comp. 317 (2001) 443

Given that the system is highly ordered but not periodic ....an ideal spin-glass system





Model system: *is there a difference between a Heisenberg and non-Heisenberg spinglass?*

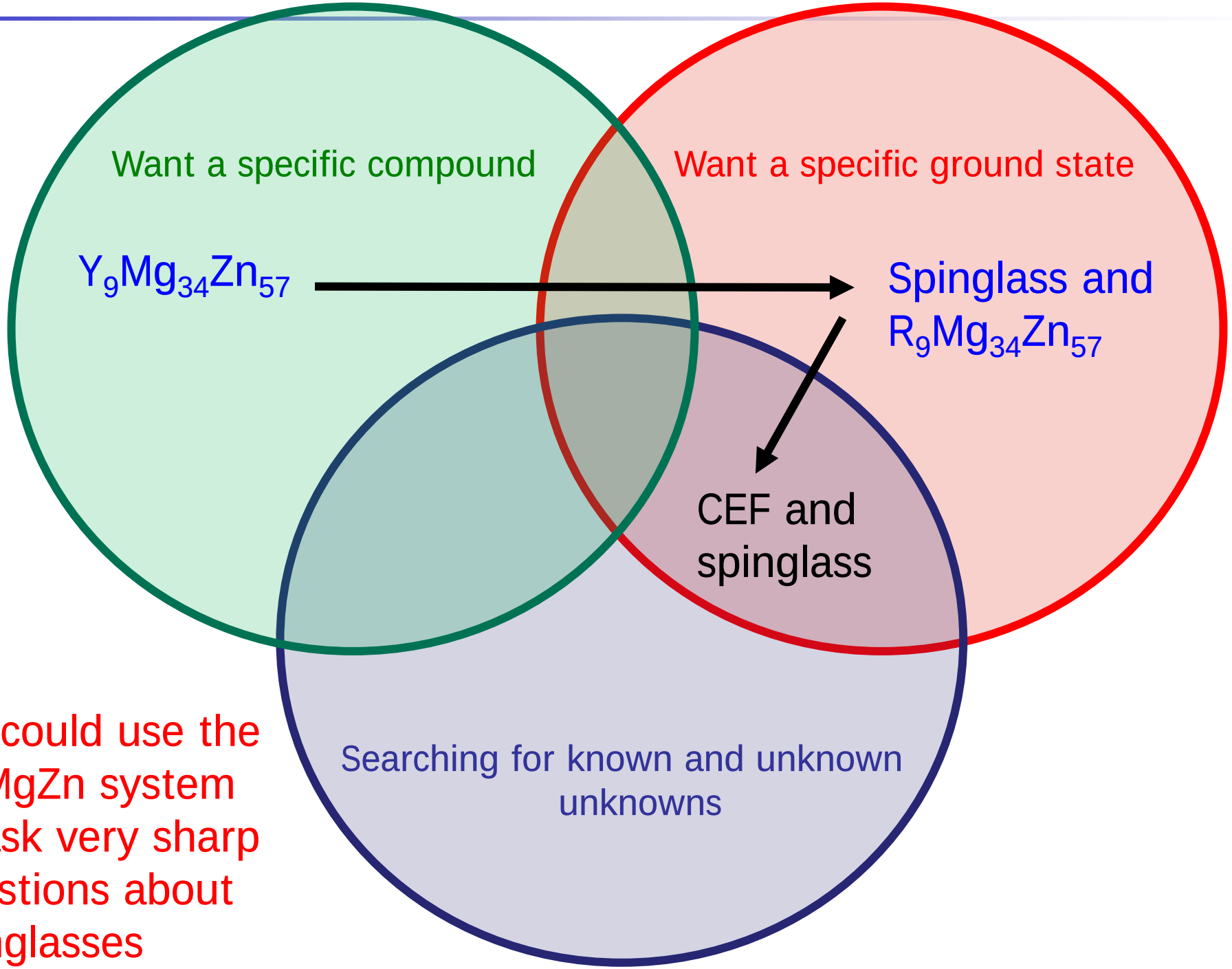
A floor covered with marbles is slippery.

If each marble is non-spherical, then the floor will be less slippery and more inclined to seize up.

A spin glass comprised of spherically symmetric moments (Gd) freezes at a lower temperature than a spin glass comprised of non-spherically symmetric moments (due to crystalline electric field splitting).

Key insight: for spinglasses we can replace "random" with "aperiodic".

Fisher et al., PRB 59 (1999) 308, and Canfield and Fisher, J. Alloys and Comp. 317 (2001) 443



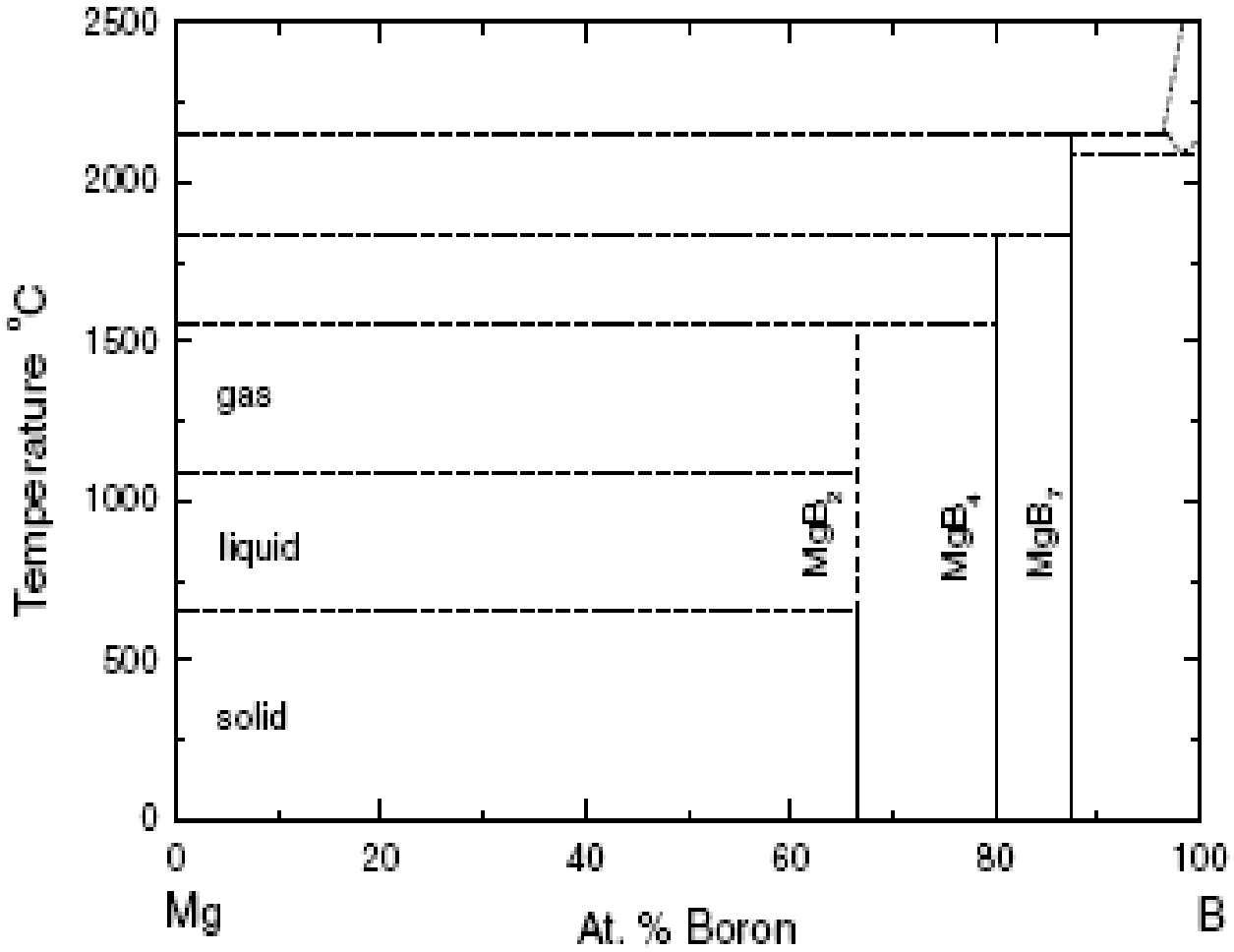
We could use the i-RMgZn system to ask very sharp questions about spinglasses

In early 2001 there were rumors that MgB_2 may superconduct near 40 K.

Want a specific compound

In early 2001 there were rumors that MgB_2 may superconduct near 40 K.

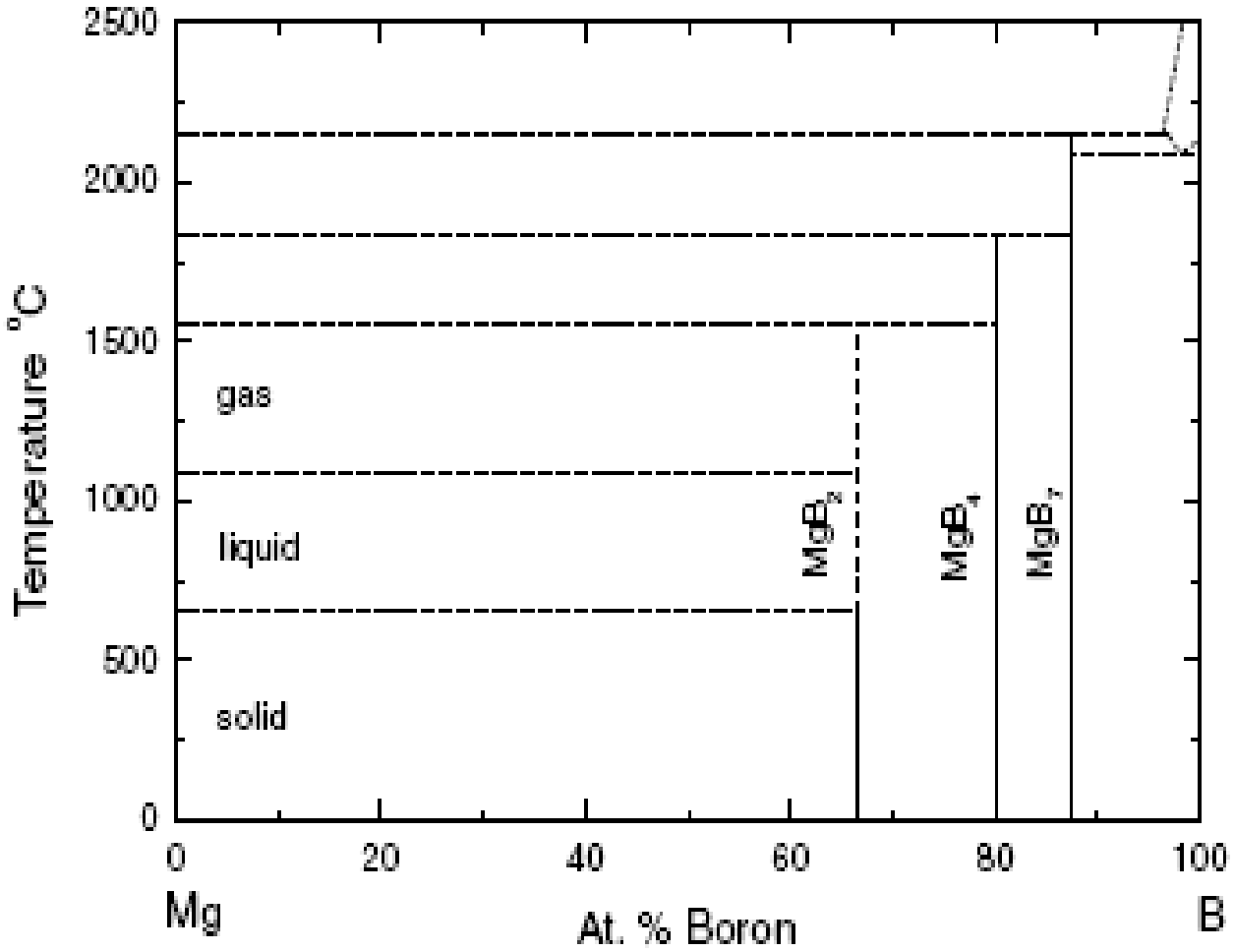
Want a specific compound



At ambient pressure, this is a very inauspicious phase diagram. There is no exposed liquidus line at all.

In early 2001 there were rumors that MgB_2 may superconduct near 40 K.

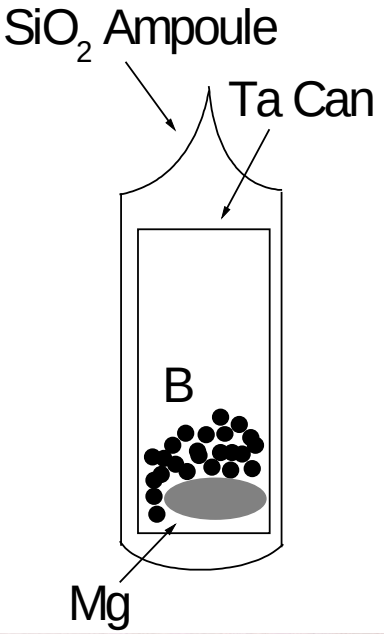
Want a specific compound

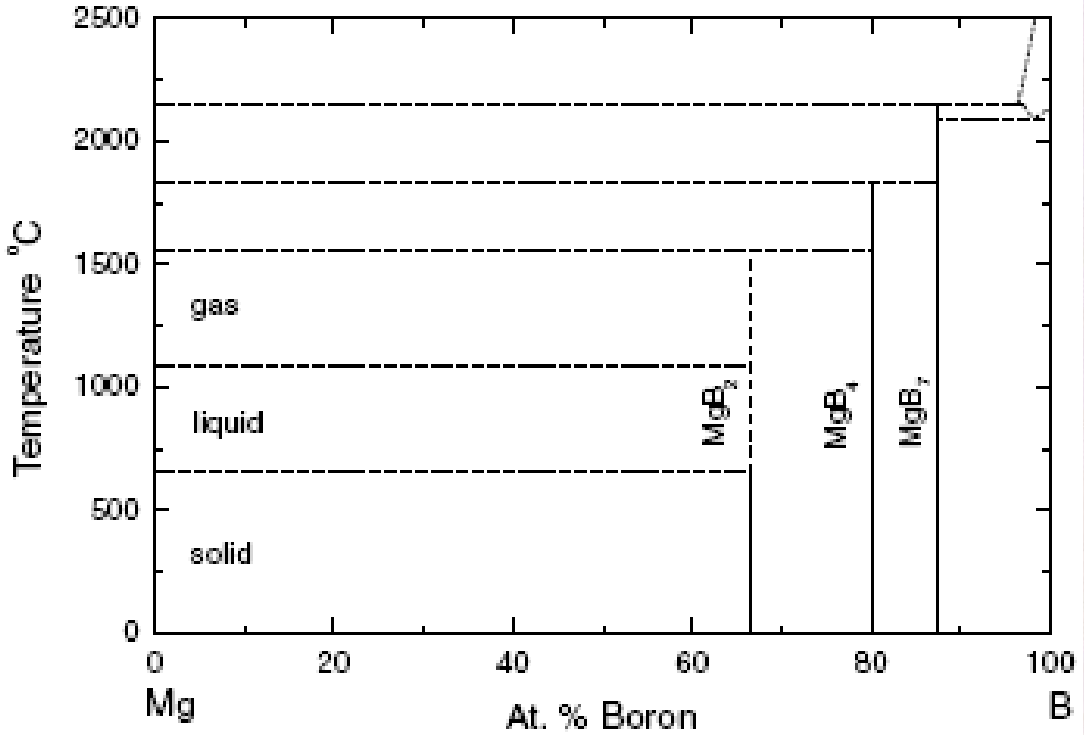


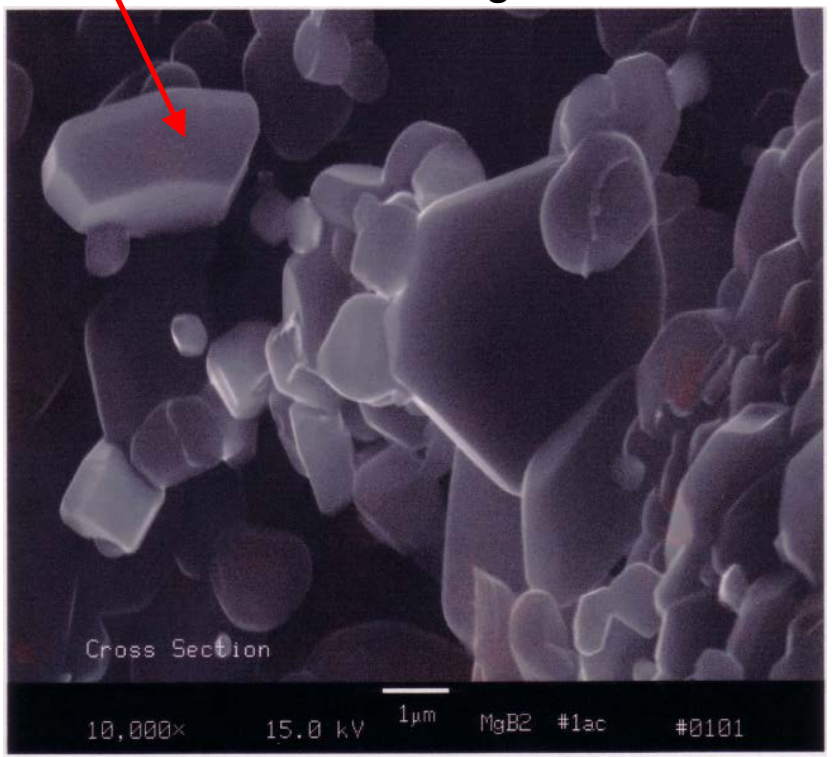
We actually tried over 100 growths with various ternary and even quaternary melts….

At ambient pressure, this is a very inauspicious phase diagram. There is no exposed liquidus line at all.

On the other hand, we found that at 950 °C, although the B powder is no where close to melting, it will react with Mg vapor (~1/3 atm. at 950 °C) to form MgB_2 *within as little as 3 hours*.







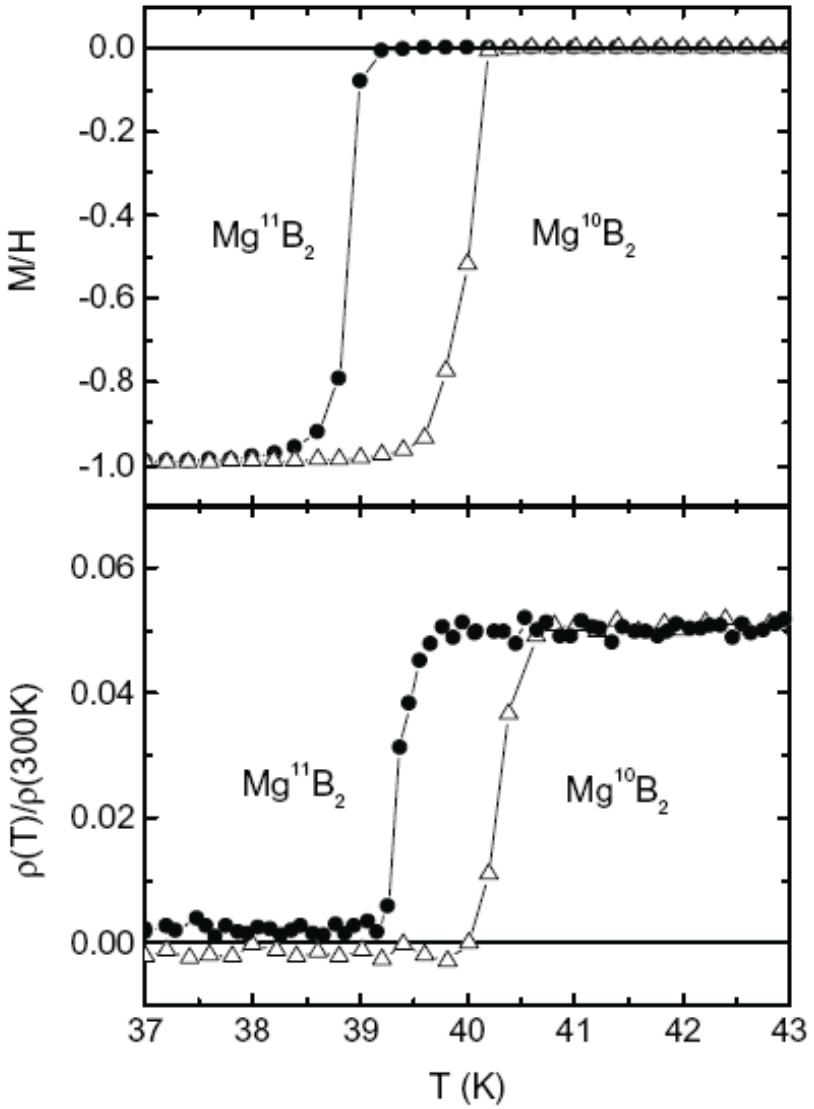
Boron Isotope Experiment

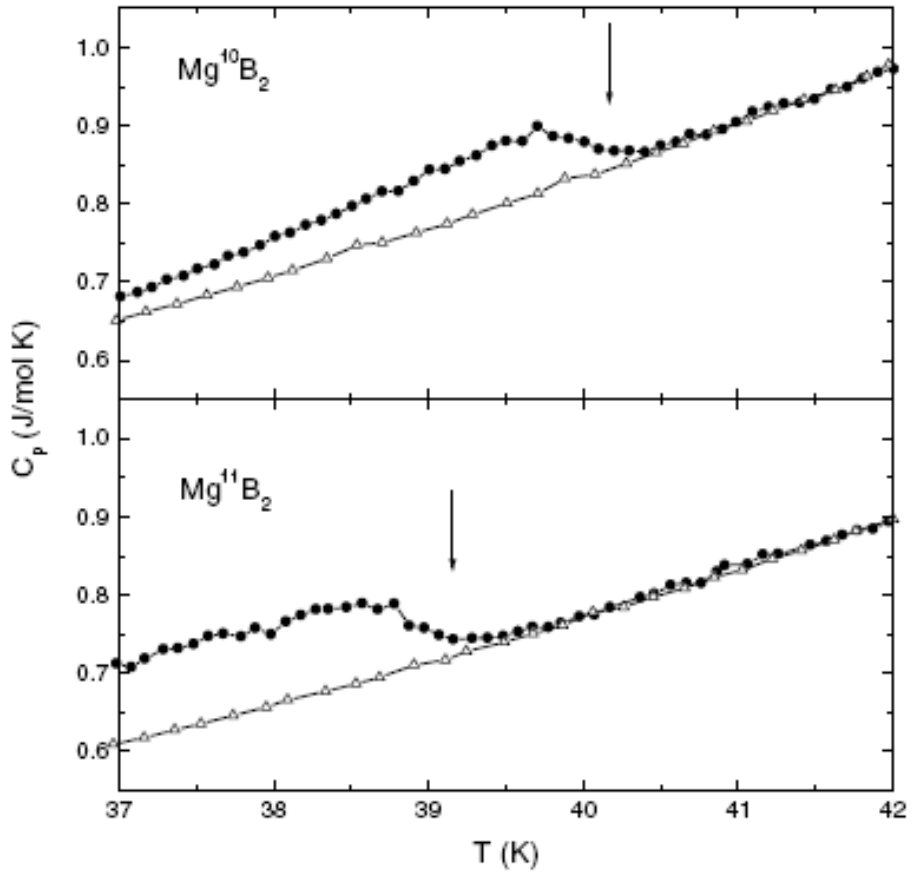
$\Delta T = 1.0$ K

(for simplest model expected $\Delta T_C \sim 0.85$)

$T_C \sim M^{\alpha_B}$, $\alpha_B = 0.26$

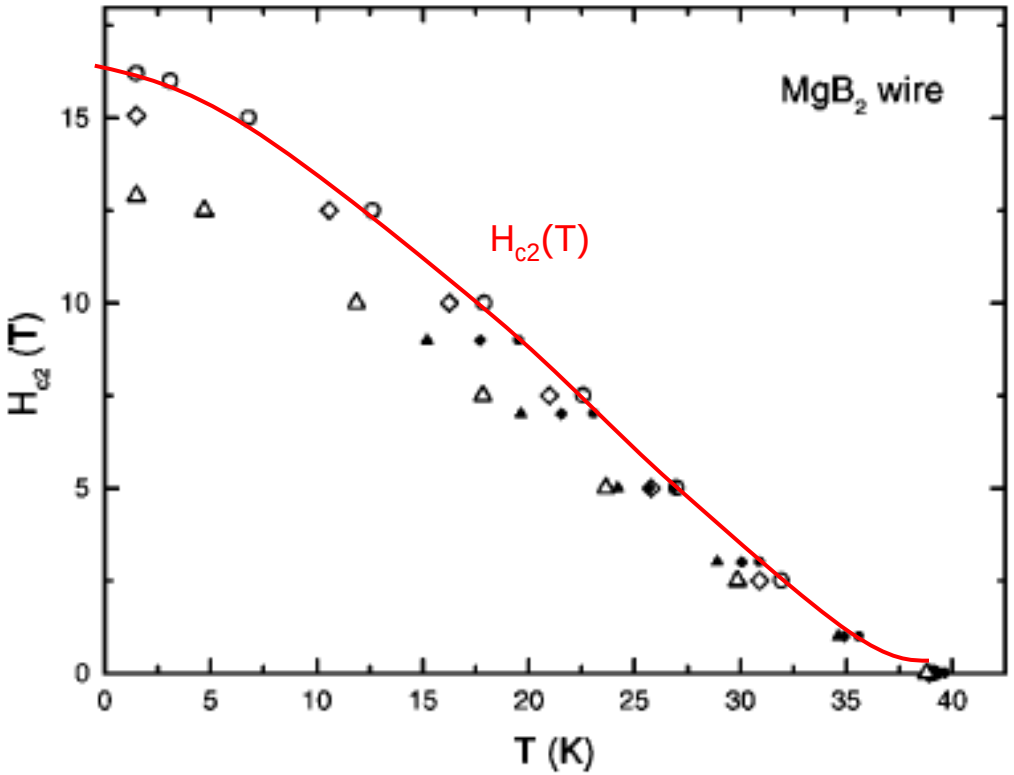
Consistent with phonon-mediated BCS.

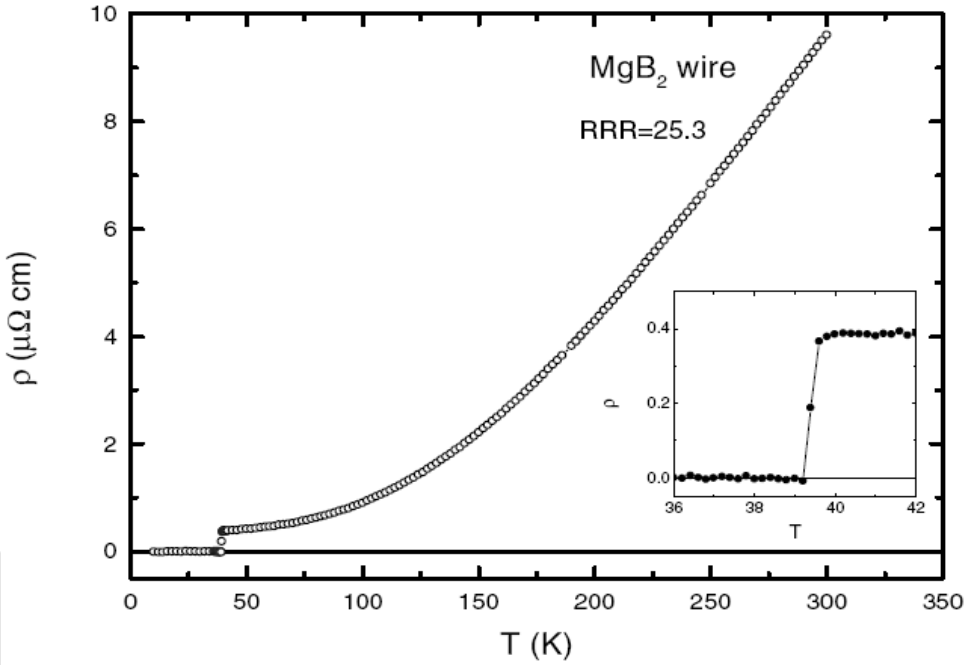


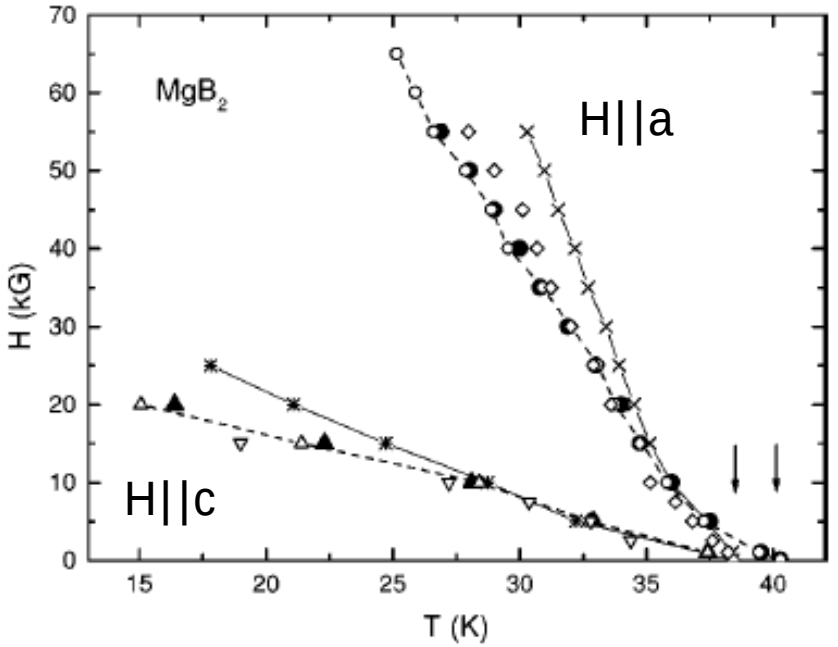


VOLUME 86, NUMBER 9 PHYSICAL REVIEW LETTERS 26 FEBRUARY 2001

Very quickly, high purity MgB_2 was found to be a very good metal, with a relatively low but anisotropic $H_{c2}(T)$

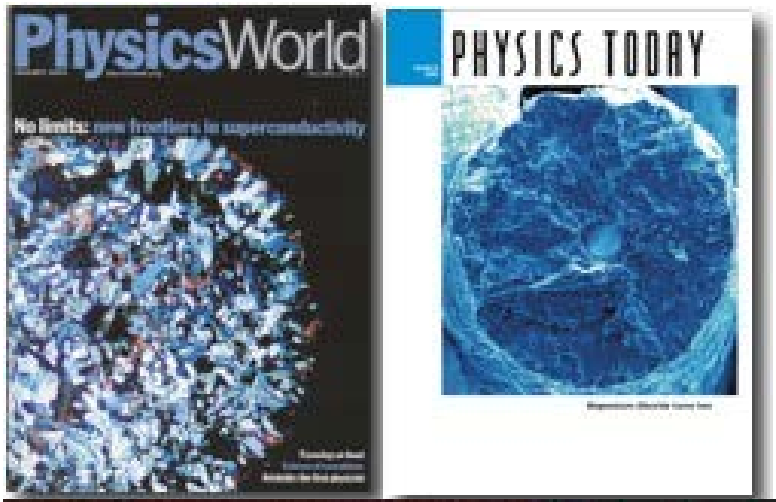






VOLUME 86, NUMBER 11 PHYSICAL REVIEW LETTERS 12 MARCH 2001
P.C. Canfield, D.K. Finnemore, S.L. Bud'ko, J.E. Ostenson, G. Lapertot,* C.E. Cunningham,† and C. Petrovic
PHYSICAL REVIEW B, VOLUME 63, 220503(R)
S. L. Bud'ko, C. Petrovic, G. Lapertot,* C. E. Cunningham,† and P. C. Canfield

Sometimes you can do a lot with polycrystalline samples....



VOLUME 86, NUMBER 9 PHYSICAL REVIEW LETTERS 26 FEBRUARY 2001

Boron Isotope Effect in Superconducting MgB_2

VOLUME 86, NUMBER 11 PHYSICAL REVIEW LETTERS 12 MARCH 2001

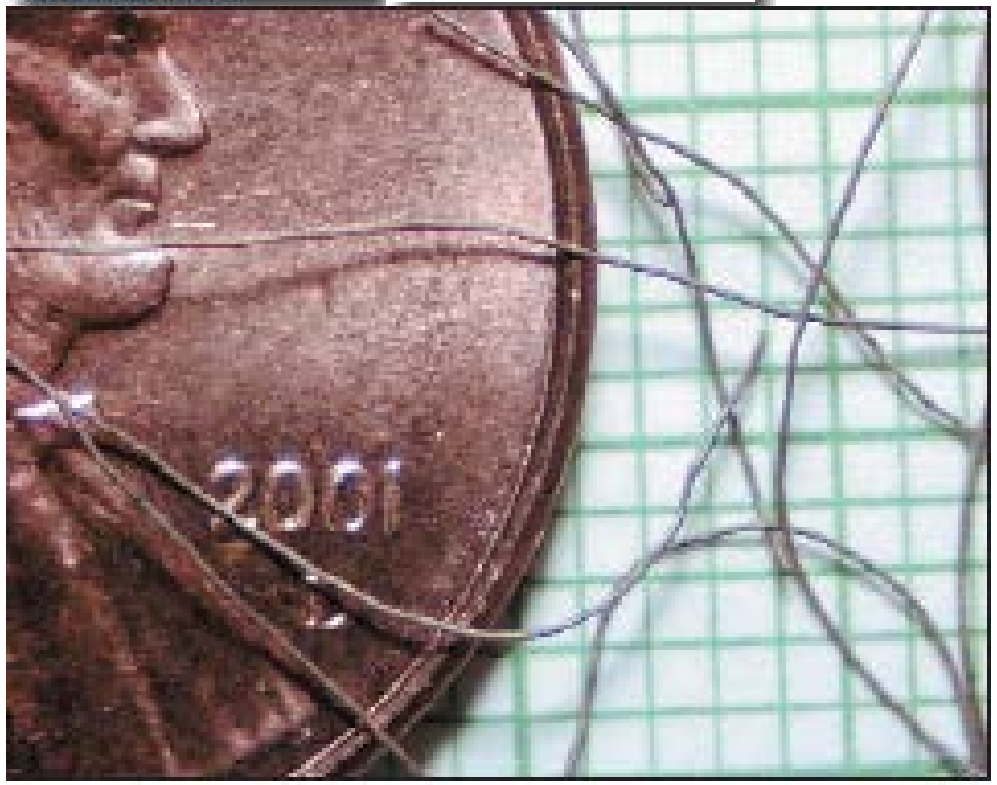
Thermodynamic and Transport Properties of Superconducting $Mg^{10}B_2$

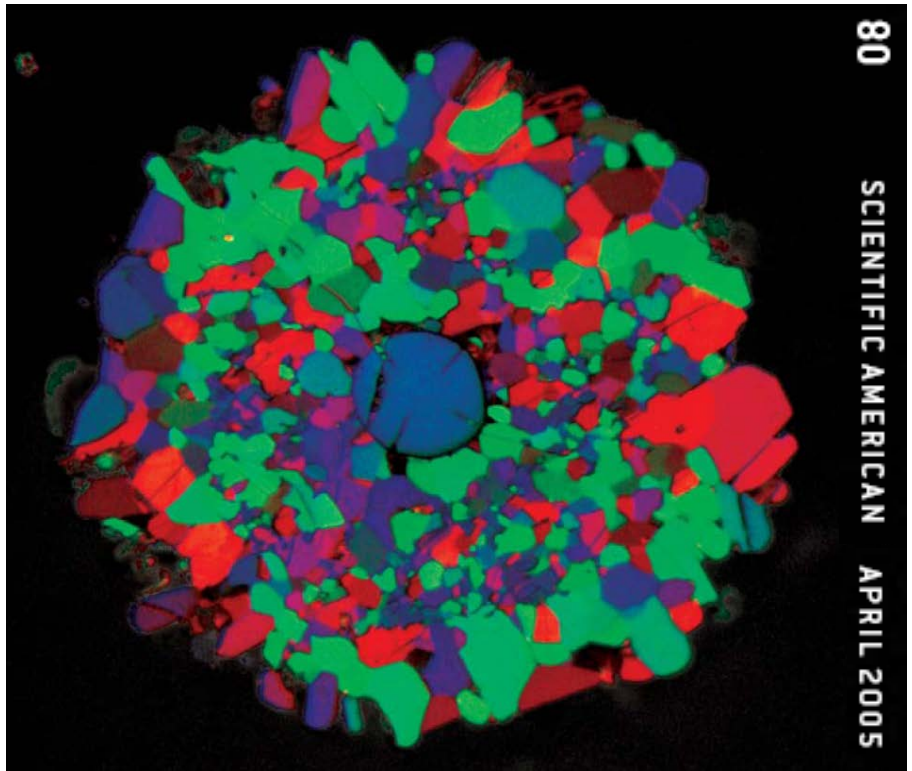
VOLUME 86, NUMBER 11 PHYSICAL REVIEW LETTERS 12 MARCH 2001

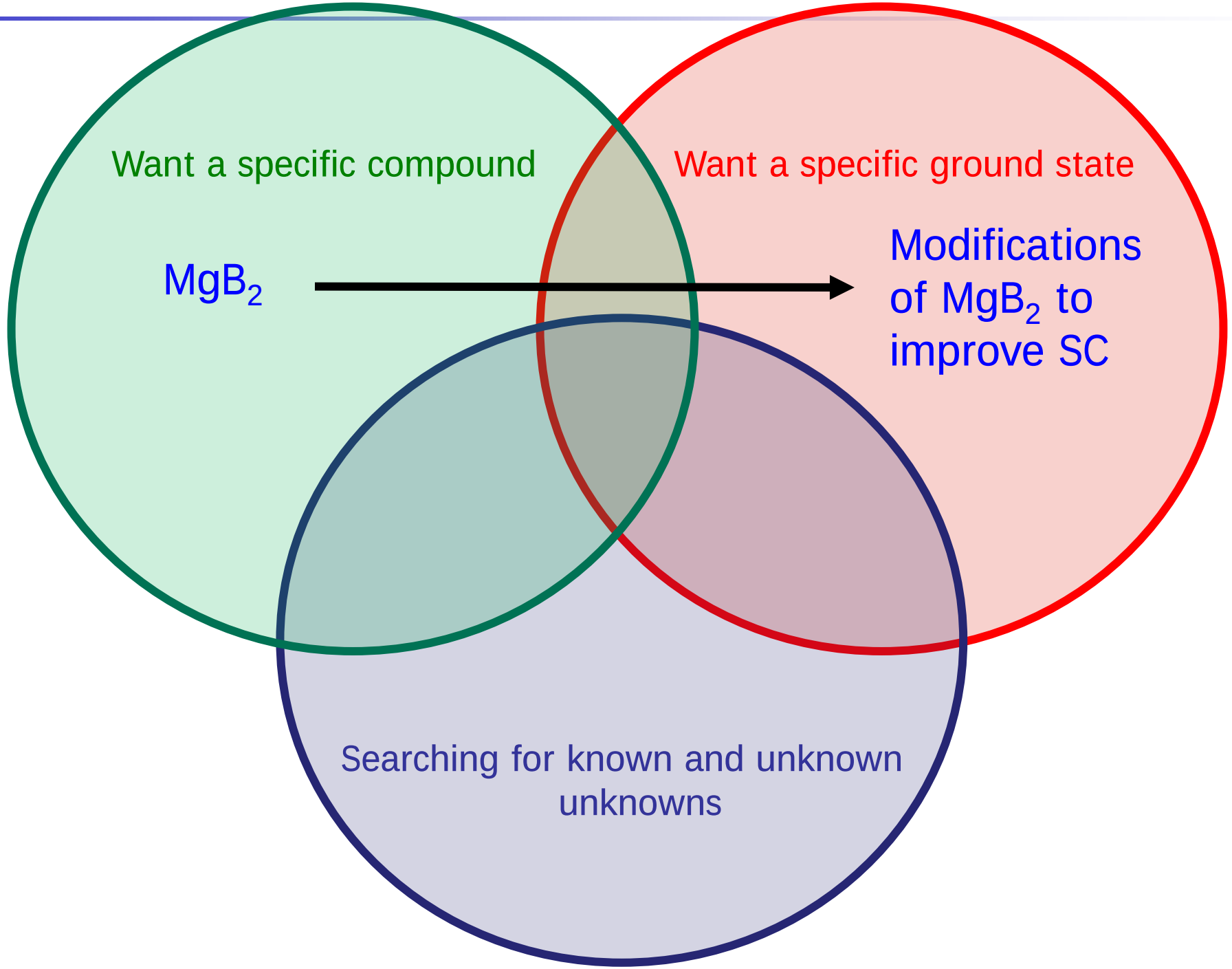
Superconductivity in Dense MgB_2 Wires

VOLUME 87, NUMBER 4 PHYSICAL REVIEW LETTERS 23 JULY 2001

Anisotropy of Superconducting MgB_2 as Seen in Electron Spin Resonance and Magnetization Data



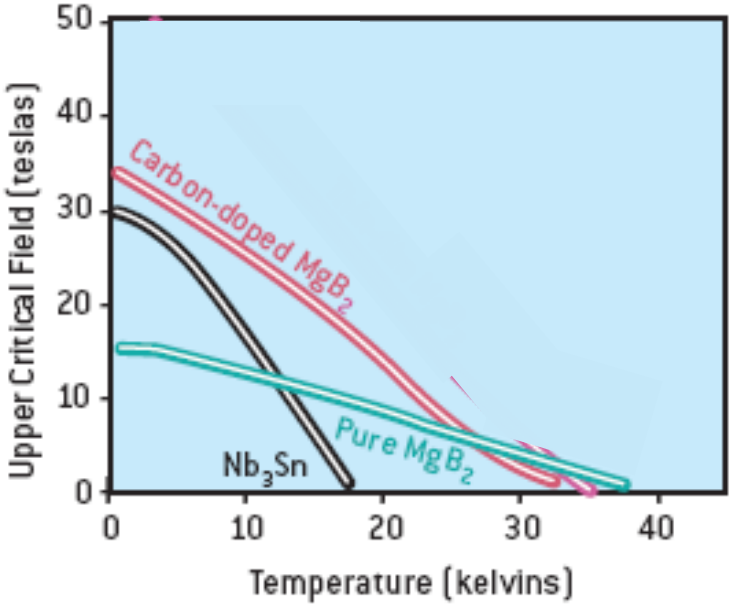


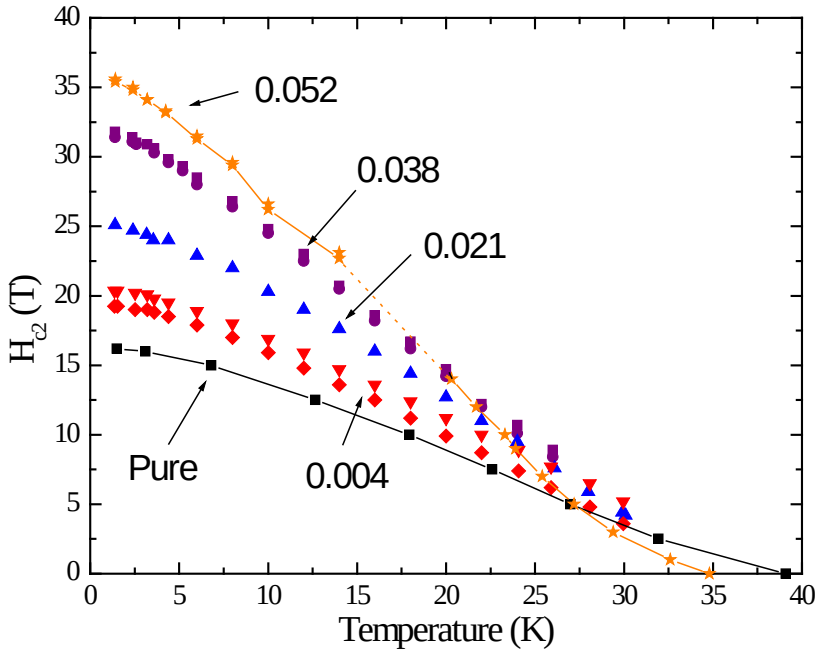

Want a specific compound
Want a specific ground state
MgB2
Modifications of MgB2 to improve SC
Searching for known and unknown unknowns

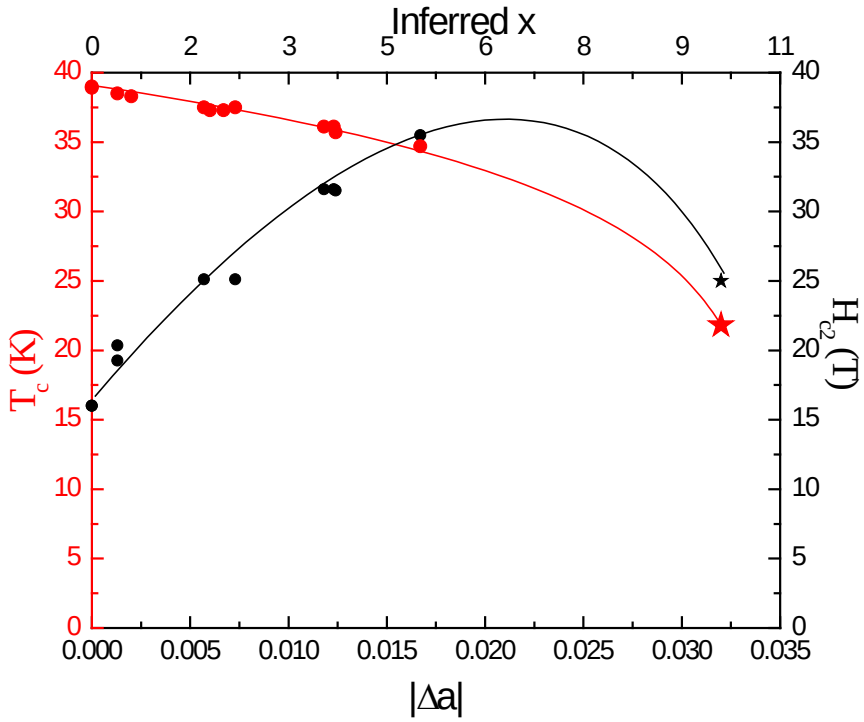
Although high purity MgB_2 has a rather low, and rather anisotropic, $H_{c2}(T)$ curve, we discovered how to systematically improve it....*Dramatically*.

$Mg(B_{1-x}C_x)_2$ studies

Tuning of T_c and H_{c2} with light carbon doping makes MgB_2 superior to Nb_3Sn (in H-T space).

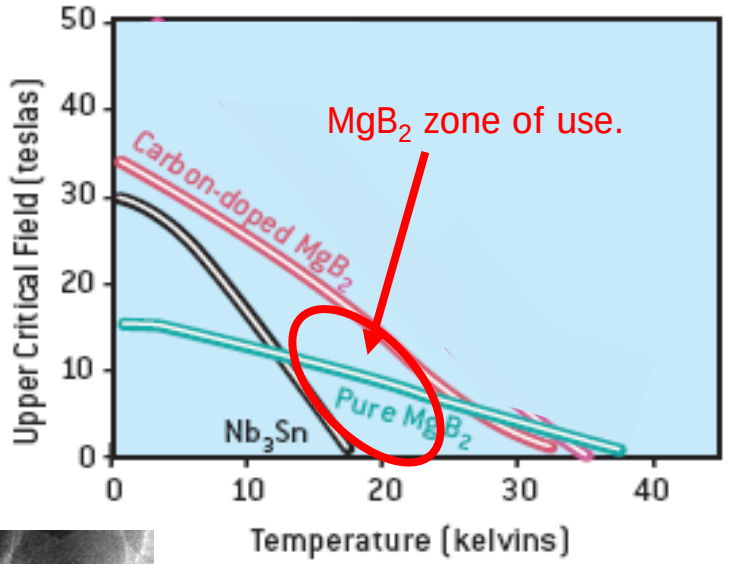


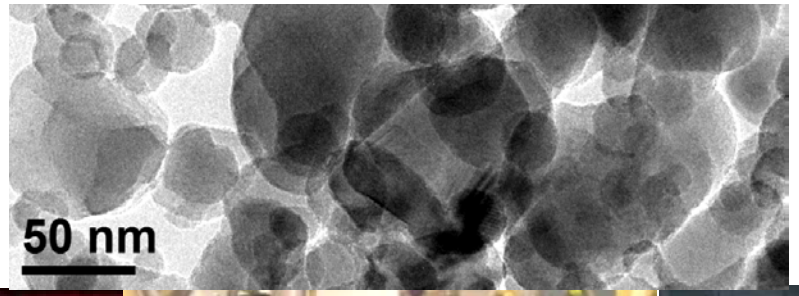


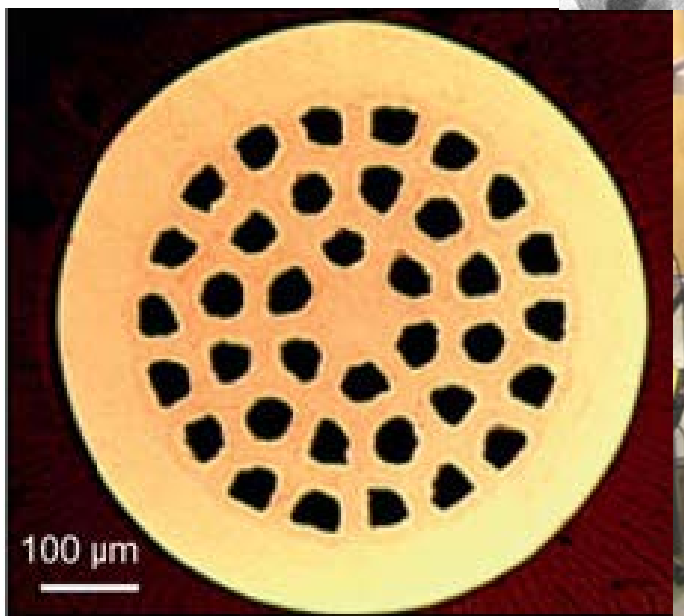


Phys. Rev. Lett. 92, 217003 (2004)

At this point MgB_2 is becoming an applied superconductor. Its appeal is the fact that it can be cooled to 20 K (well below its T_c and a temperature with a reasonable H_{c2}) with closed cycle refrigerators or He gas. This makes is much cheaper to use. MgB_2 wires are now being developed with MRI units in mind.







In 2008 we wanted to grow pure and K-substituted $BaFe_2As_2$.

Want a specific compound

In 2008 we wanted to grow pure and K-substituted $BaFe_2As_2$.

Want a specific compound

Within 14 hours of reading of superconductivity in K-doped $BaFe_2As_2$ we had grown sizable single crystals of these materials and started studying their physical properties.

In 2008 we wanted to grow pure and K-substituted $BaFe_2As_2$.

Want a specific compound

PHYSICAL REVIEW B 78, 014507 (2008)

Anisotropic thermodynamic and transport properties of single-crystalline $Ba_{1-x}K_xFe_2As_2$ ($x=0$ and 0.45)

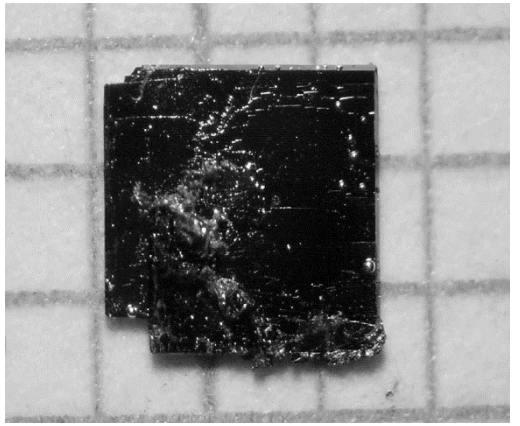
N. Ni,[1,2] S. L. Bud'ko,[1,2] A. Kreyssig,[1,2] S. Nandi,[1,2] G. E. Rustan,[1,2] A. I. Goldman,[1,2] S. Gupta,[1,3] J. D. Corbett,[1,3] A. Kracher,[1] and P. C. Canfield[1,2]

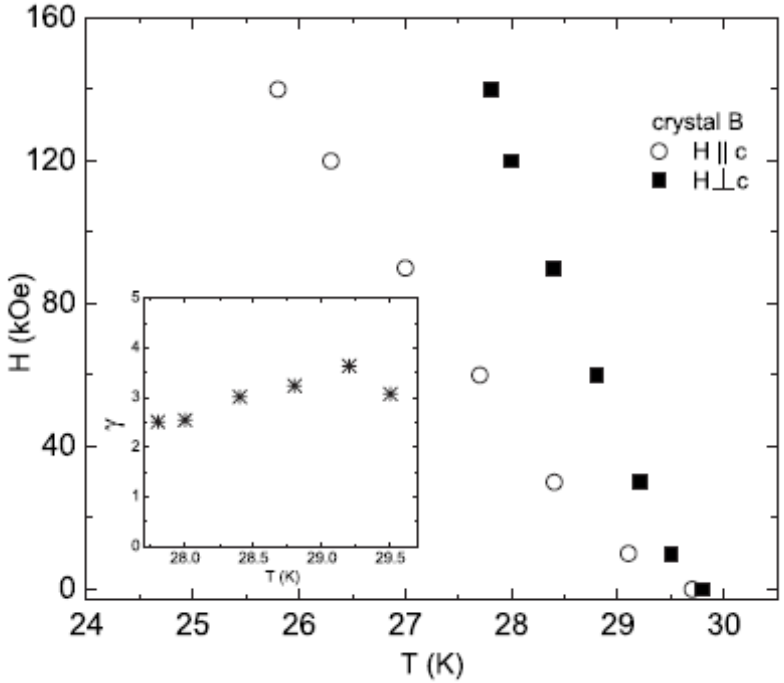
[1]*Ames Laboratory US DOE, Iowa State University, Ames, Iowa 50011, USA*

[2]*Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

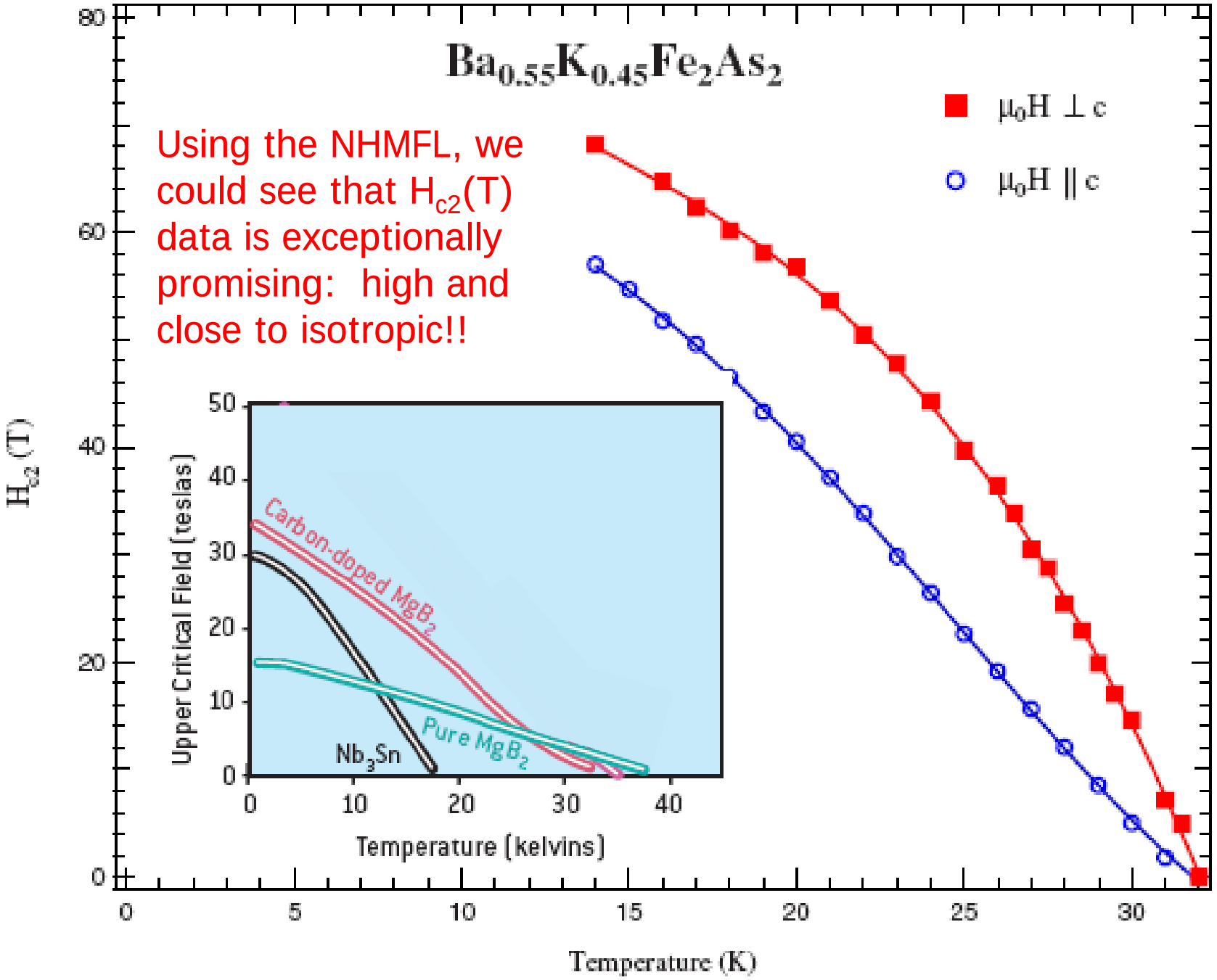
[3]*Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA*

(Received 11 June 2008; revised manuscript received 18 June 2008; published 10 July 2008)



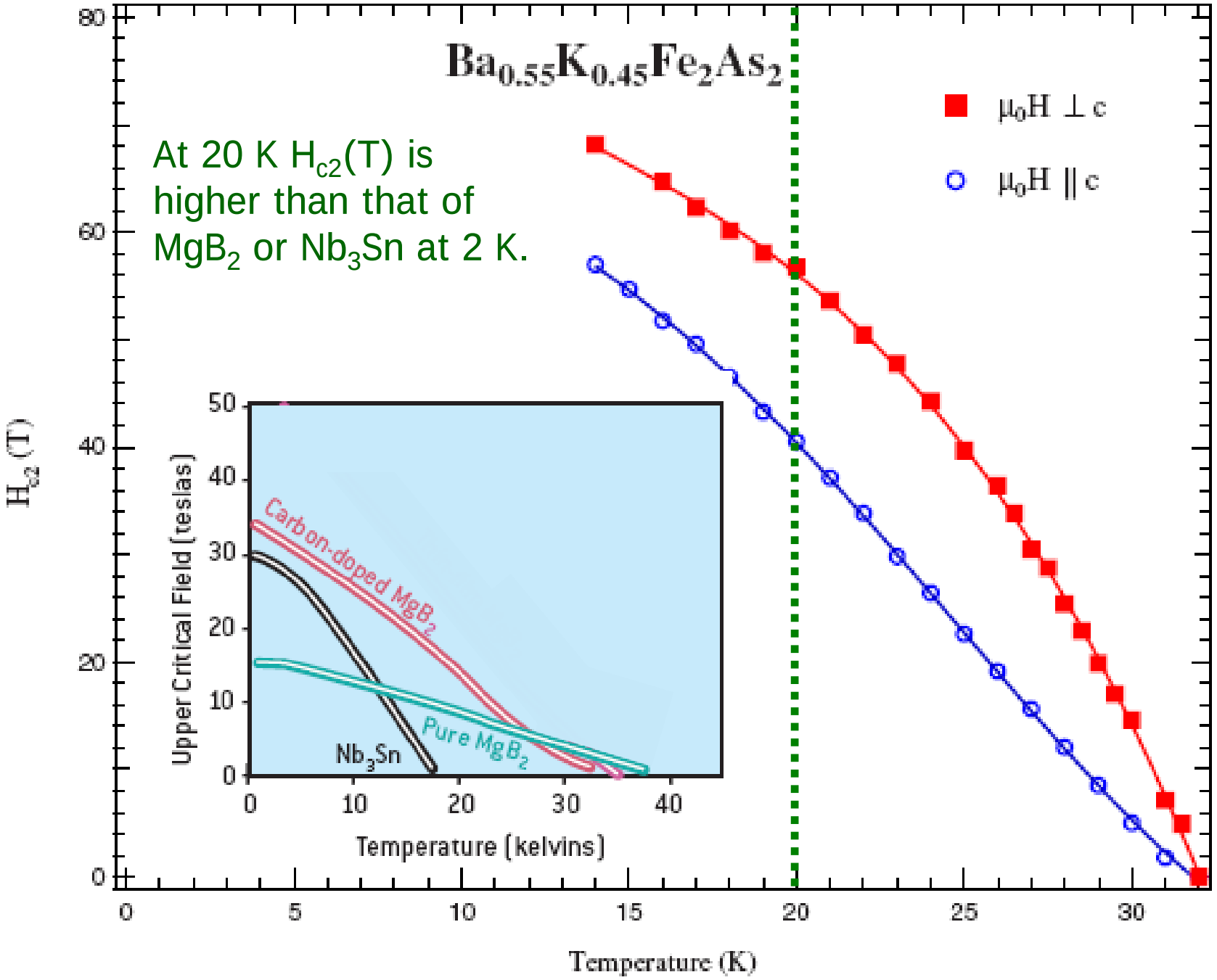


This allowed for clear sense that (i) $H_{c2}(T)$ was not too anisotropic and (ii) $H_{c2}(T)$ was going to be BIG even with T_c less than 30 K.



PHYSICAL REVIEW B 78, 220505(R) (2008)

PAUL C. CANFIELD AND SERGEY L. BUD'KO

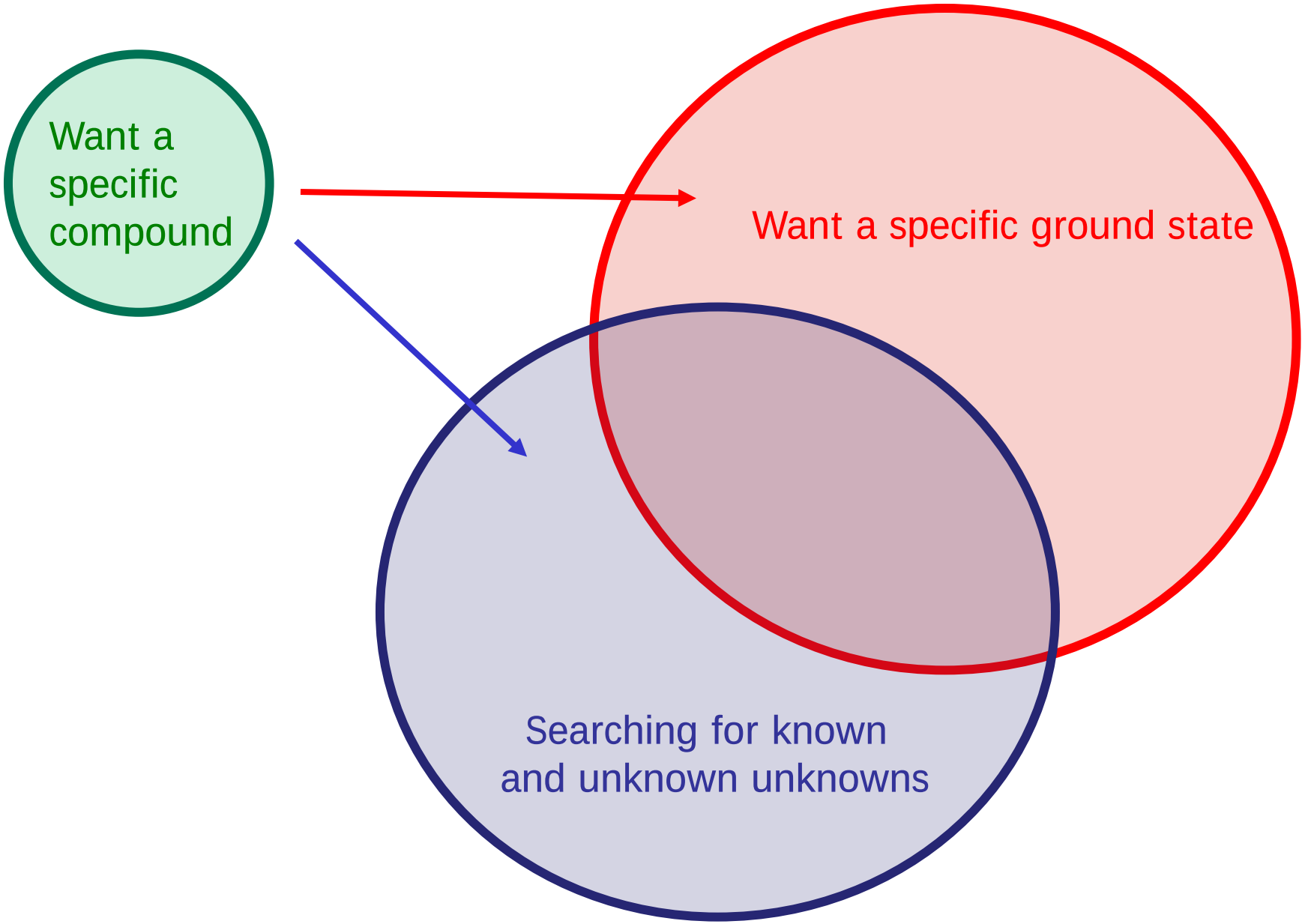


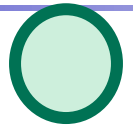
At 20 K $H_{c2}(T)$ is higher than that of MgB_2 or Nb_3Sn at 2 K.

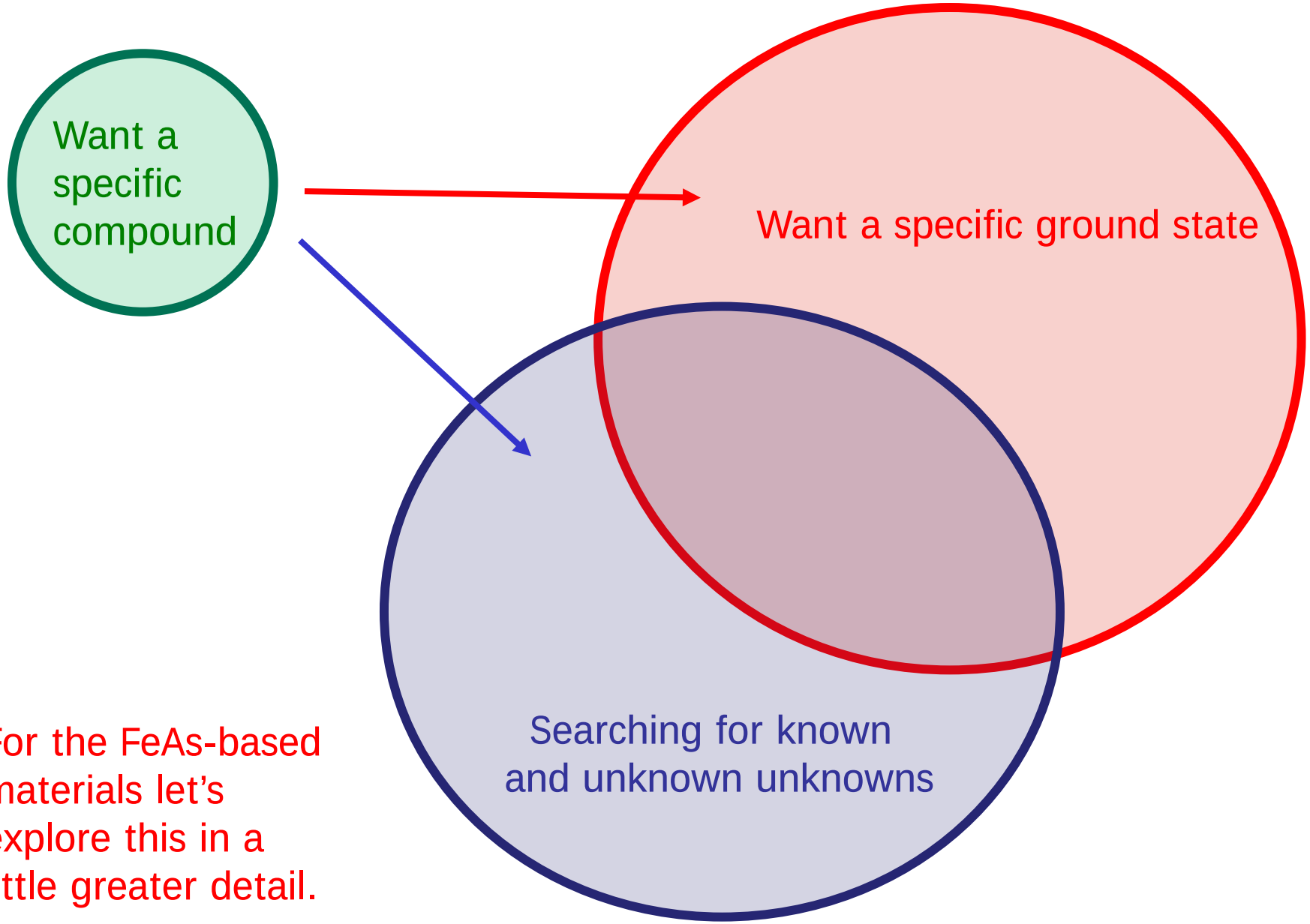
PHYSICAL REVIEW B 78, 220505(R) (2008)

PAUL C. CANFIELD AND SERGEY L. BUD'KO

Often success in ◯ directly feeds into other motivations.



Often success in  directly feeds into other motivations.



For the FeAs-based materials let's explore this in a little greater detail.

Starting with $BaFe_2As_2$, we want to determine range and rules of superconductivity.

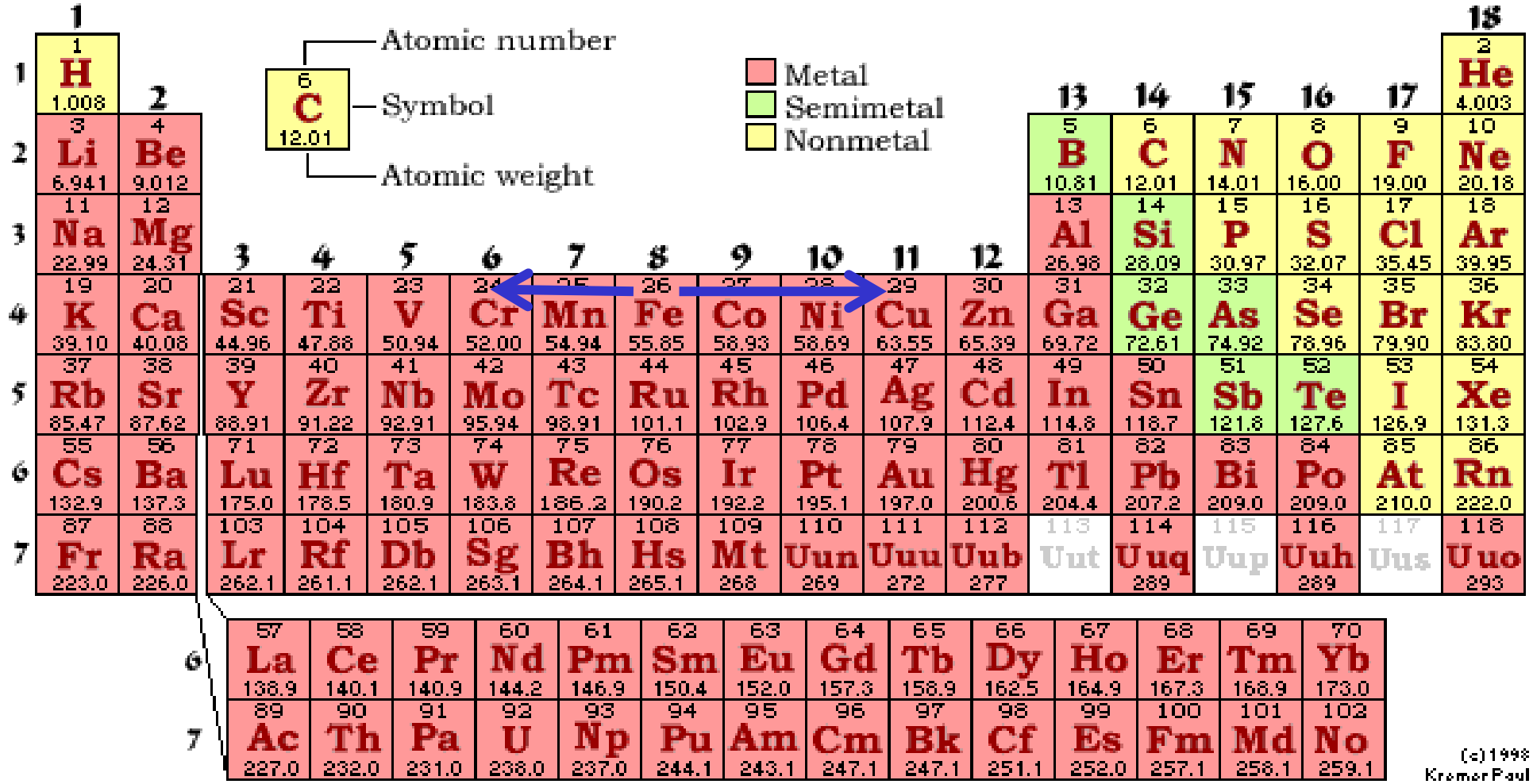
Want a specific ground state

Starting with $BaFe_2As_2$, we want to determine range and rules of superconductivity.

Want a specific ground state

Start with $BaFe_2As_2$

Explore the 3-d row to extent possible



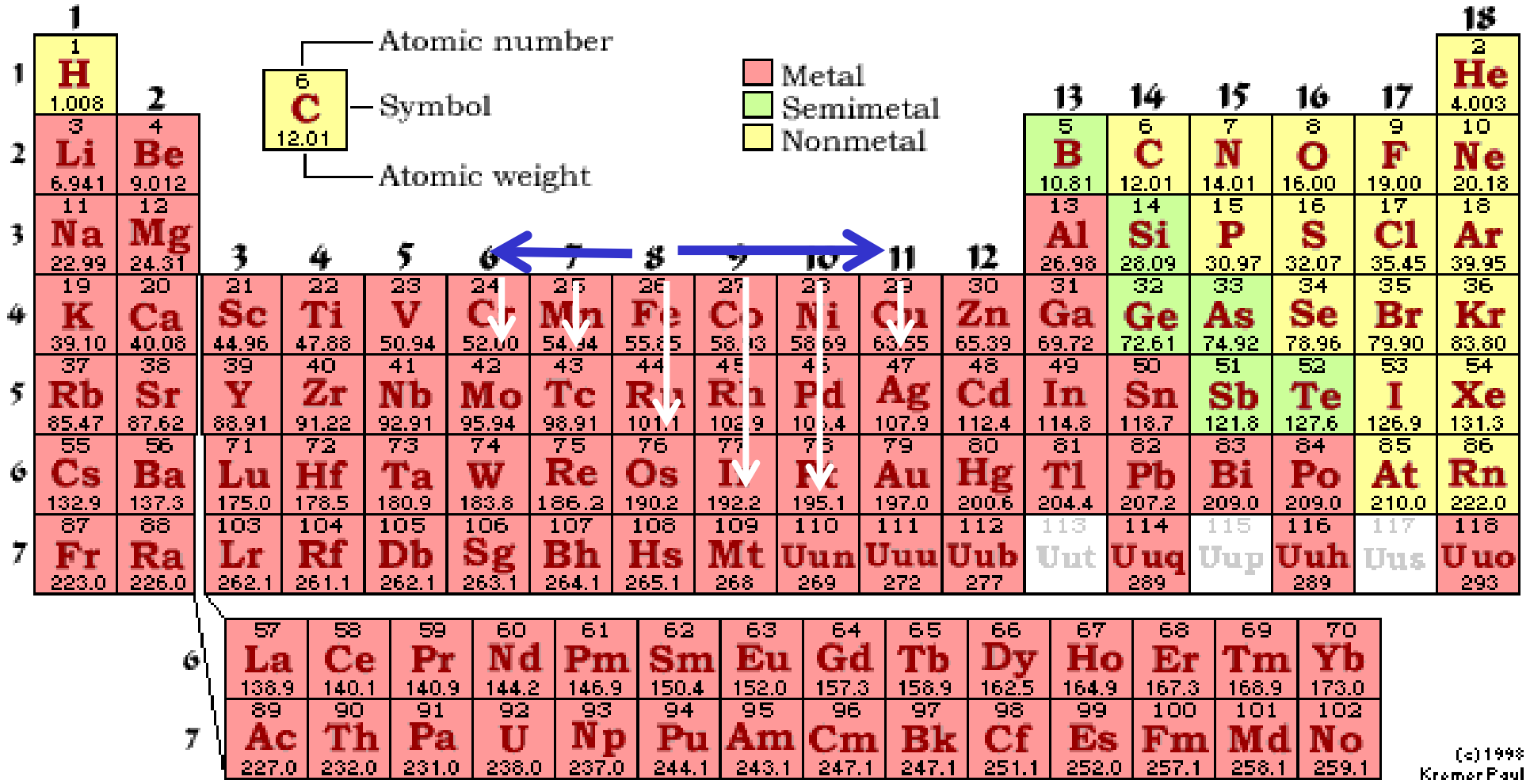
Starting with $BaFe_2As_2$, we want to determine range and rules of superconductivity.

Want a specific ground state

Start with $BaFe_2As_2$

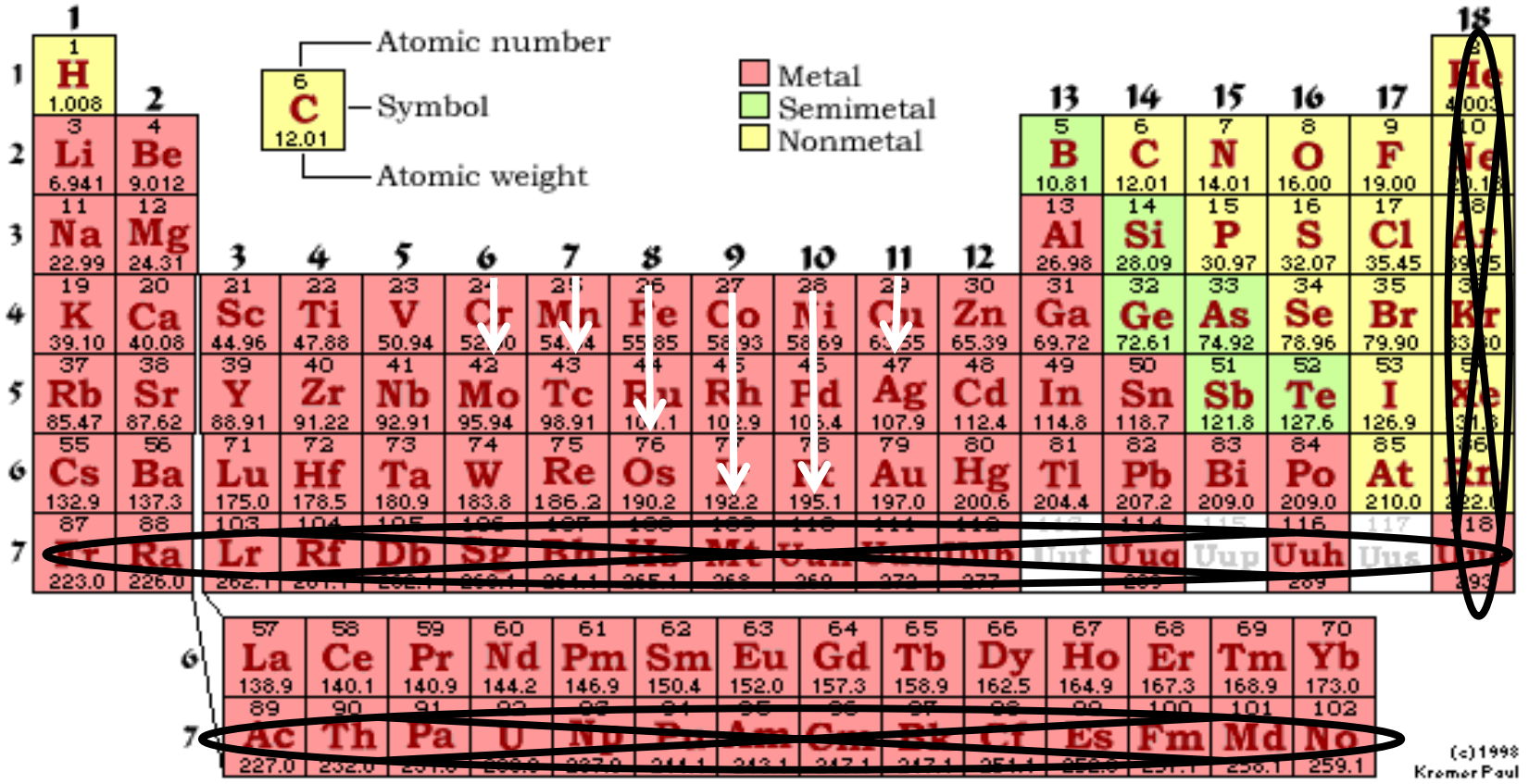
Explore the 3-d row to extent possible

Move down columns to 4-d and 5-d



(c) 1998 Kramer Paul

This reduces the phase space dramatically.



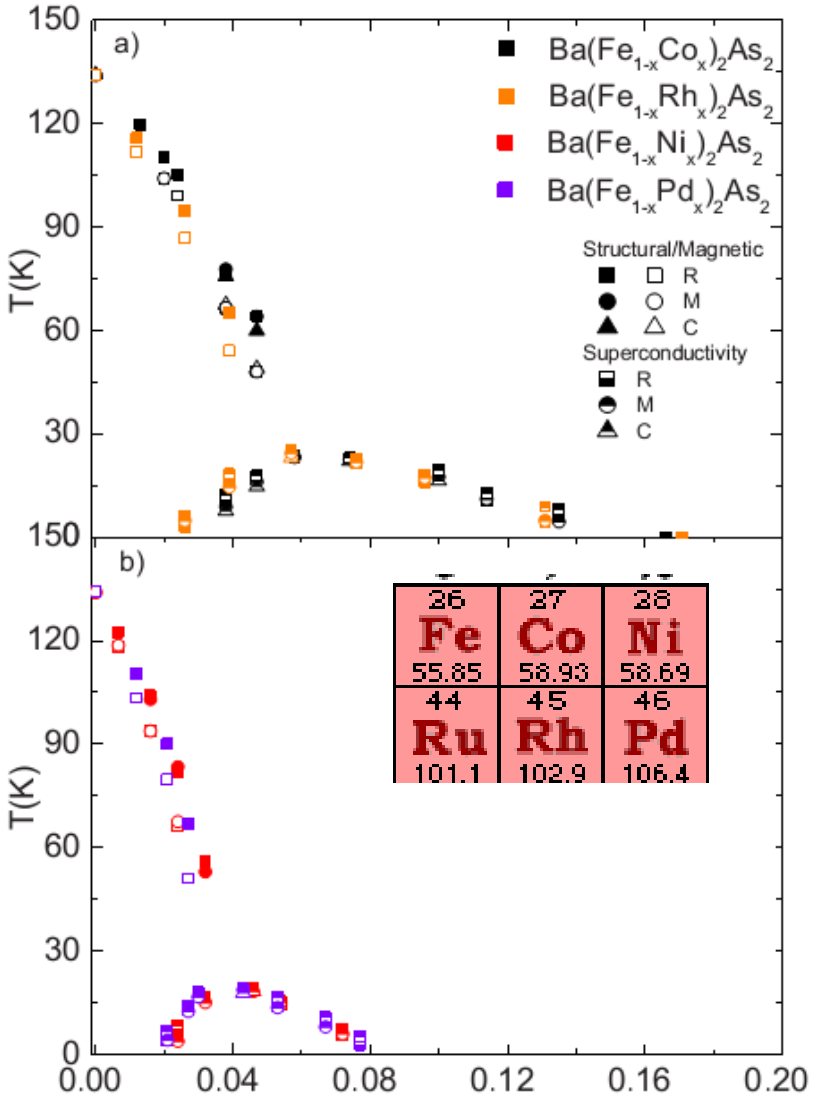
INSTEAD OF

Binary compounds: (80!/78!2!) x 3 ~ 10^4

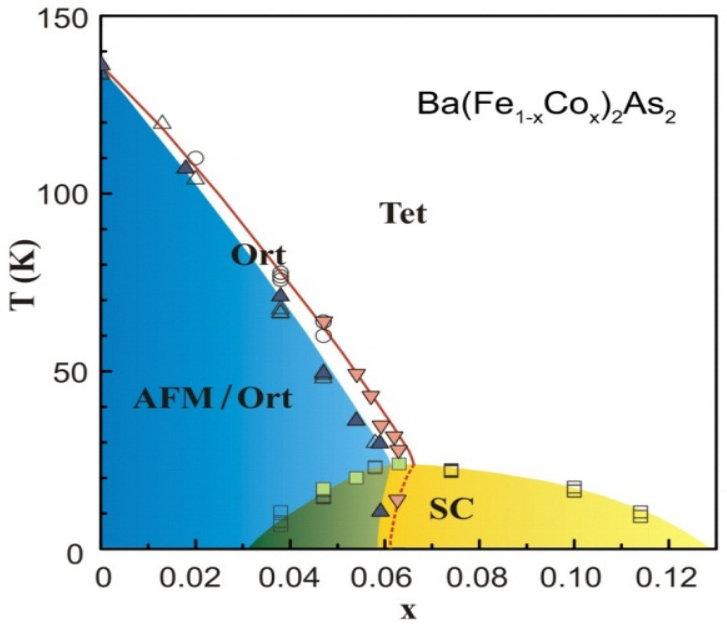
Ternary compounds: (100!/97!3!) x 8 ~ 10^6

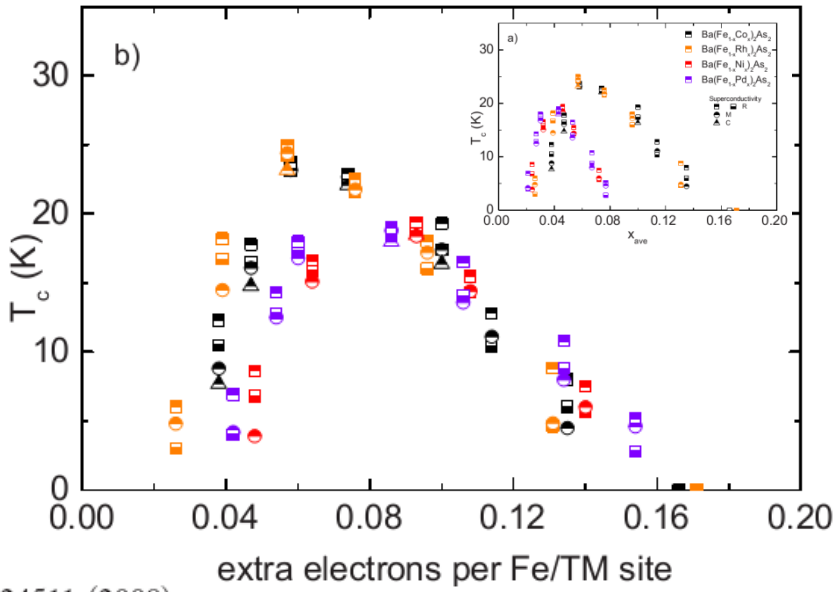
Now we are talking about less than a dozen substitution series.

The results of these substitutional studies helped define the physics of the Fe-based superconductors.



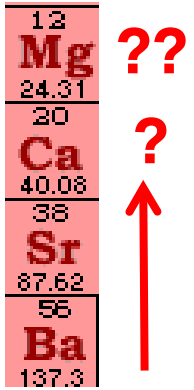
x WDS





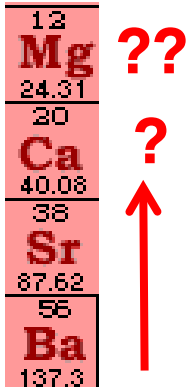
PHYSICAL REVIEW B 80, 024511 (2009)

unknowns



What happens if we try to go further up the column? Does either $CaFe_2As_2$ and/or $MgFe_2As_2$ exist?

unknowns



What happens if we try to go further up the column? Does either $CaFe_2As_2$ and/or $MgFe_2As_2$ exist?

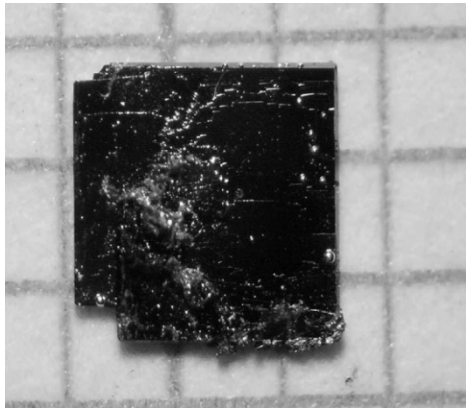
unknowns

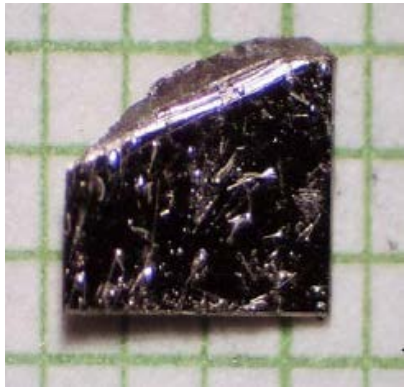
$BaFe_2As_2$ and $SrFe_2As_2$ were known compounds before we grew the first single crystals....

PHYSICAL REVIEW B 78, 014507 (2008)

Anisotropic thermodynamic and transport properties of single-crystalline $Ba_{1-x}K_xFe_2As_2$ ($x=0$ and 0.45)

N. Ni,[1,2] S. L. Bud'ko,[1,2] A. Kreyssig,[1,2] S. Nandi,[1,2] G. E. Rustan,[1,2] A. I. Goldman,[1,2] S. Gupta,[1,3] J. D. Corbett,[1,3] A. Kracher,[1] and P. C. Canfield[1,2]
[1]*Ames Laboratory US DOE, Iowa State University, Ames, Iowa 50011, USA*
[2]*Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[3]*Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA*
(Received 11 June 2008; revised manuscript received 18 June 2008; published 10 July 2008)





PHYSICAL REVIEW B 78, 024516 (2008)

Structural transition and anisotropic properties of single-crystalline $SrFe_2As_2$

J.-Q. Yan,[1] A. Kreyssig,[1,2] S. Nandi,[1,2] N. Ni,[1,2] S. L. Bud'ko,[1,2] A. Kracher,[1] R. J. McQueeney,[1,2] R. W. McCallum,[1,3] T. A. Lograsso,[1] A. I. Goldman,[1,2] and P. C. Canfield[1,2]
[1]*Ames Laboratory, US DOE, Iowa State University, Ames, Iowa 50011, USA*
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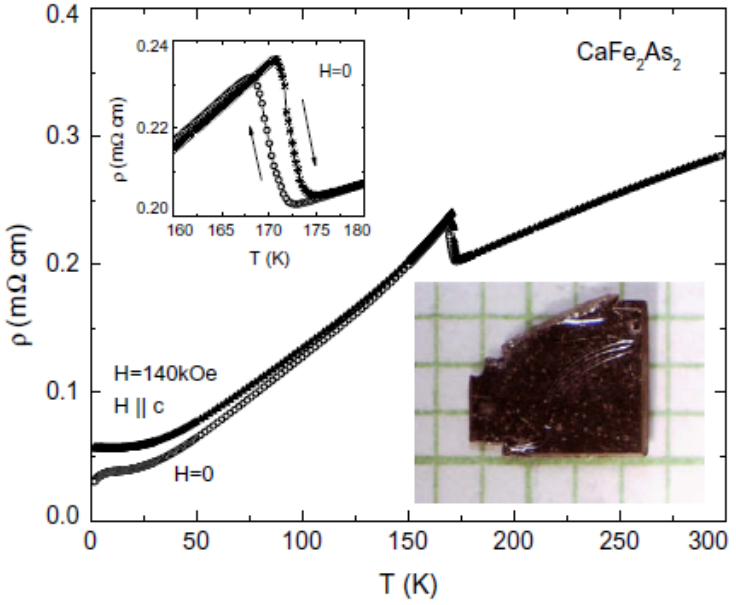
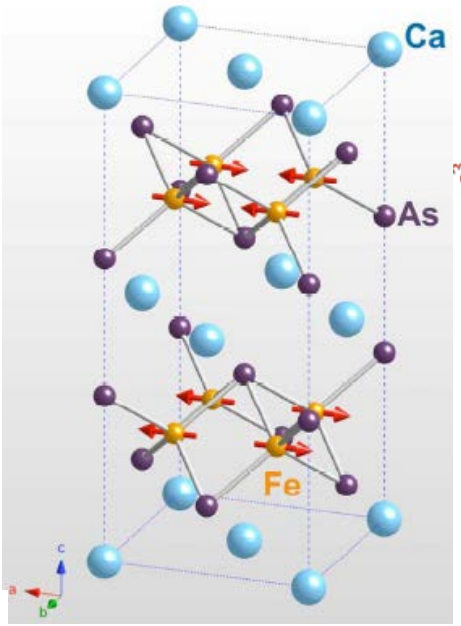
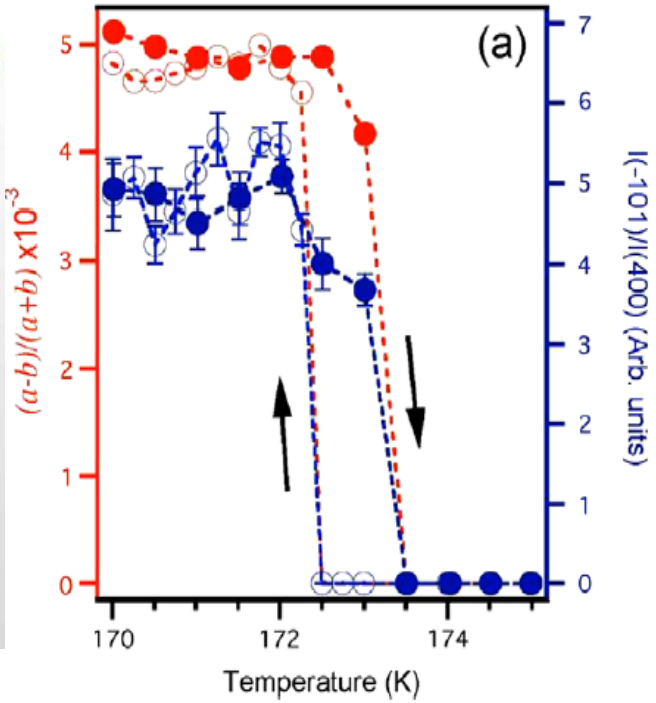
(Received 18 June 2008; published 23 July 2008)

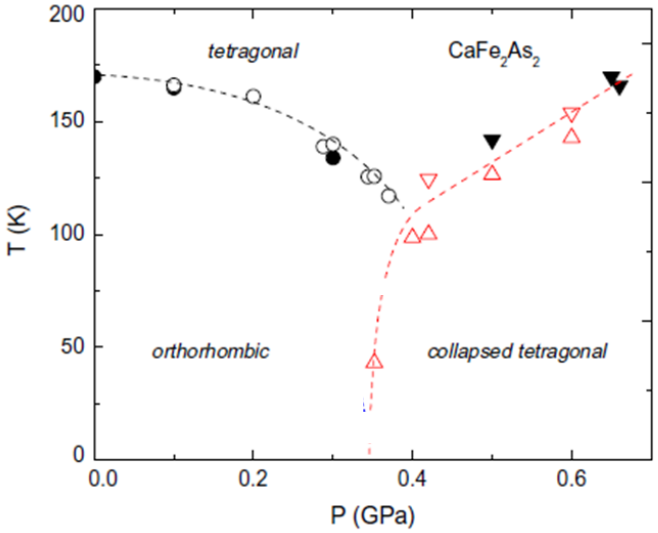
$CaFe_2As_2$ was discovered as the result of single crystal growth. It is the extreme member of the AFe_2As_2 series.

unknowns









First order structural / AF transition at 170 K at ambient pressure and exceptionally pressure sensitive.

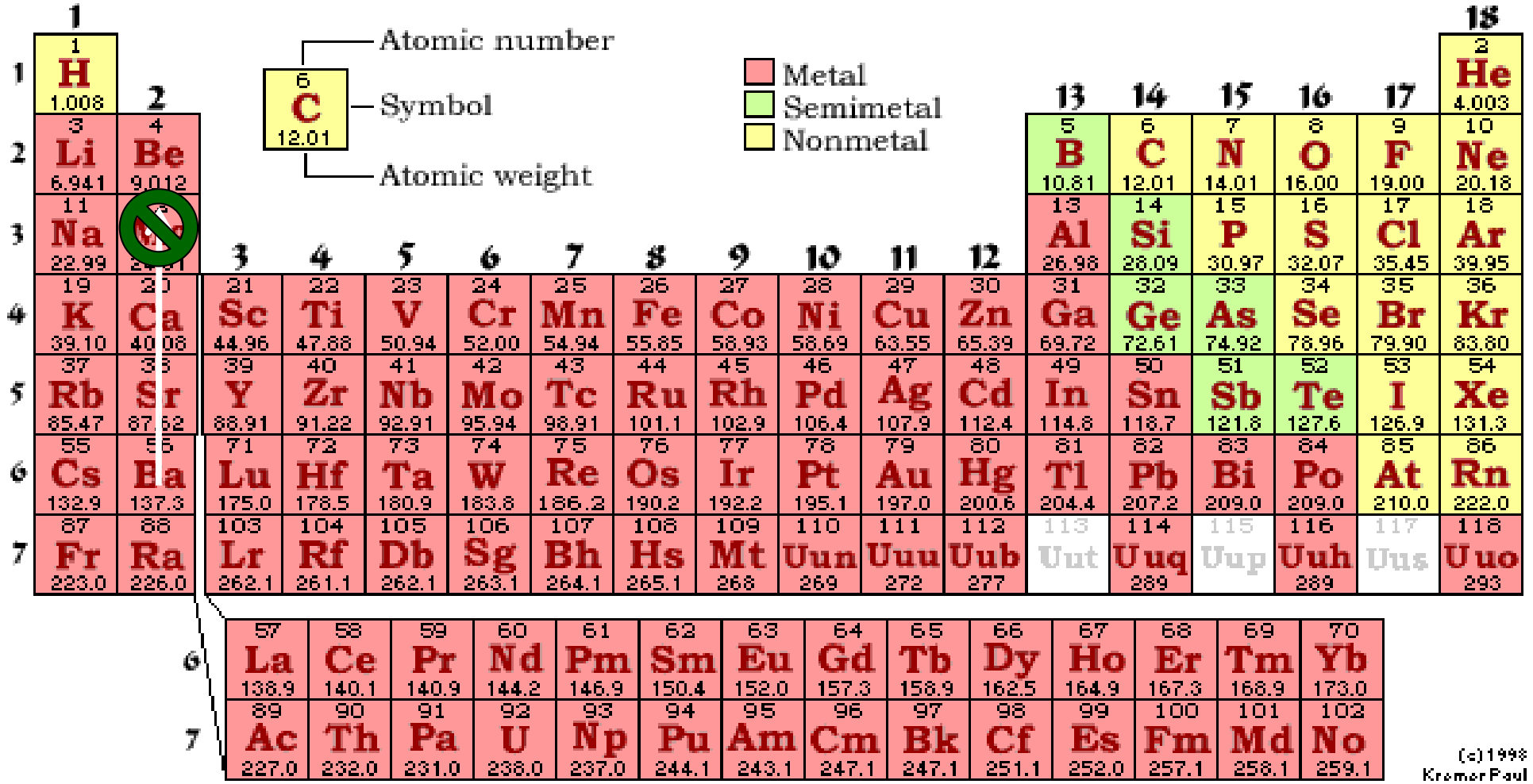
A concise summary of a dozen 2008 / 2009 papers on the basic properties:

Physica C 469 (2009) 404–412

Clearly there were attempts to get Mg to go into the lattice as well, both as substitution and as line compound.

unknowns

These attempts failed to produce any Mg substitution.

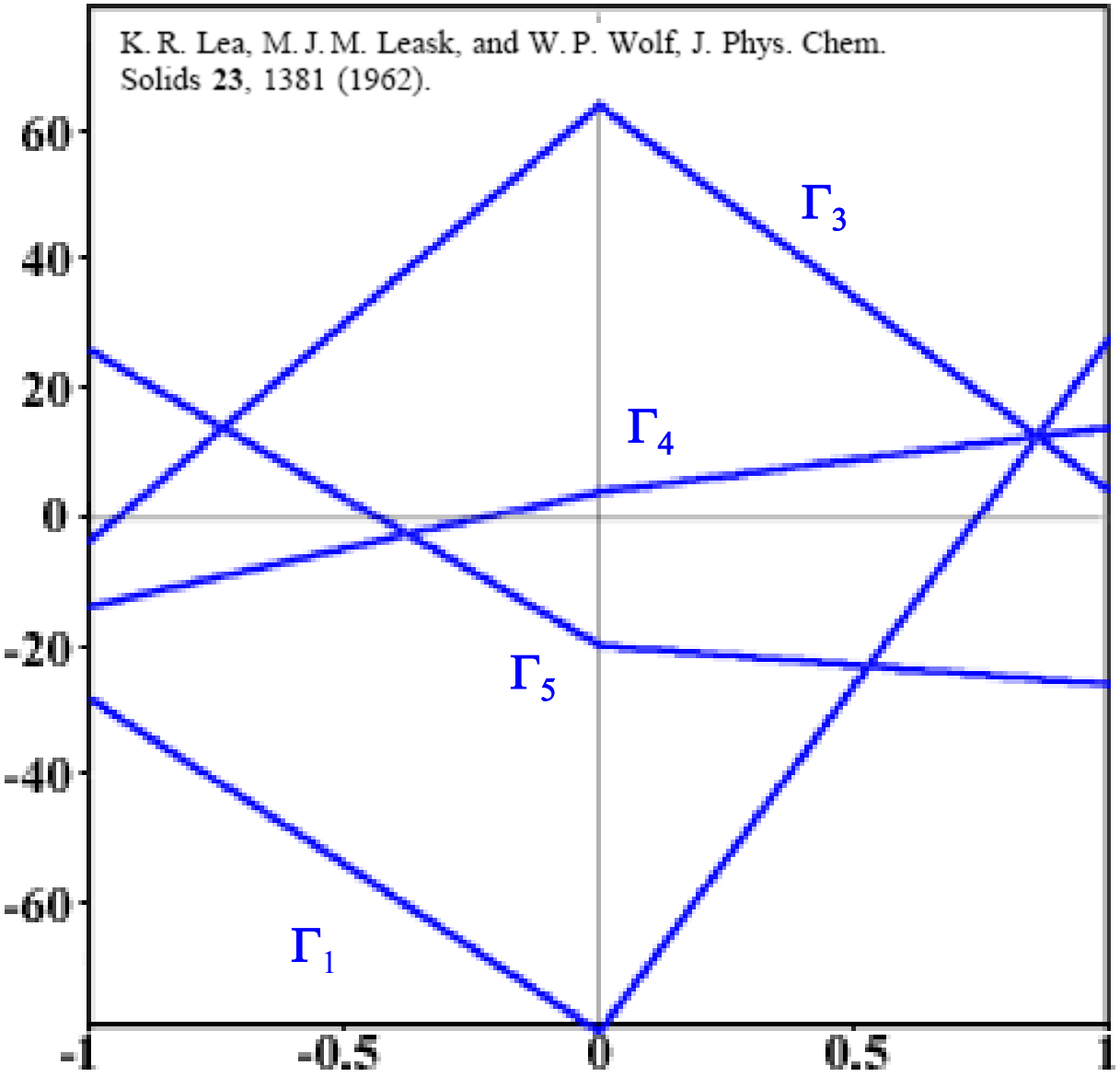


Let’s look a little more explicitly at how “Want a specific ground state” reduces phase space and provides clear guidance and motivation to searches when it is used as a first step..

Want a specific ground state

Want to find a Pr-based compound that manifests a clear heavy Fermion ground state. Given that Pr^{3+} is non-Kramers: Can entropy be preserved in Pr-based samples to low enough temperatures to allow for hybridization?

CEF splitting for Pr^{3+} in cubic point symmetry



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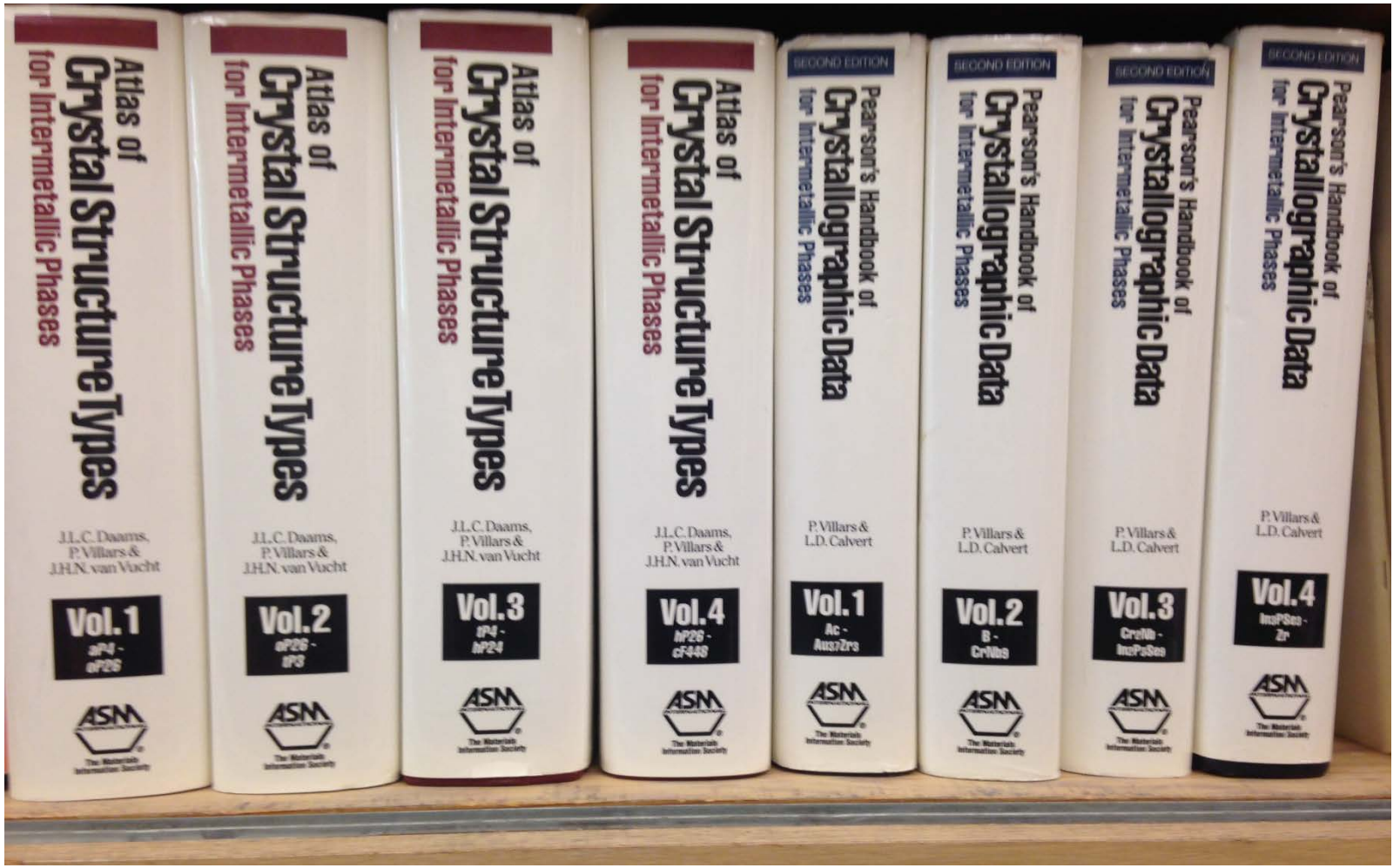
NOTE: in cubic point symmetry the Γ_3 state is a non-magnetic doublet and can, sometimes, be the ground state.

The desired ground state can help constrain the search.

Use data bases aggressively



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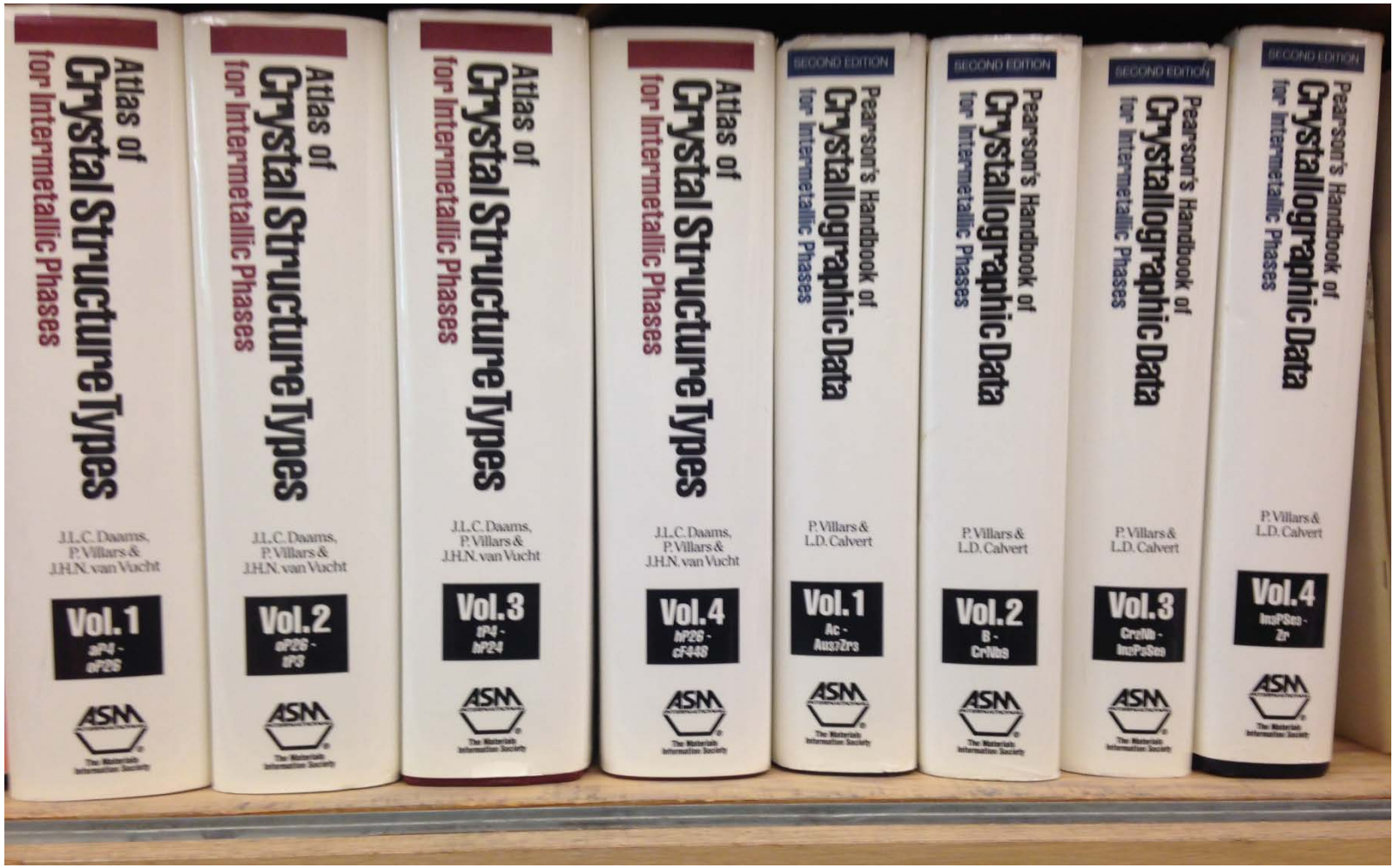
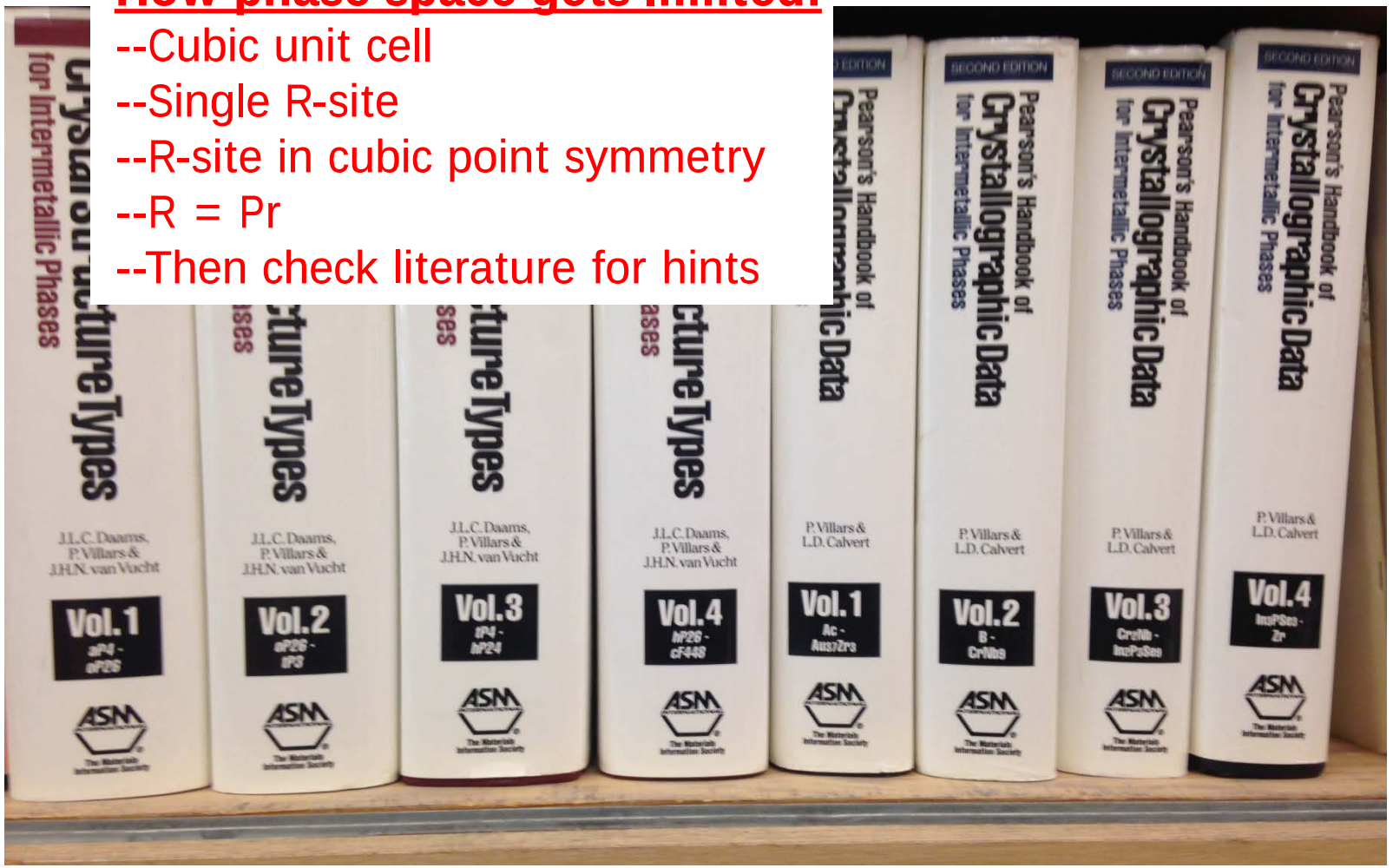


When I was doing this, Pearson's Handbook was still actually books.

The desired ground state can help constrain the search.

How phase space gets limited:

--Cubic unit cell
--Single R-site
--R-site in cubic point symmetry
--R = Pr
--Then check literature for hints



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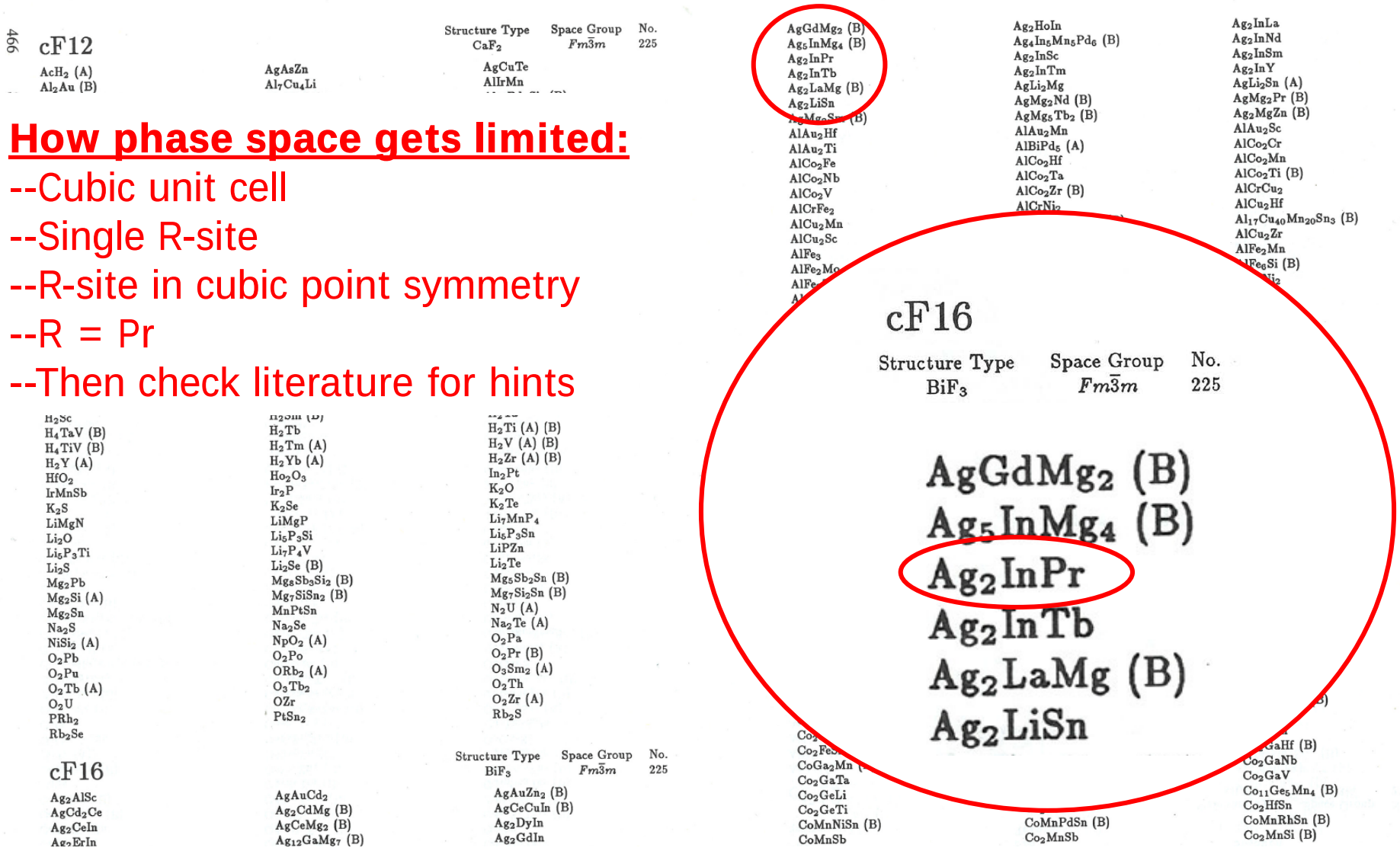


One of many pages from Pearson's Handbook of crystallographic data....

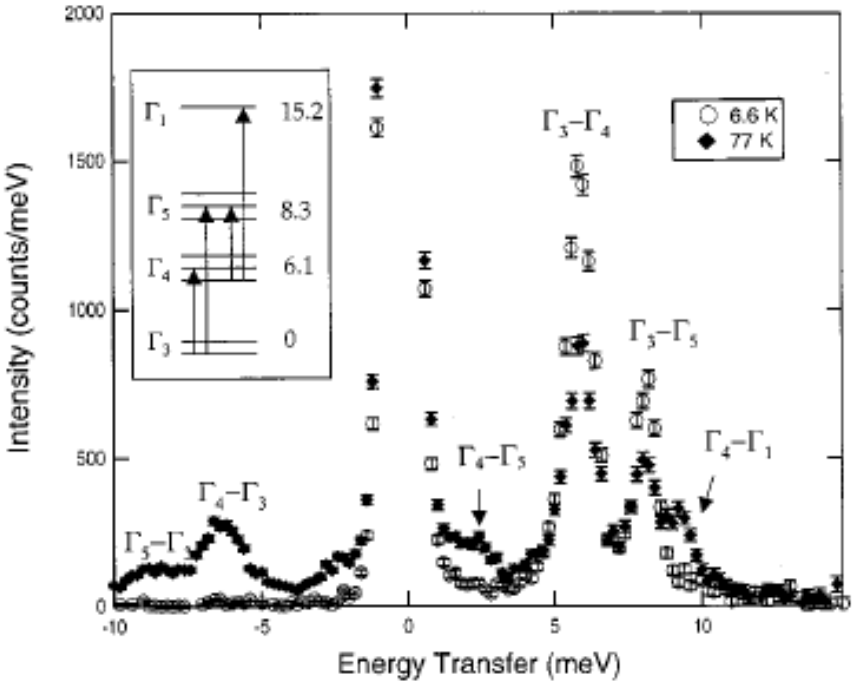
$PrAg_2In$ matched the cascade of requirements:

Cubic unit cell

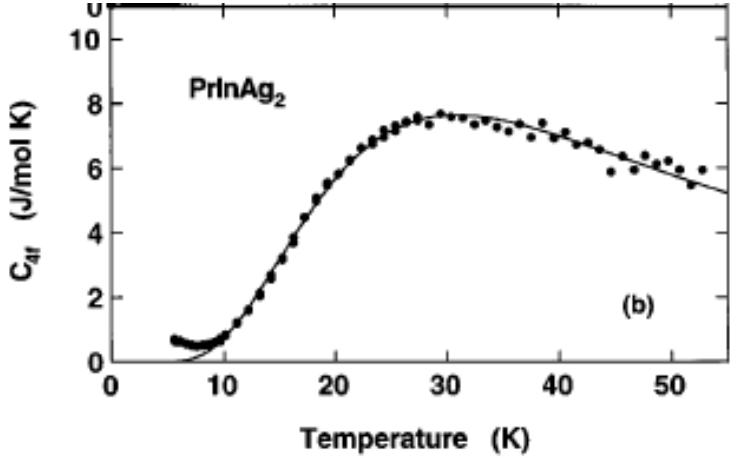
Cubic point symmetry for Pr

Γ_3 CEF groundstate

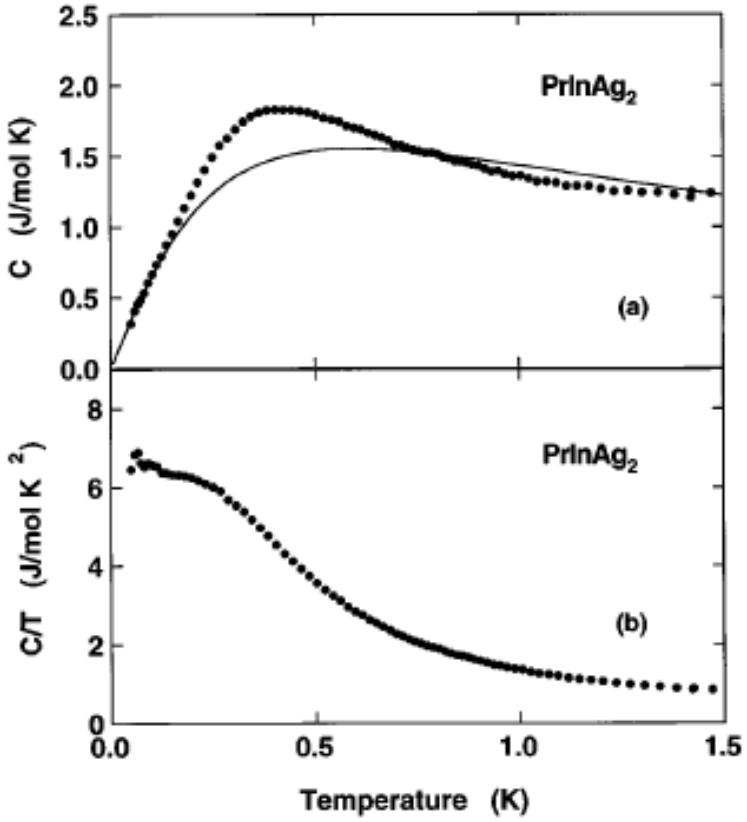
Large C/T for T < 300 mK



Kelly et al., PRB 61 (2000) 1831



Yatskar et al., PRL 77 (1996) 3637



$PrAg_2In$

Can entropy be preserved in Pr-based samples to low enough temperatures to allow for hybridization?
Yes, if done carefully….cubic unit cell, cubic point symmetry.

Can a Pr-based sample go heavy?
Yes, but it is fundamentally different physics since the heavy fermion ground state is evolving from a non-magnetic CEF level. My pet theory is dynamic screening of Jahn-Teller distortion as mechanism for entropy transfer….

$PrAg_2In$ opened the area of Pr-based heavy fermion research and generalized the idea of preservation of entropy as a route to heavy fermion ground states. This system inspired several searches for other examples.

A wider “Want a specific ground state” search is associated with the idea of fragile magnets.

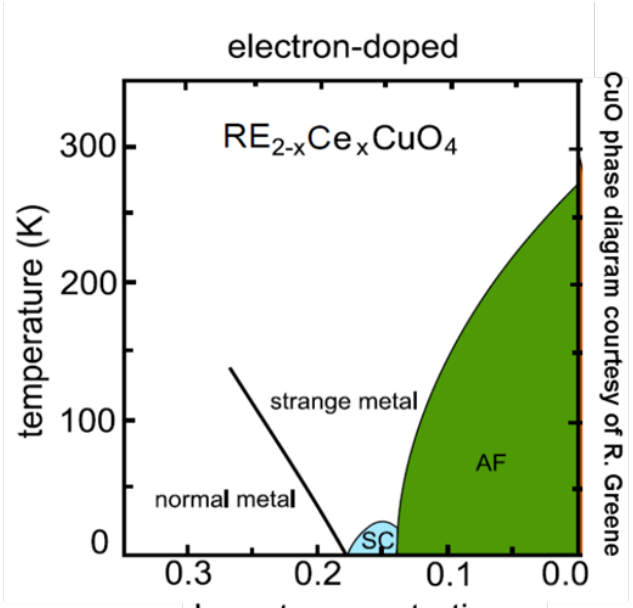
This, more modern effort, incorporates and employs computational work to narrow phase space.

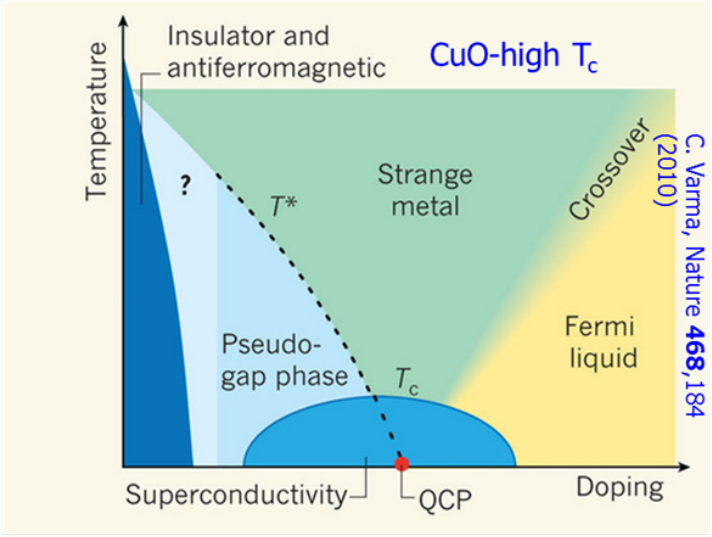
Want more high-T_c superconductors

Want a specific ground state

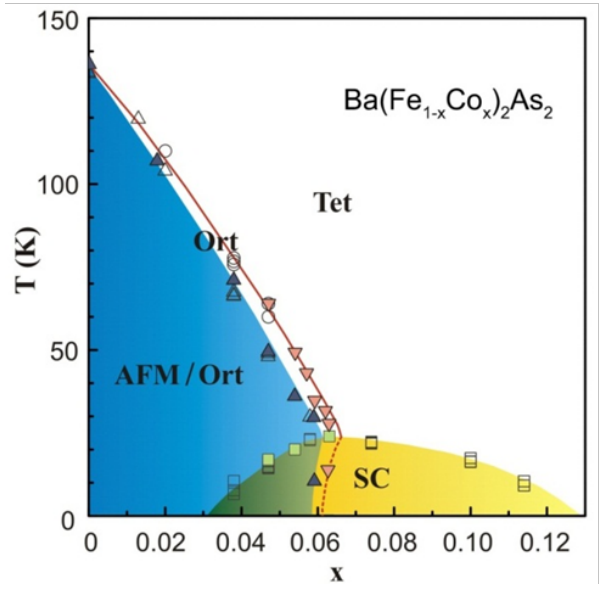
Want more high-T_c superconductors

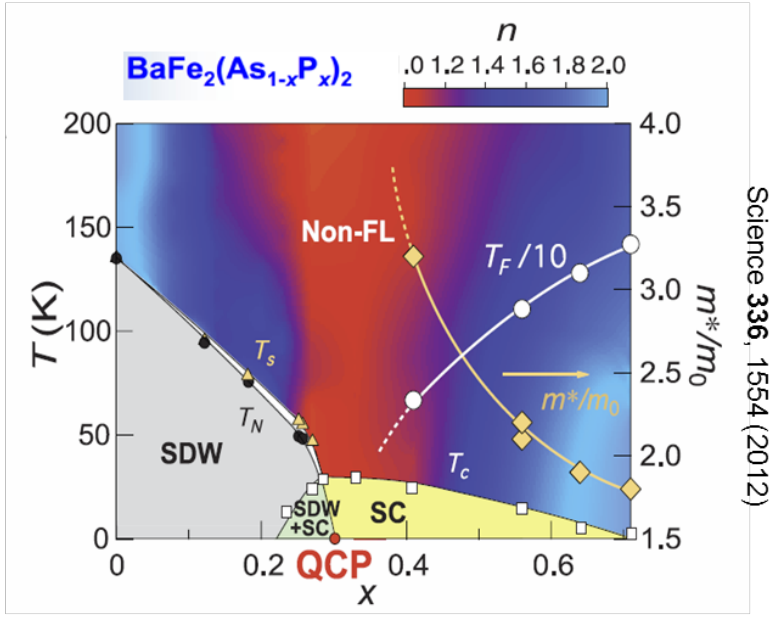
Want a specific ground state





Cu-based

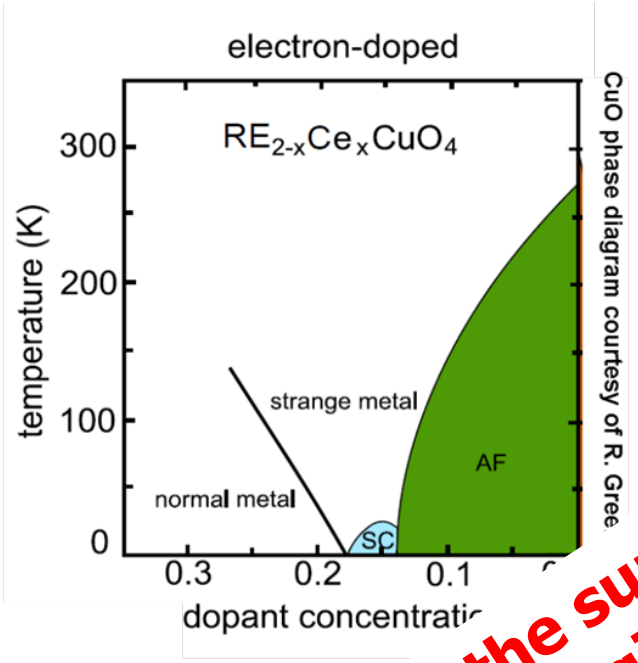


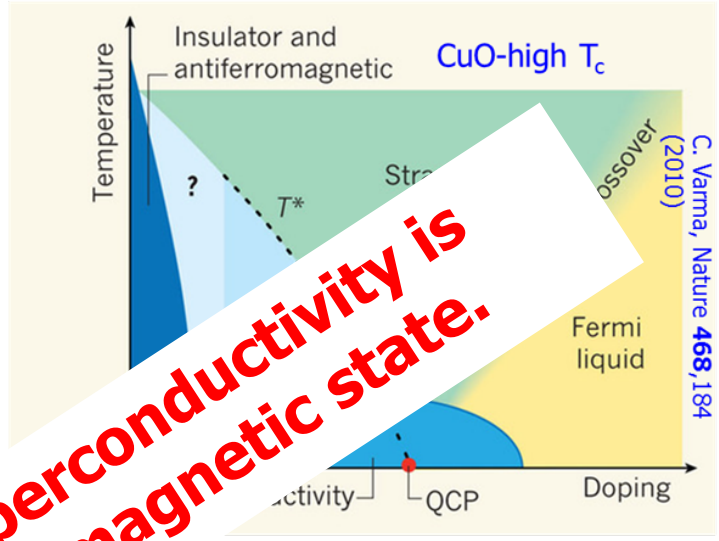


Science 336, 1554 (2012)

Fe-based

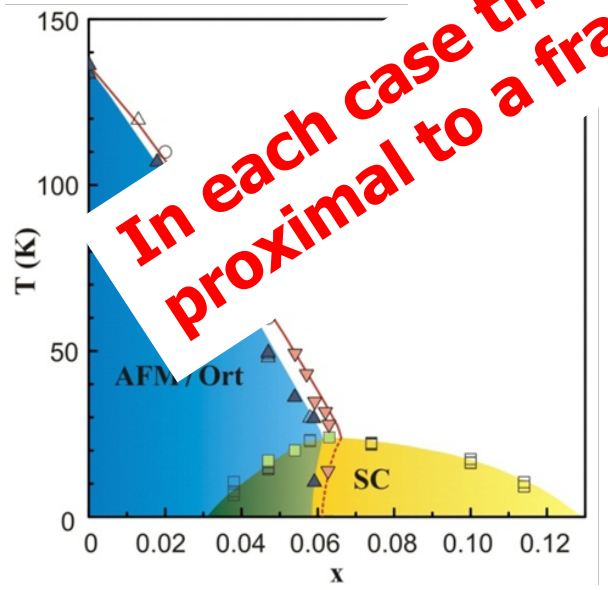
Want a specific ground state

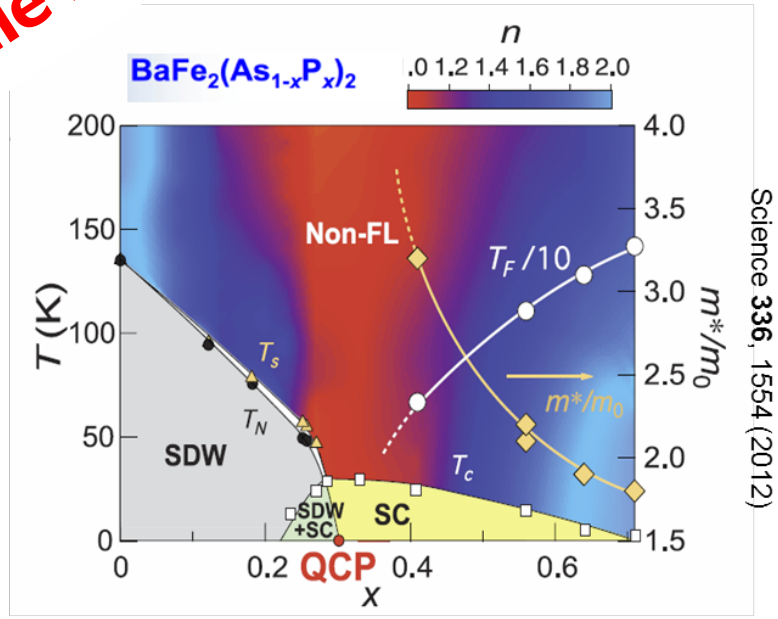




In each case the superconductivity is proximal to a fragile magnetic state.

Cu-based

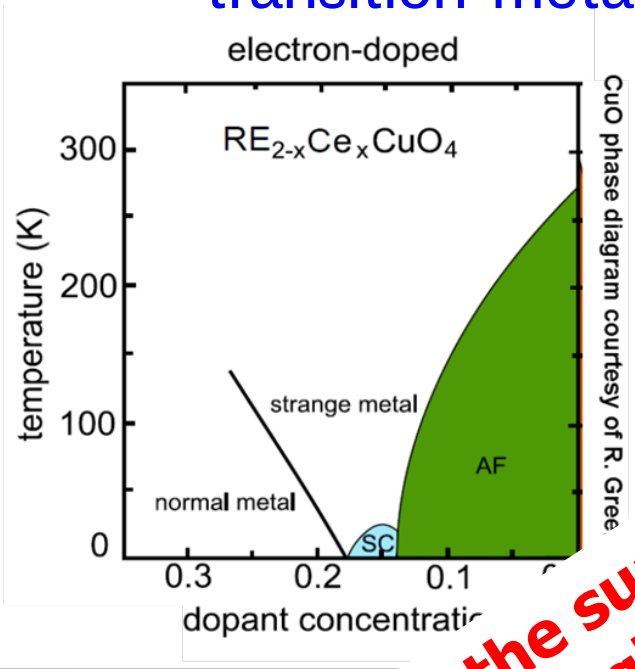


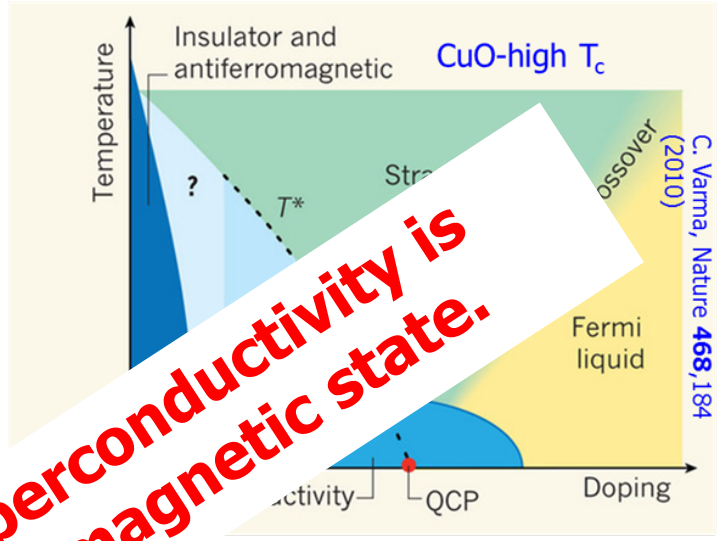


Fe-based

Let's rephrase our desire....We want to find transition-metal-based fragile magnets

Want a specific ground state





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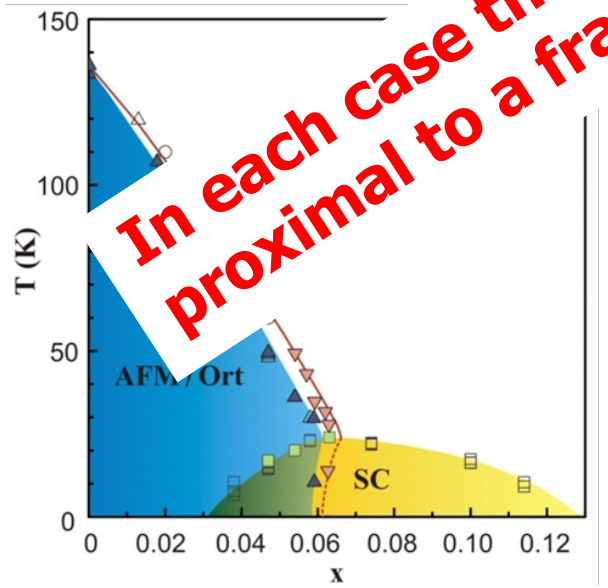
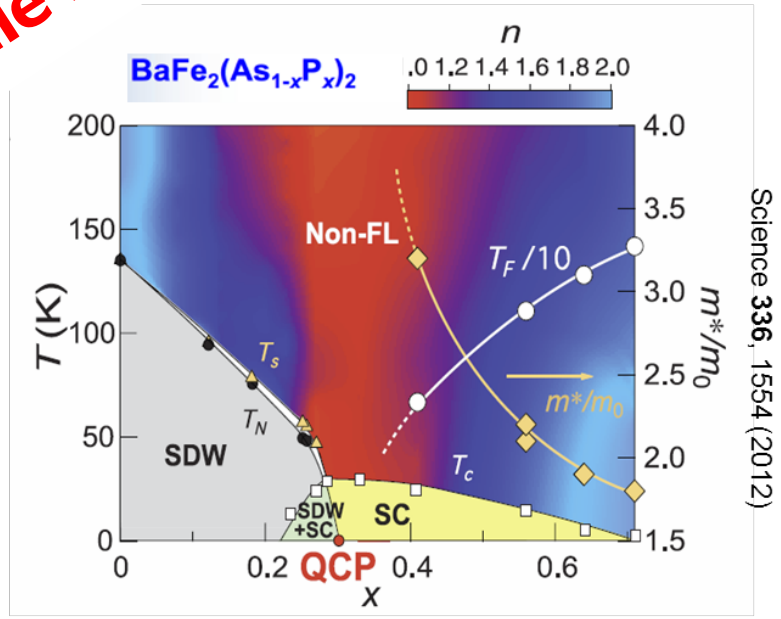
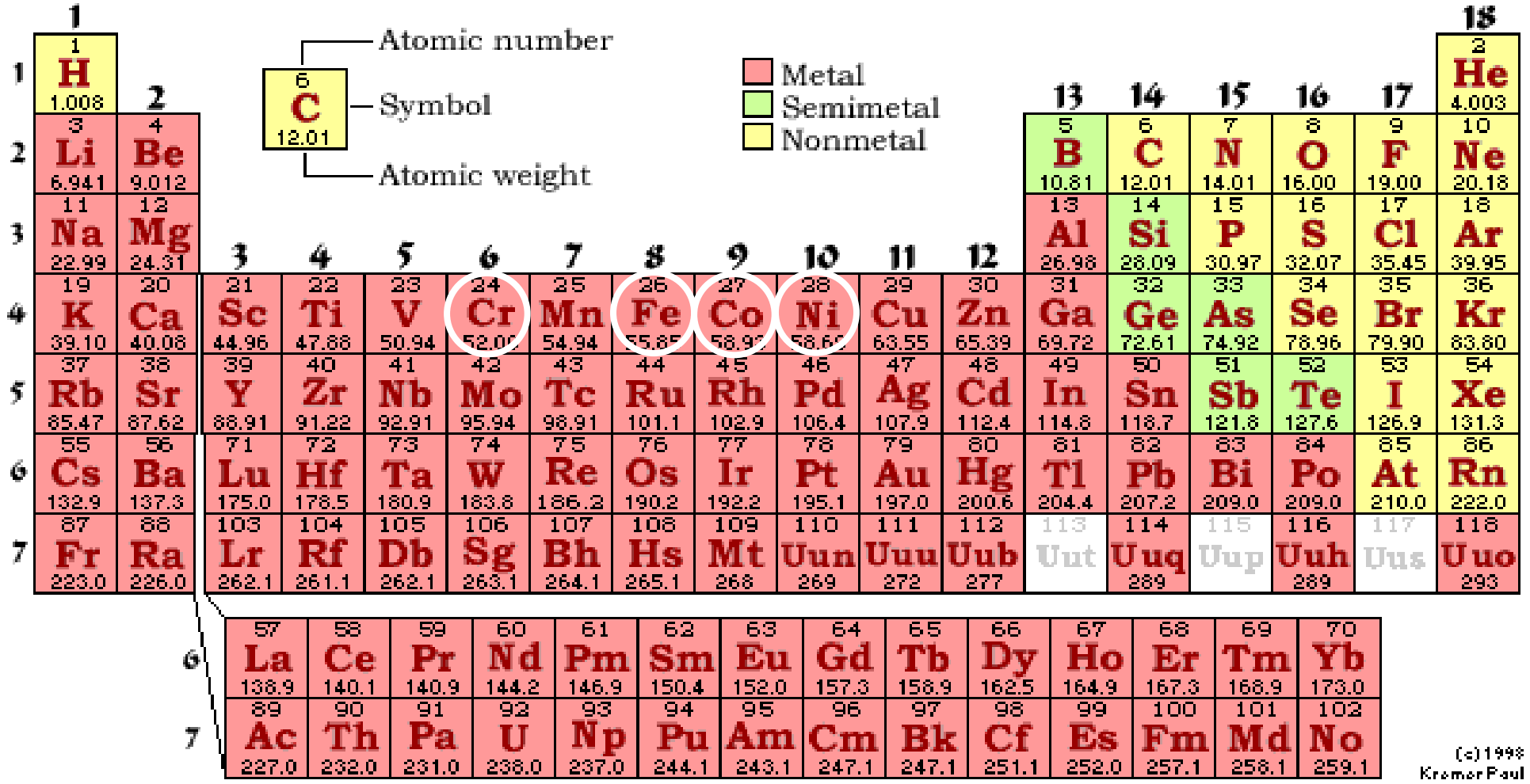


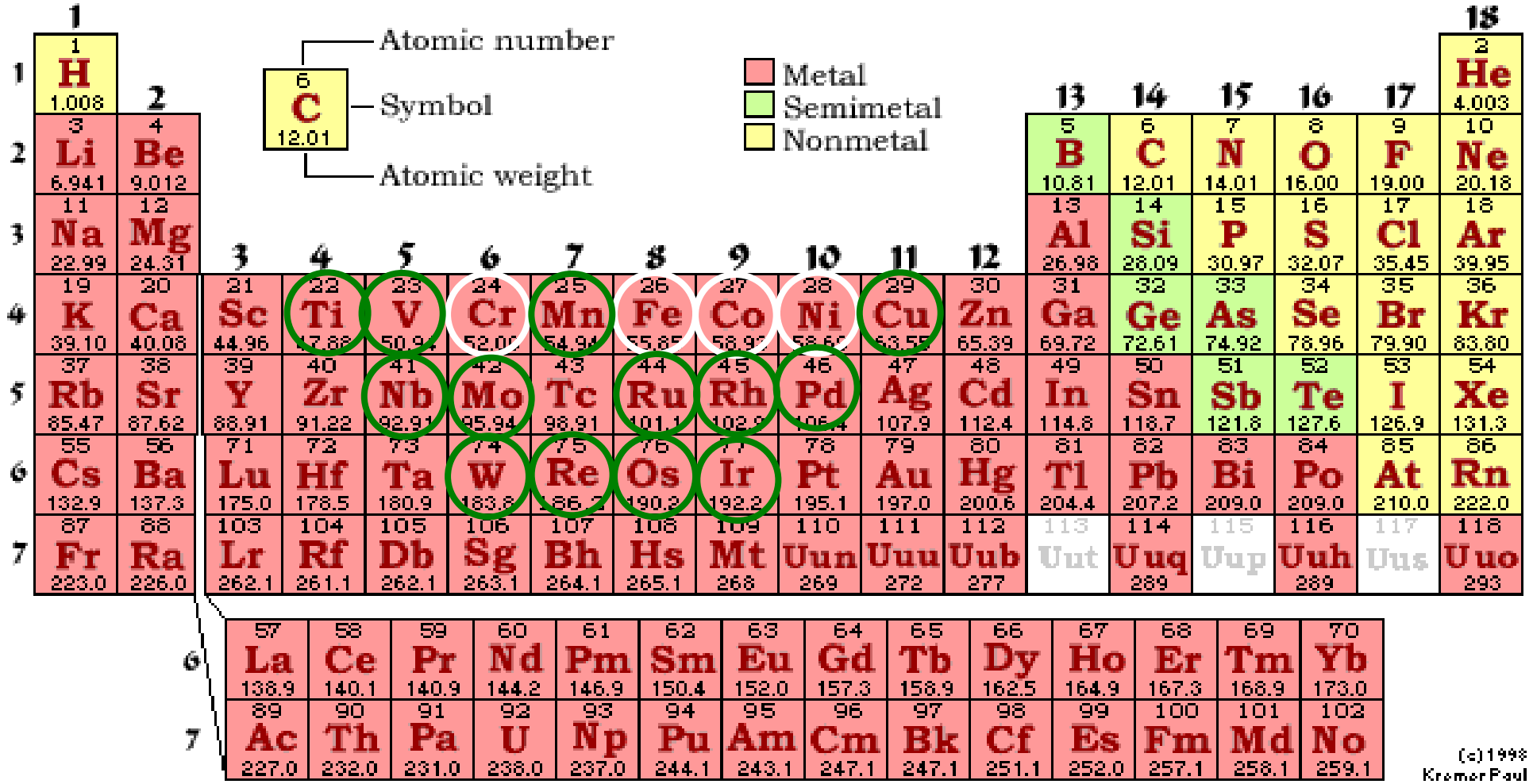


Fe-based

We can start limiting phase space by focusing on only the more likely transition metals.



We can start limiting phase space by focusing on only the more likely transition metals. We can expand to other later, as possible....



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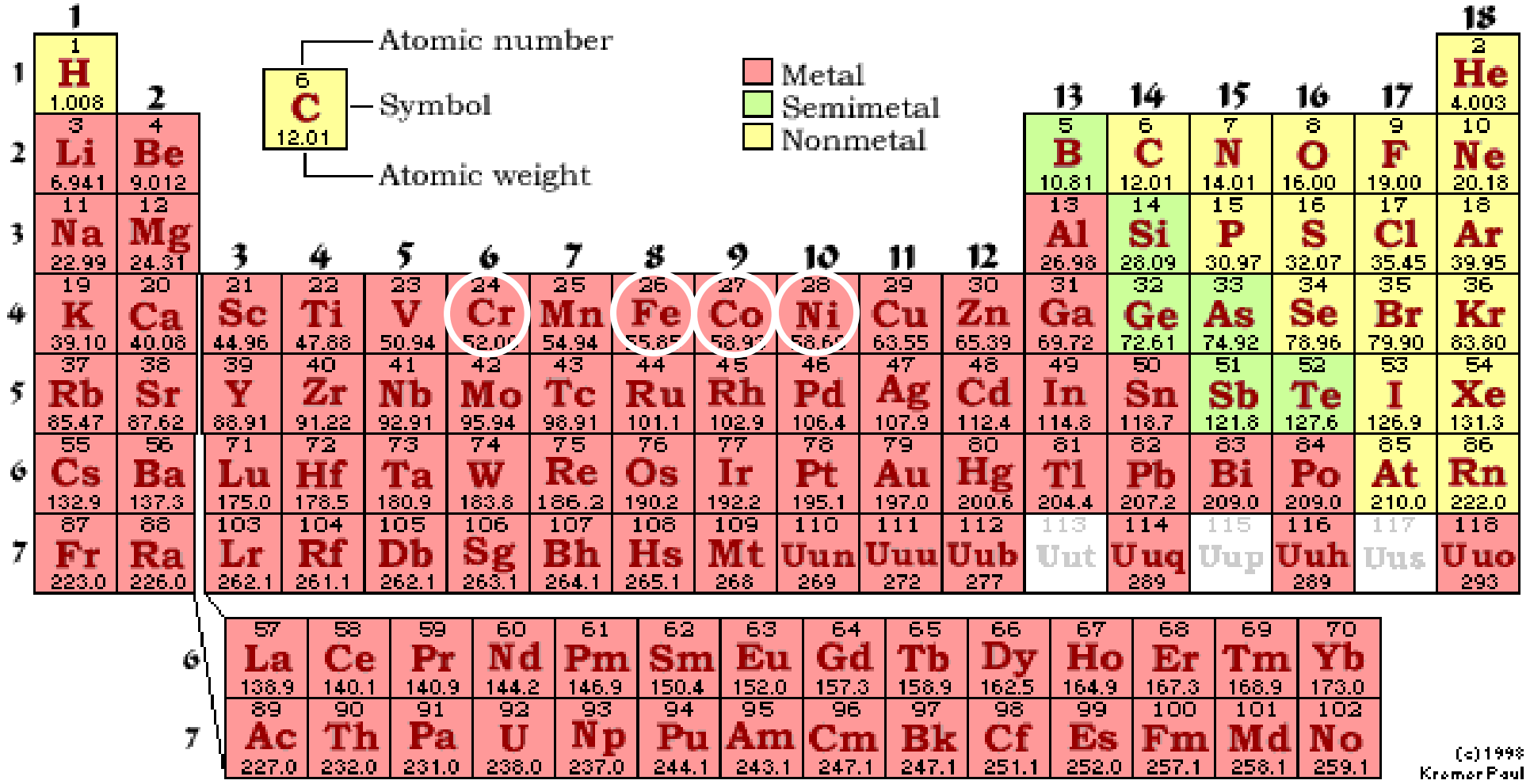

But even just these four transition metals cover a substantial phase space

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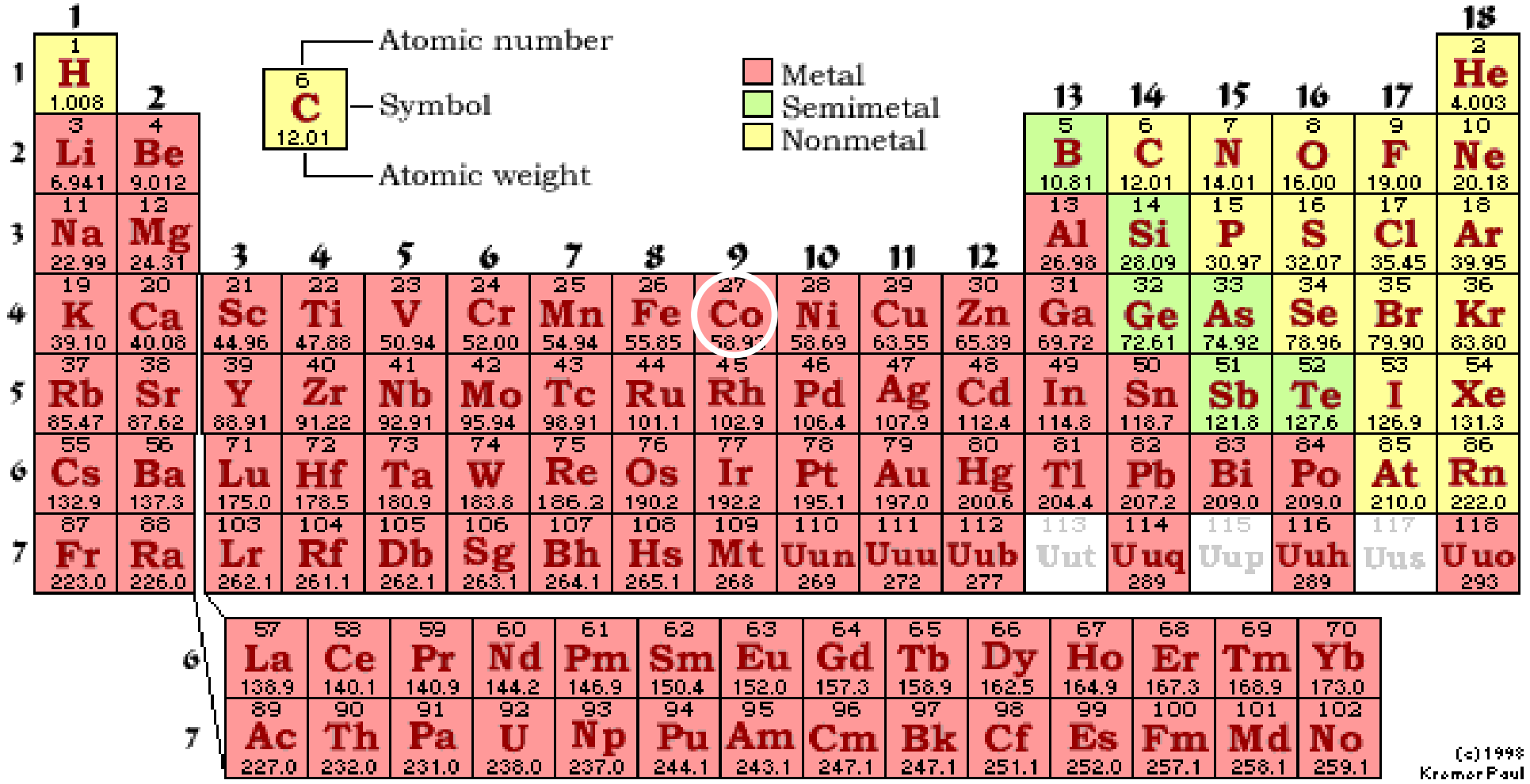
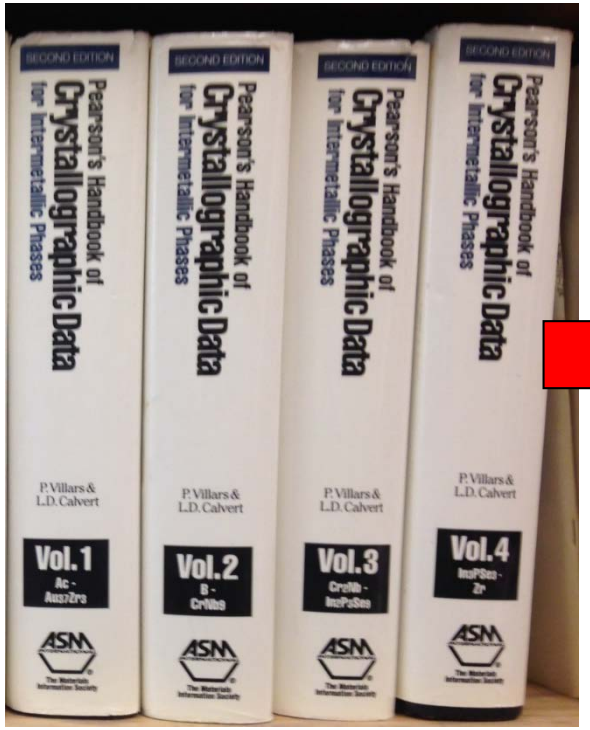
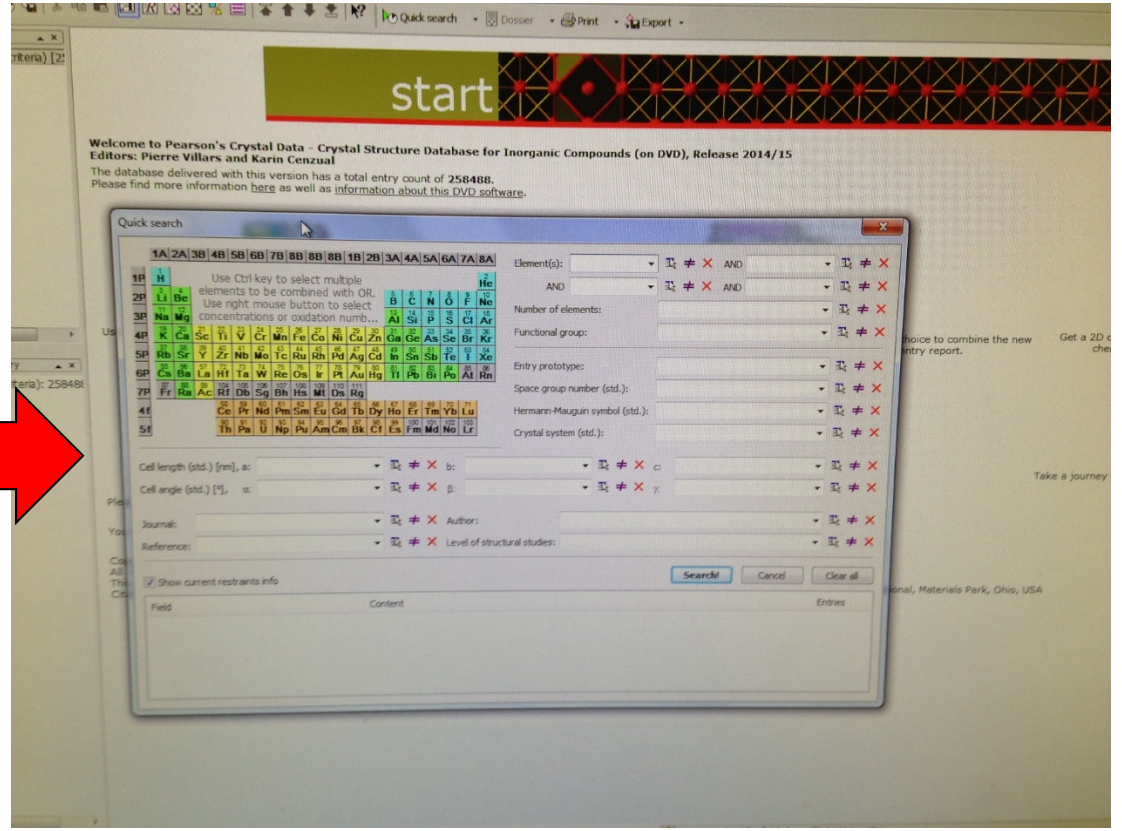


As an example, we can look at just cobalt





-Now the advantage of computerized searches becomes key.

-Make “cuts” on known compounds.

i.e. use Pearson’s Crystallographic software to look for subsets

e.g. tetragonal unit cell, ternary compound, Co-bearing (1158)

This is a big and difficult search.

We propose to devise ways to make it easier.

We are using computational efforts to help identify “fragility”.

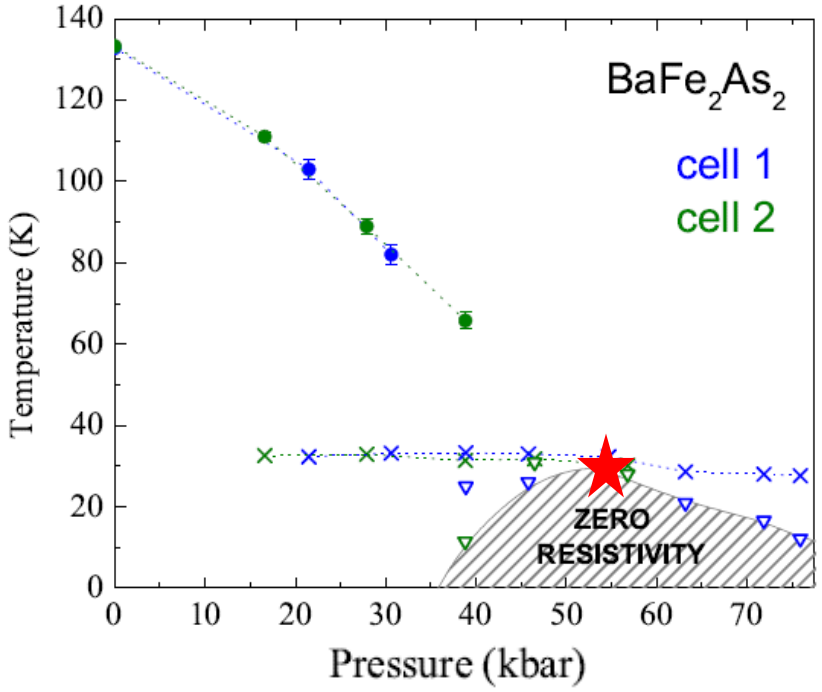
We want something that indicates a degree of fragility of the phase transition.

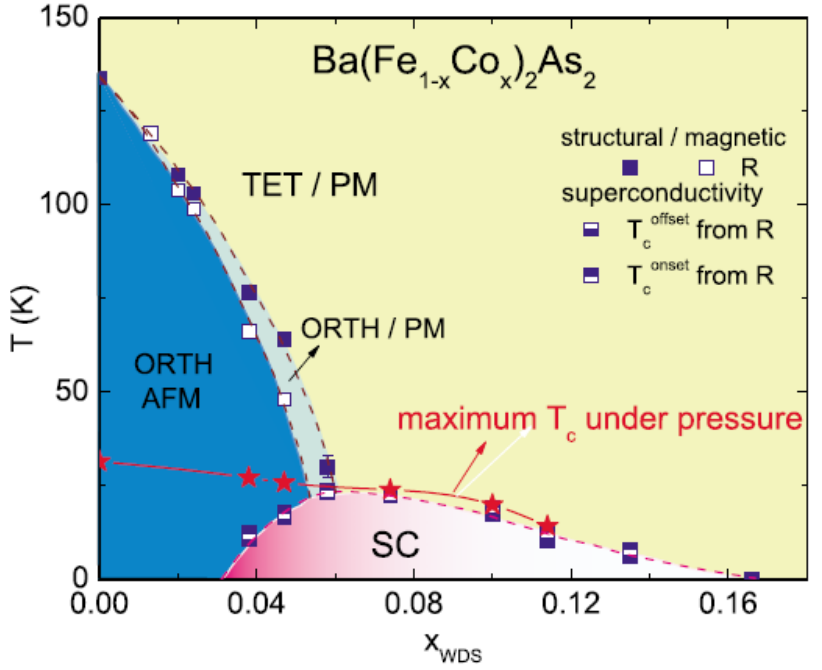
Computation of pressure effects on a pure compound is much easier / reliable than computation of substitution effects.

Grossly, this means we focus on band width more than band filling, but even that is a good start.

Fortunately there is often a correlation between pressure sensitivity and response to substitution.

Phys. Rev. B **79**, 224518 (2009)





PHYSICAL REVIEW B **82**, 024519 (2010)

The search for “fragile magnet superconductors”.

Experimentally:

We will identify promising candidate materials, both through data mining / literature search and also through exploration based on experience and intuition.

We will use our ability to measure magnetization and electrical transport under pressures of up to ~ 1, 2, or 8 GPa to help determine degree of fragility.

We will use chemical substitution to help determine degree of fragility.

Systems that can have their magnetic transitions driven to zero will be studied in detail

Computationally:

We will provide benchmark data for computational efforts to use to develop methodologies for identification of “fragility”.

Once methodologies are considered to be reliable, we will use them to make first cut identifications of candidate materials.

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We have started trying to do this.

The third motivation has two parts:
Searching for known unknowns is something we have seen already.

Studies of rare earth series: RX_nY_m

known unknowns

runs across the series

RBiPt

RSb_2

RNi_2Ge_2

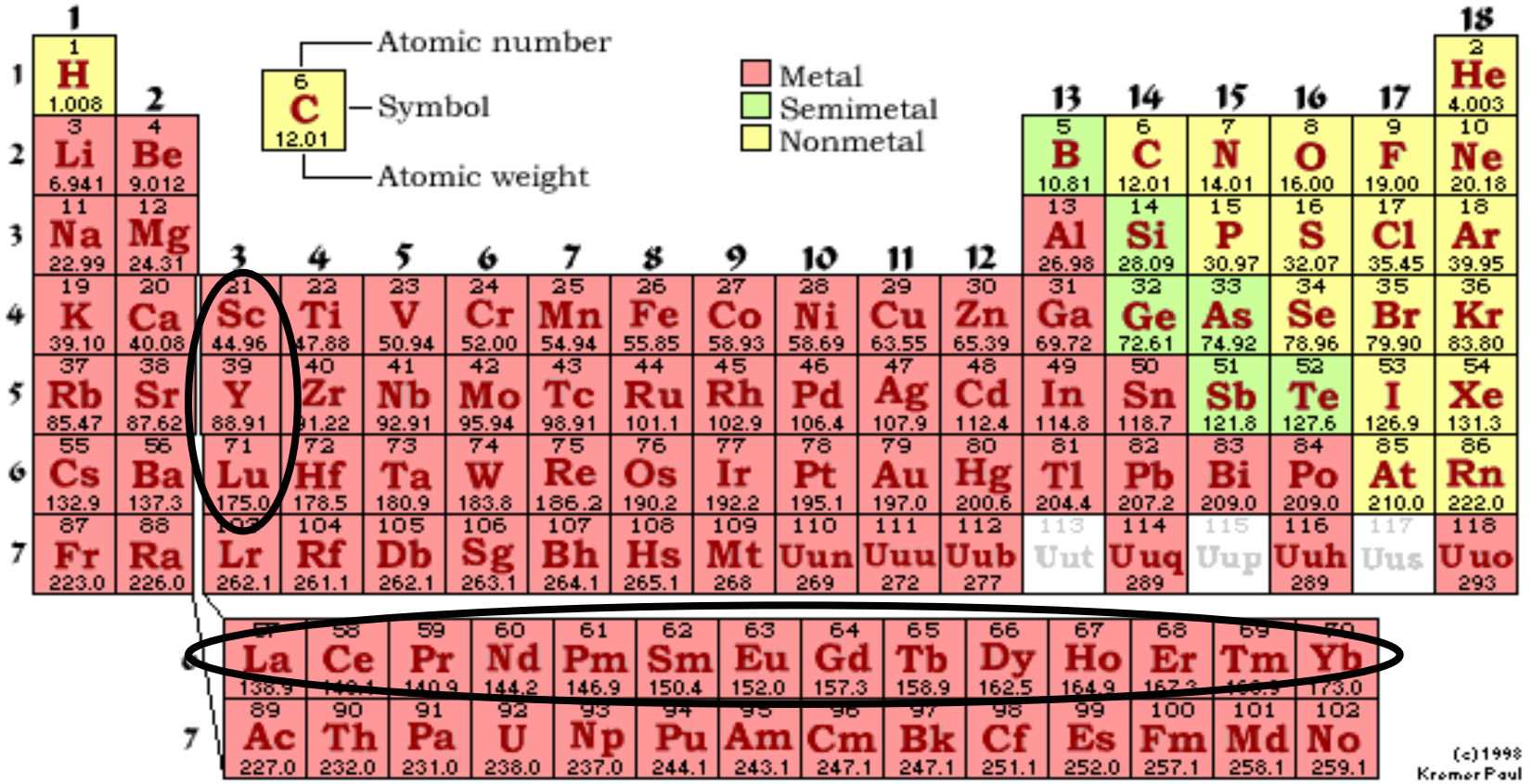
RNi_2B_2C

$RAgSb_2$

RAgGe

i-R-Mg-Zn

RT_2Zn_{20}



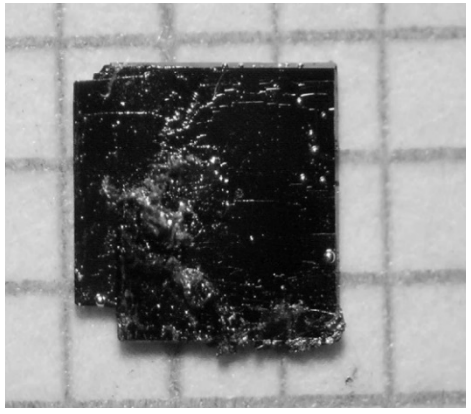
Such explorations have led to many discoveries associated with local and itinerant magnetism and superconductivity

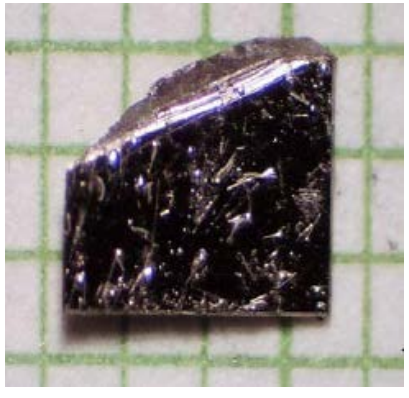
Explorations of a given crystal structure / class

PHYSICAL REVIEW B 78, 014507 (2008)

Anisotropic thermodynamic and transport properties of single-crystalline $Ba_{1-x}K_xFe_2As_2$ ($x=0$ and 0.45)

N. Ni,[1,2] S. L. Bud'ko,[1,2] A. Kreyssig,[1,2] S. Nandi,[1,2] G. E. Rustan,[1,2] A. I. Goldman,[1,2] S. Gupta,[1,3] J. D. Corbett,[1,3] A. Kracher,[1] and P. C. Canfield[1,2]
[1]*Ames Laboratory US DOE, Iowa State University, Ames, Iowa 50011, USA*
[2]*Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[3]*Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA*
(Received 11 June 2008; revised manuscript received 18 June 2008; published 10 July 2008)



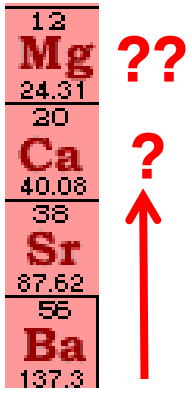


PHYSICAL REVIEW B 78, 024516 (2008)

Structural transition and anisotropic properties of single-crystalline $SrFe_2As_2$

J.-Q. Yan,[1] A. Kreyssig,[1,2] S. Nandi,[1,2] N. Ni,[1,2] S. L. Bud'ko,[1,2] A. Kracher,[1] R. J. McQueeney,[1,2] R. W. McCallum,[1,3] T. A. Lograsso,[1] A. I. Goldman,[1,2] and P. C. Canfield[1,2]
[1]*Ames Laboratory, US DOE, Iowa State University, Ames, Iowa 50011, USA*
[2]*Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[3]*Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA*
(Received 18 June 2008; published 23 July 2008)

known unknowns



$BaFe_2As_2$ and $SrFe_2As_2$ were known compounds ....What about $CaFe_2As_2$ and $MgFe_2As_2$?

The third motivation has two parts:
Searching for known unknowns is something we have seen already.

What are searches for unknown unknowns?
They are directed, but unfocused searches....

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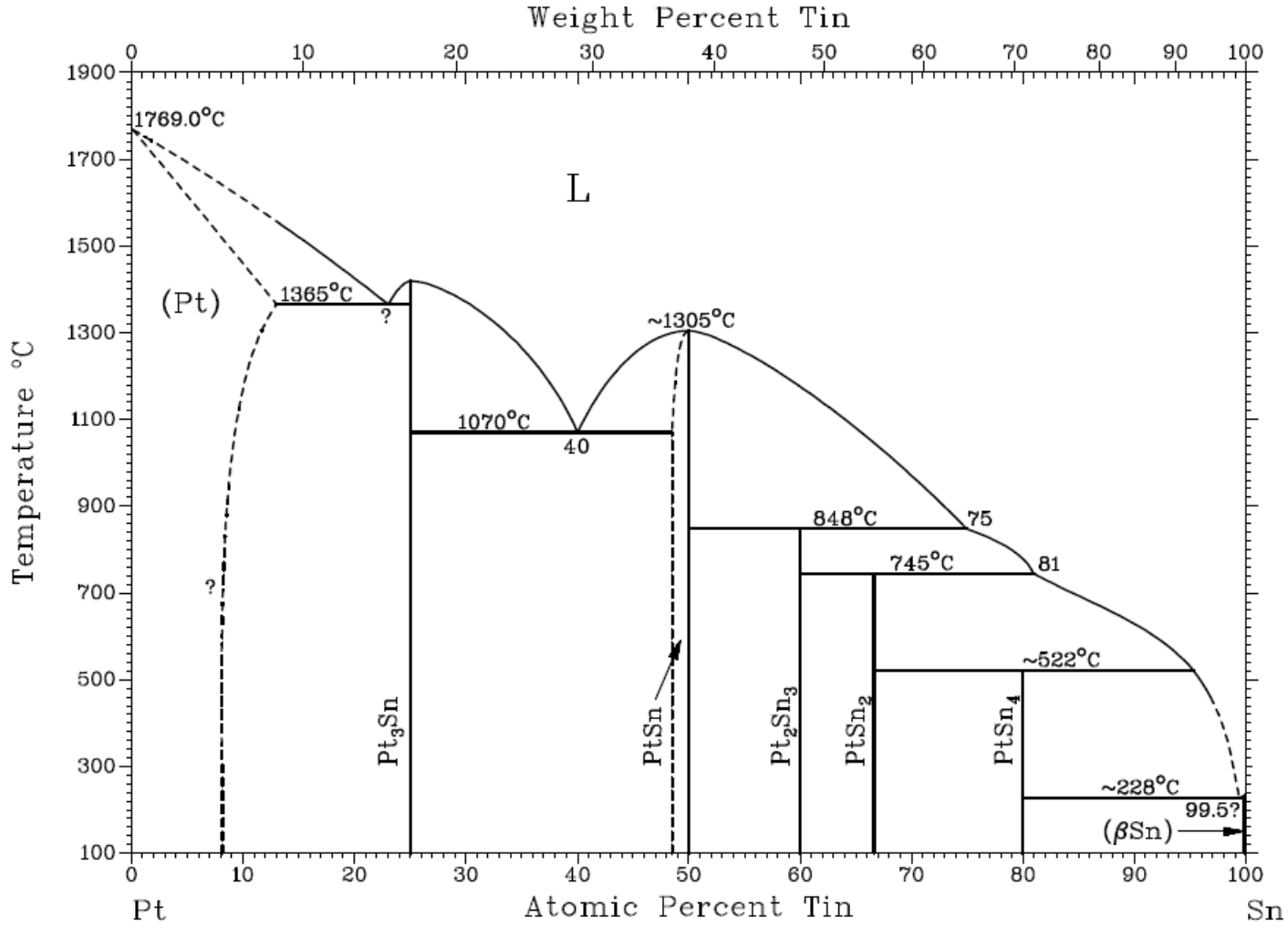
Time for
two examples:

Deep Peritectic Project

unknowns

Solution growth is particularly powerful for the growth of single crystals of compounds that have very low peritectic decomposition temperatures



In many cases, such compounds have not been grown or studied in single crystal (or even single phase) form.

We have been growing and studying such compounds. Each one leads us where it will. ***We decide whether to follow or not.***

Deep Peritectic Project

unknowns

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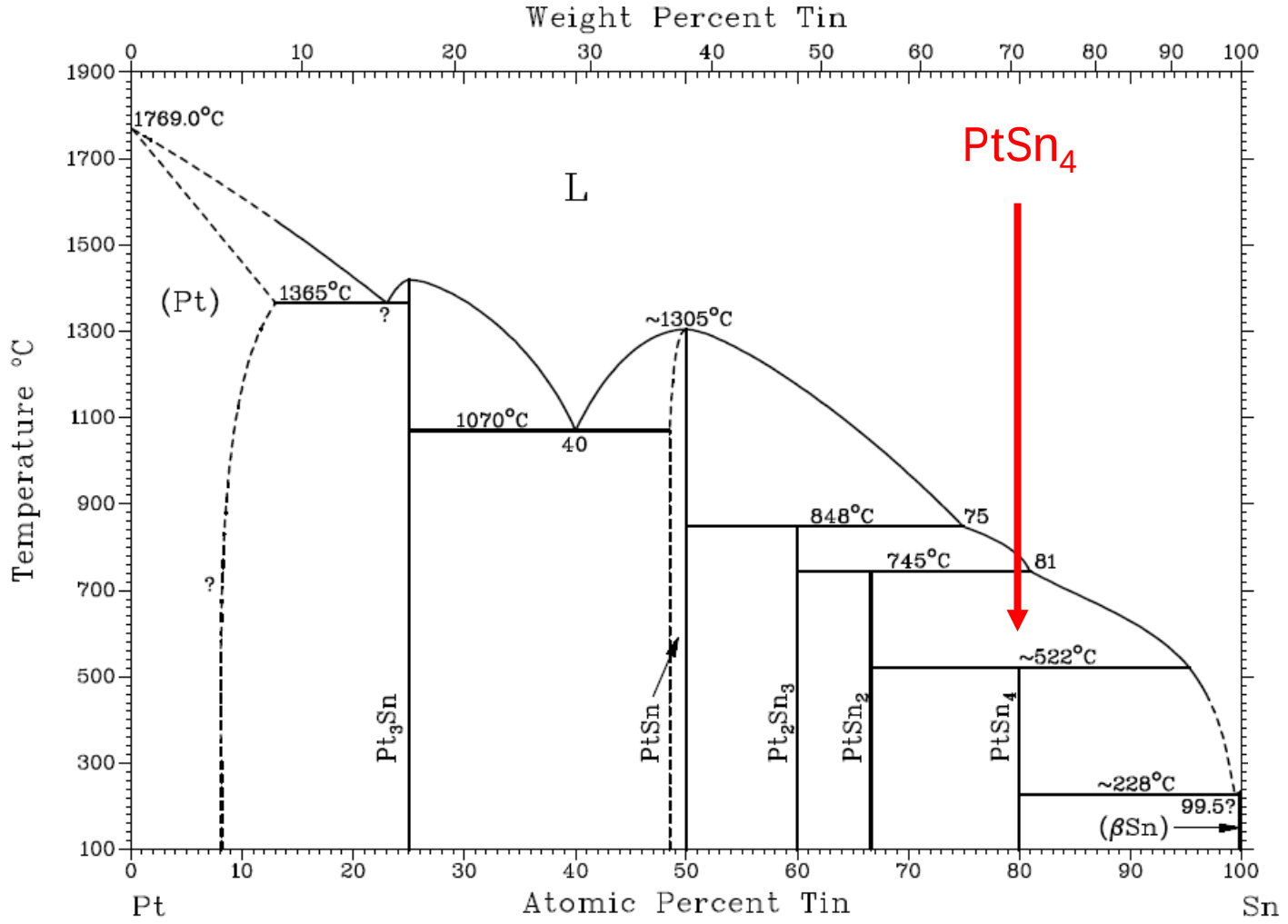
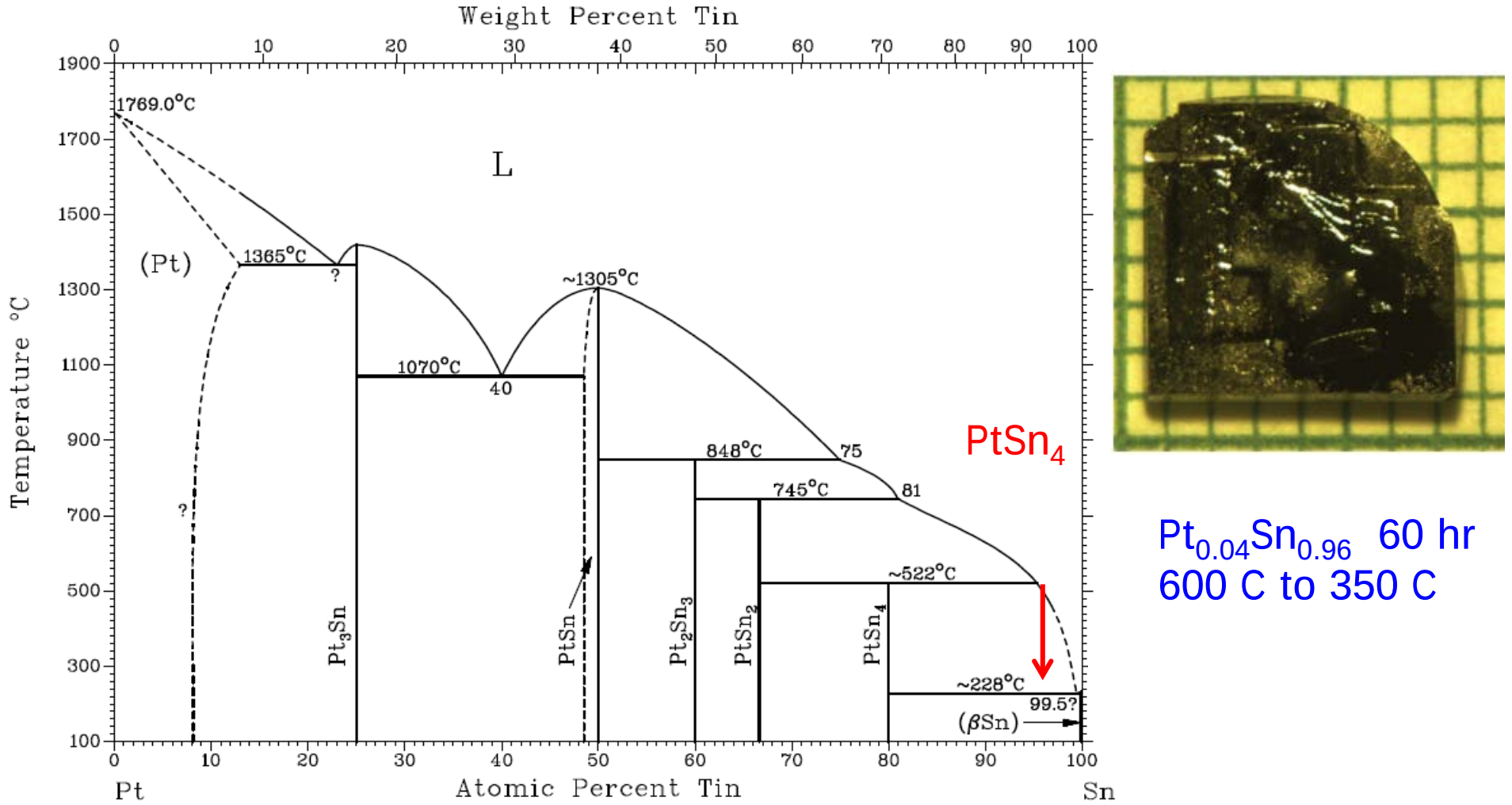


$PtSn_4$ is an example of such a compound.

Deep Peritectic Project

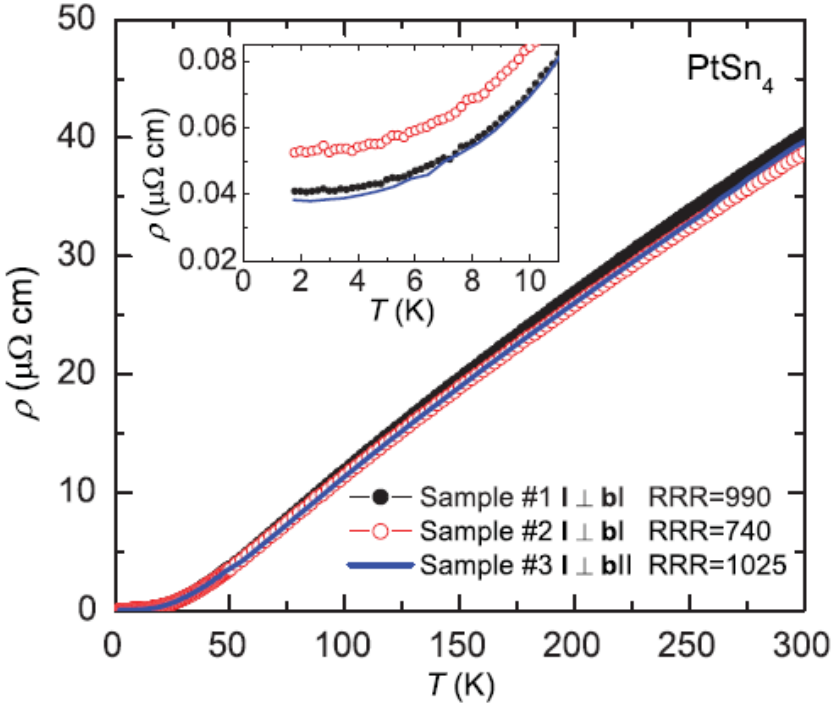
unknowns

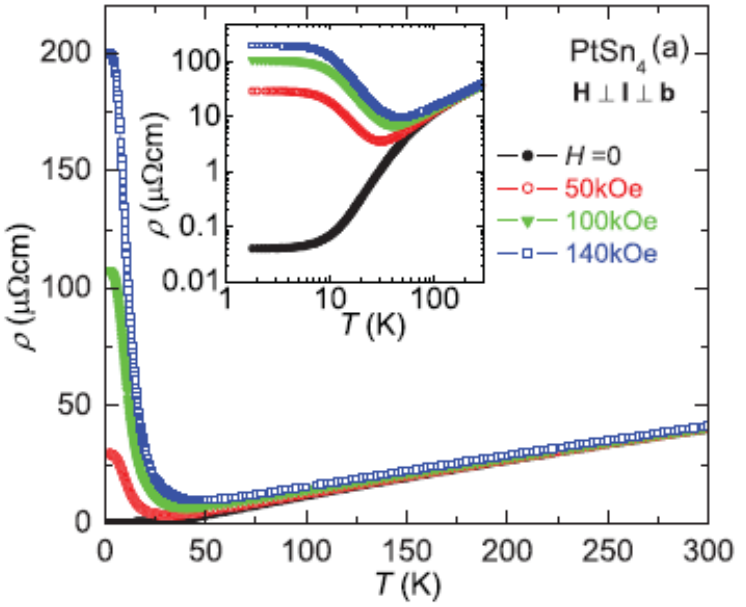
Solution growth is particularly powerful for the growth of single crystals of compounds that have very low peritectic decomposition temperatures



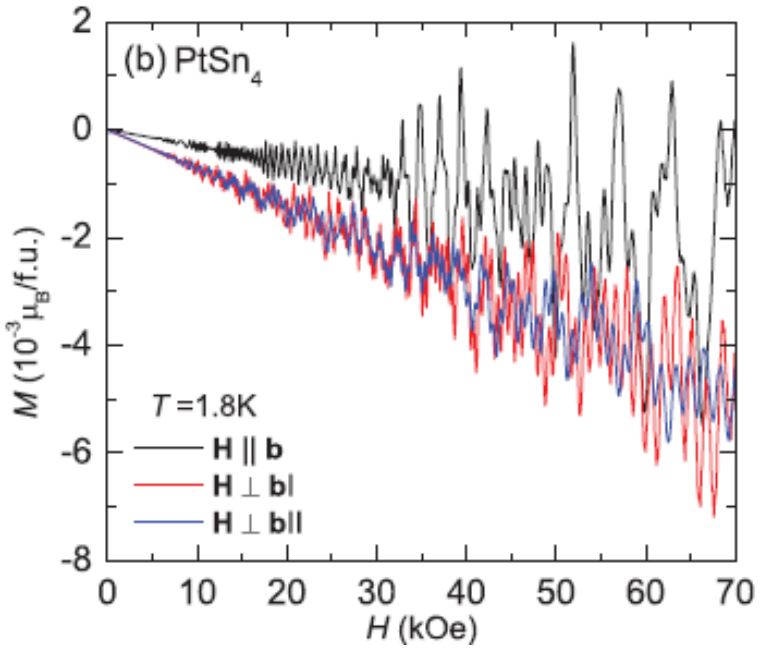
$Pt_{0.04}Sn_{0.96}$ 60 hr
600 C to 350 C

PHYSICAL REVIEW B **85**, 035135 (2012)



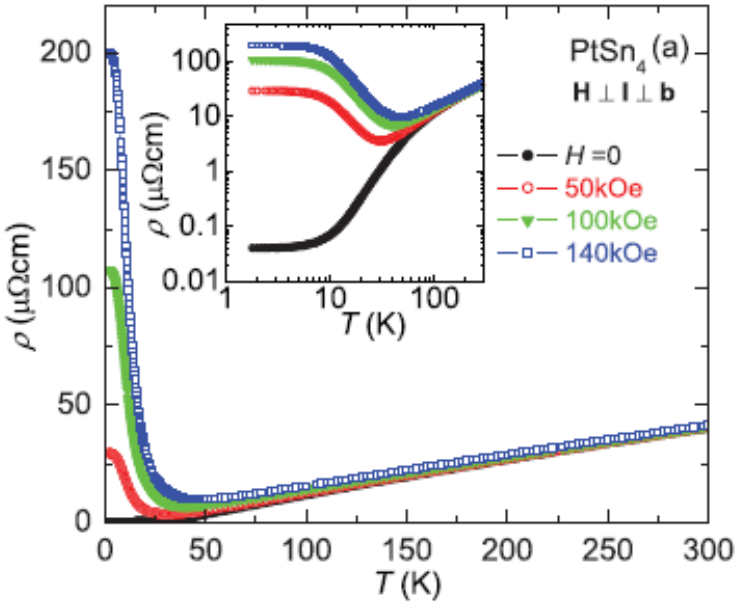


In 2012 we published an early example of what more recently has been called "titanic" or "extreme" magnetoresistance. We found $PtSn_4$ forms with remarkable purity and manifests quantum oscillations (up to high temperatures and in modest fields) in almost any property we measured.



More recently, based on its enormous field sensitivity, we examined the Fermiology of $PtSn_4$ and discovered Dirac node arcs.

PHYSICAL REVIEW B 85, 035135 (2012)

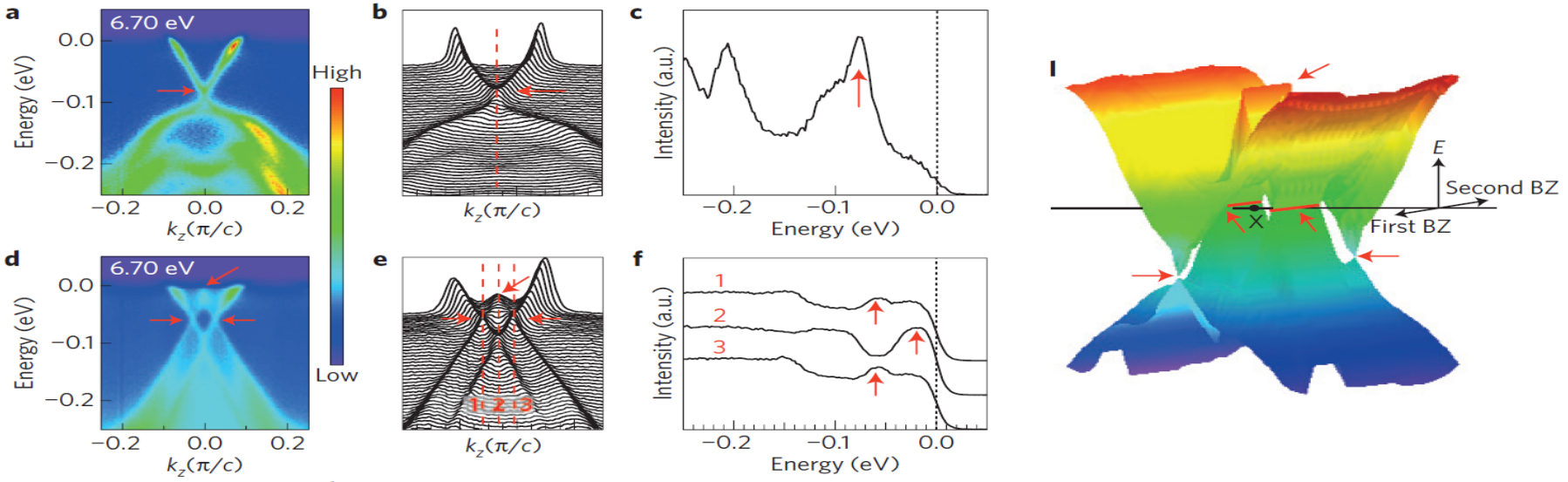


nature physics

LETTERS

PUBLISHED ONLINE: 4 APRIL 2016 | DOI: 10.1038/NPHYS3712

Dirac node arcs in $PtSn_4$

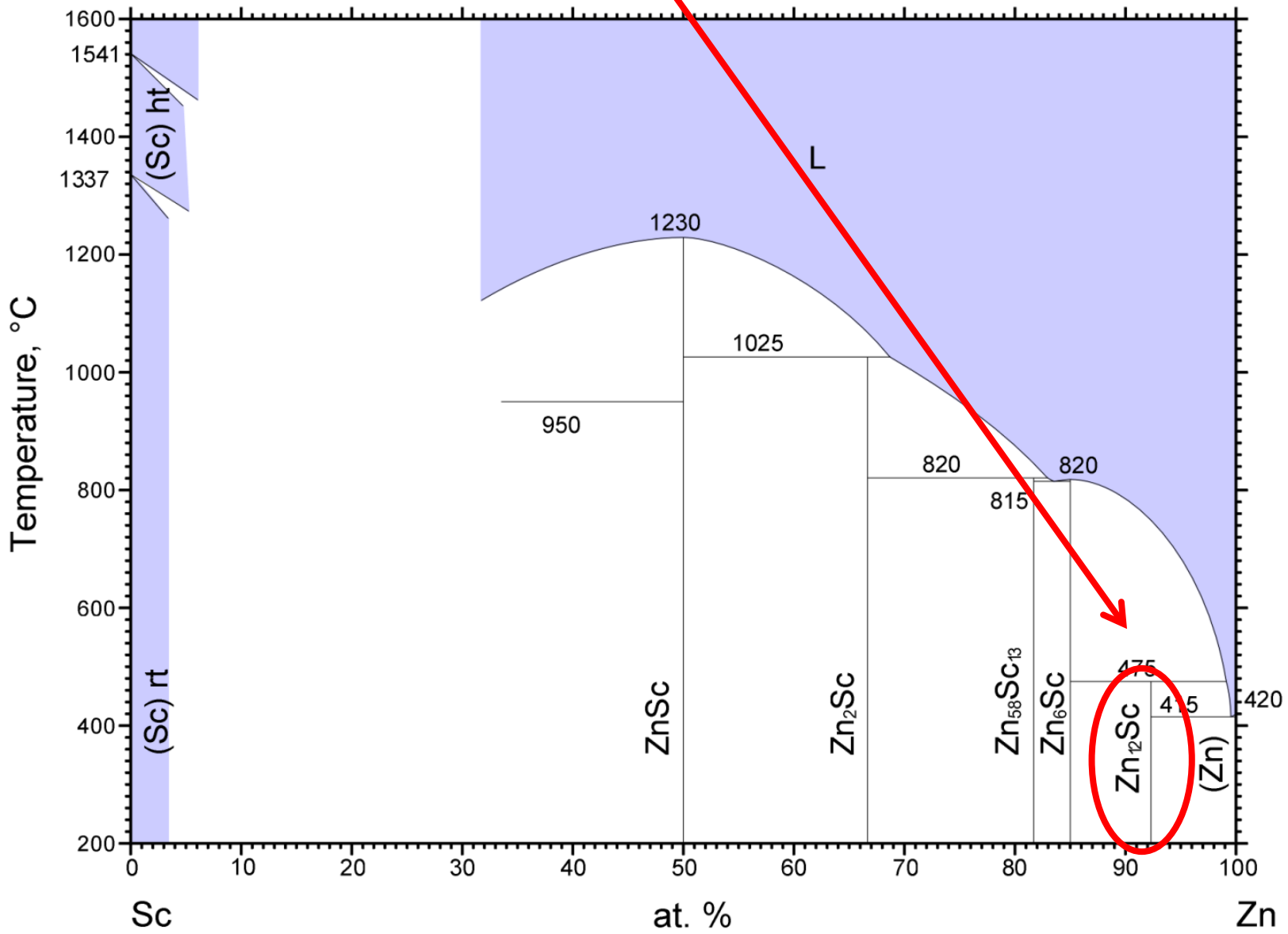


A second example of what comes from searching for unknown unknowns...

We mastered the use of Zn as a solvent growing the RT_2Zn_{20} compounds. This opened Zn up as a more general use solvent.

$ScZn_{12}$ was an attractive target.

unknowns

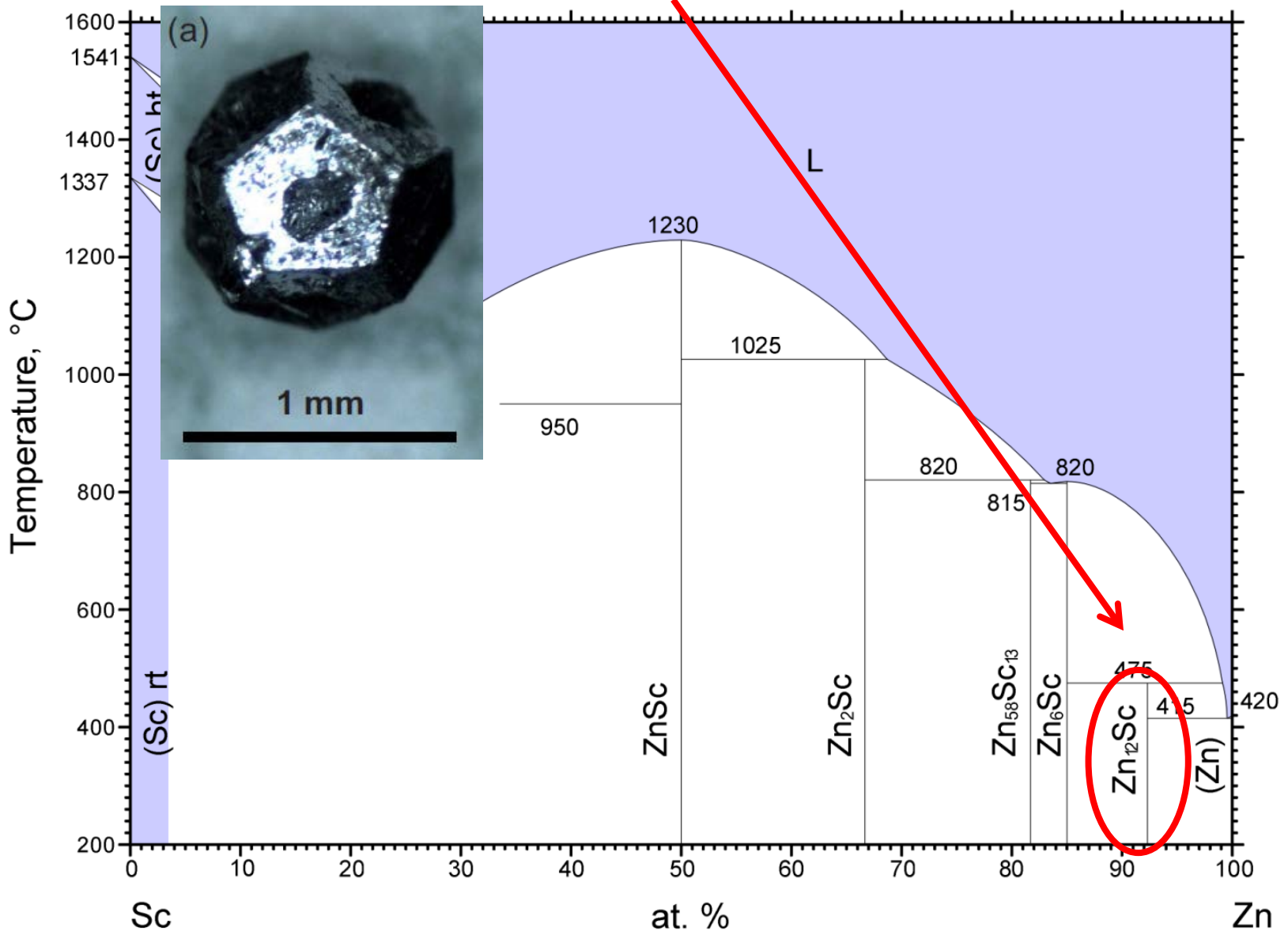


$ScZn_{12}$
$ThMn_{12}$,tI26
I4/mmm (139)

unknowns

Instead we grew this....

$ScZn_{12}$ was an attractive target.



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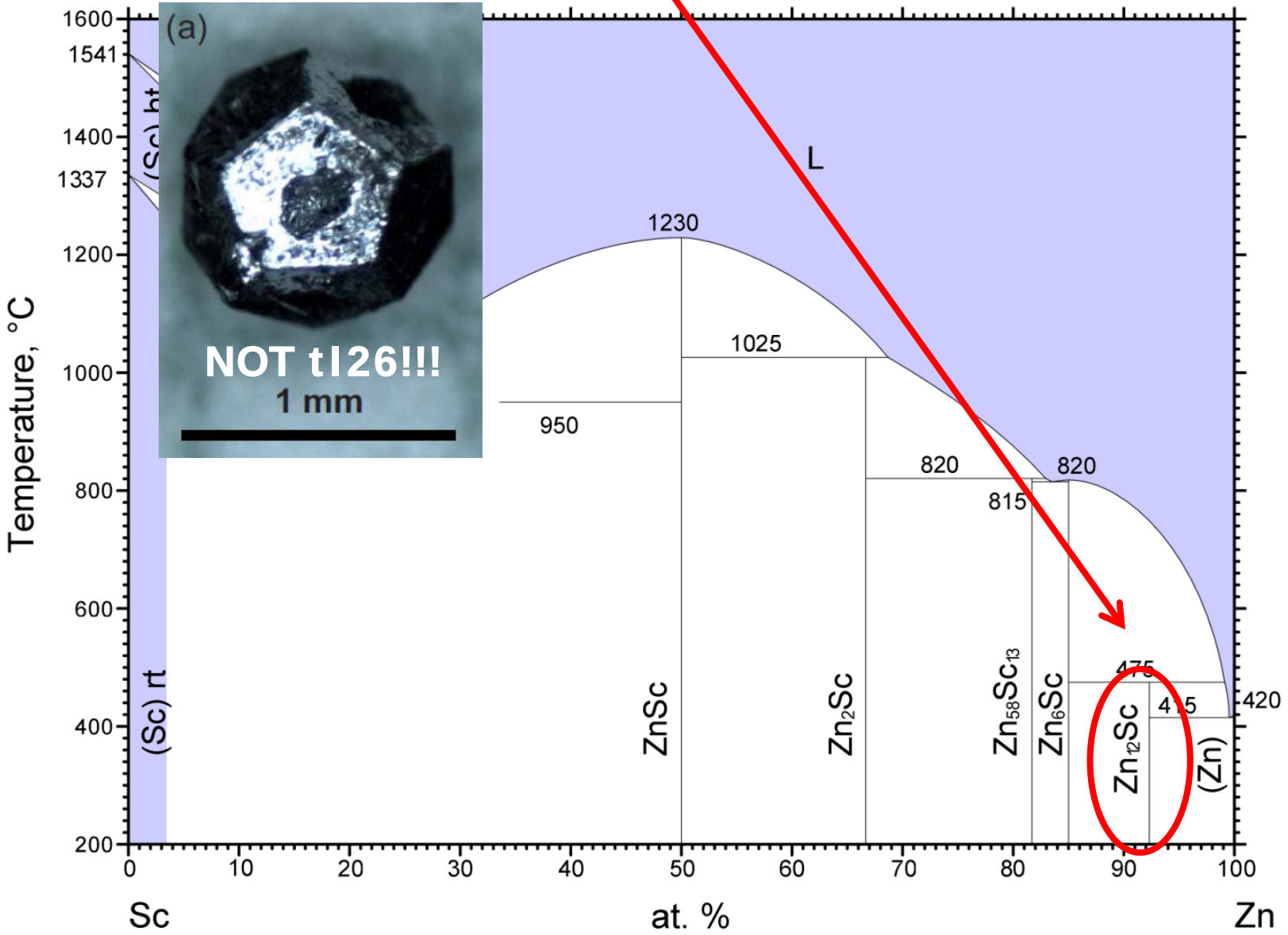
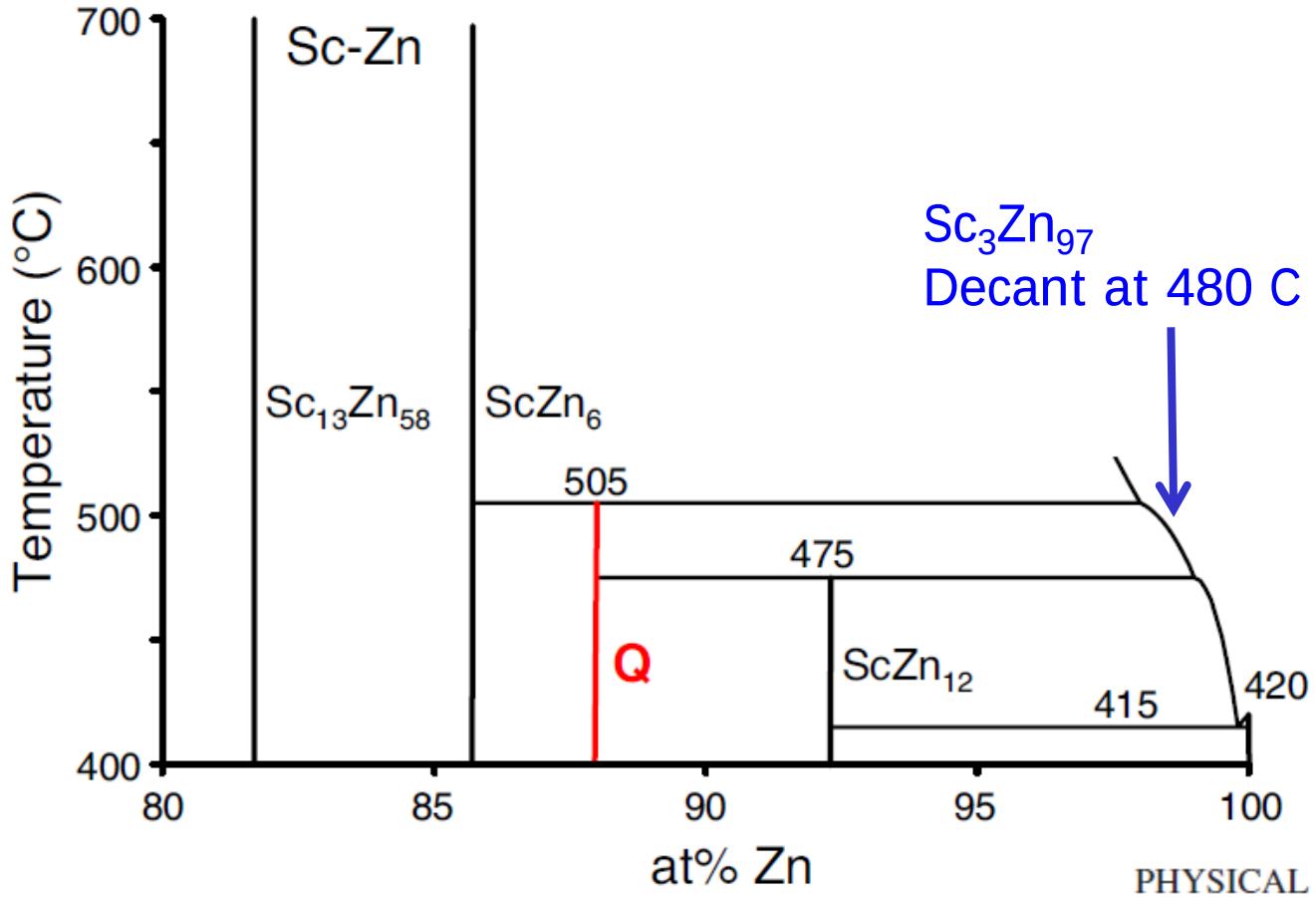
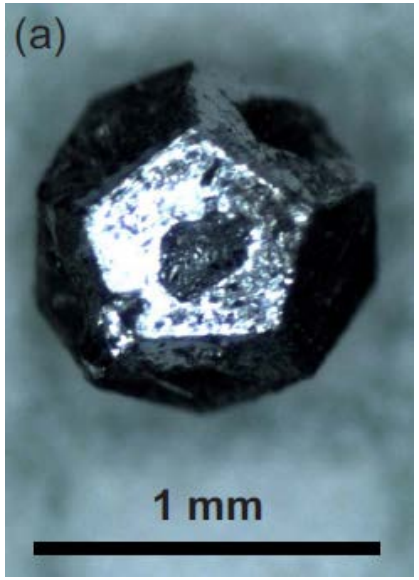


$ScZn_{12}$
$ThMn_{12}$,tI26
I4/mmm (139)

unknowns

We discovered the second known, stable binary quasicrystalline material: i-$Sc_{12}Zn_{88}$.
We also redefined the Zn-rich side of the binary Zn-Sc phase diagram.





PHYSICAL REVIEW B 81, 020201(R) (2010)

This led directly our discovery or i-RCd QCs.

nature materials

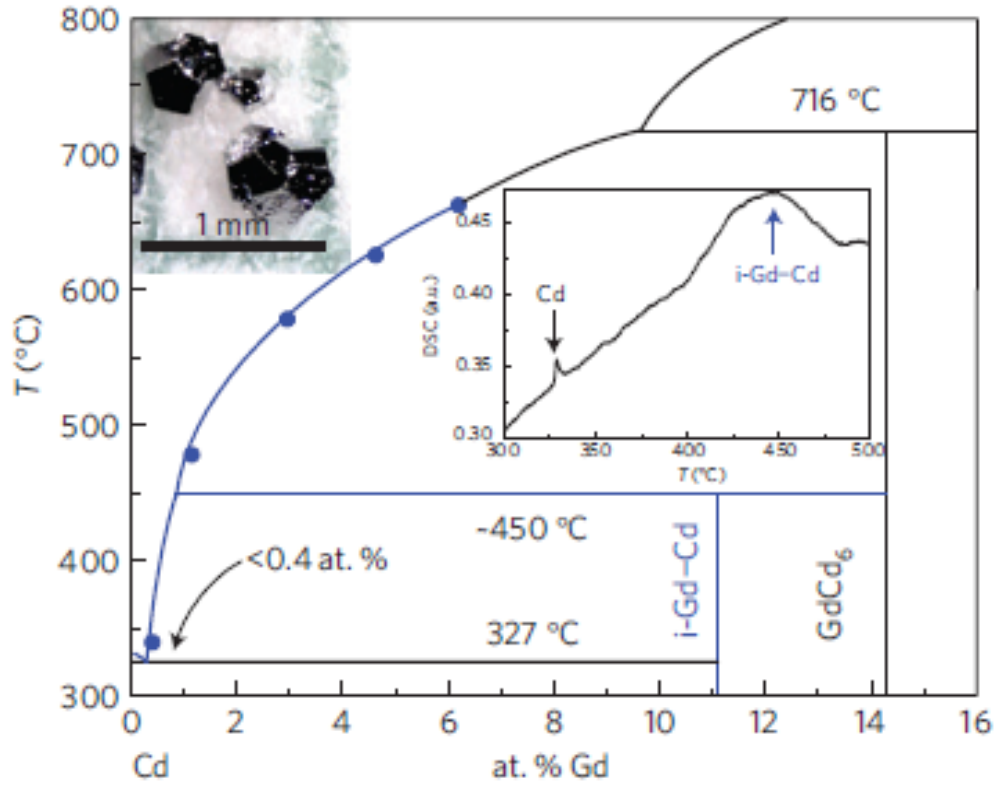
LETTERS

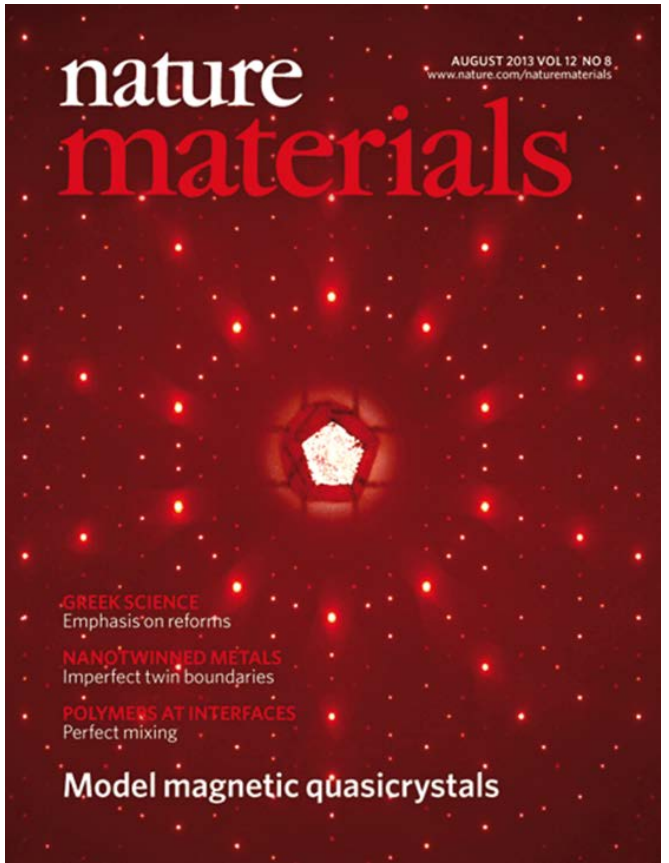
PUBLISHED ONLINE: 9 JUNE 2013 | DOI: 10.1038/NMAT3672

unknowns

A family of binary magnetic icosahedral quasicrystals based on rare earths and cadmium

Alan I. Goldman[1,2]*, Tai Kong[1,2], Andreas Kreyssig[1,2], Anton Jesche[1,2], Mehmet Ramazanoglu[1,2], Kevin W. Dennis[1], Sergey L. Bud'ko[1,2] and Paul C. Canfield[1,2]*





We find solutions

In order to grow a material out of solution, you need to have a solution that you can safely work with. Volatile elements are particularly hard to work with....

We find solutions

unknowns

In order to grow a material out of solution, you need to have a solution that you can safely work with. Volatile elements are particularly hard to work with....

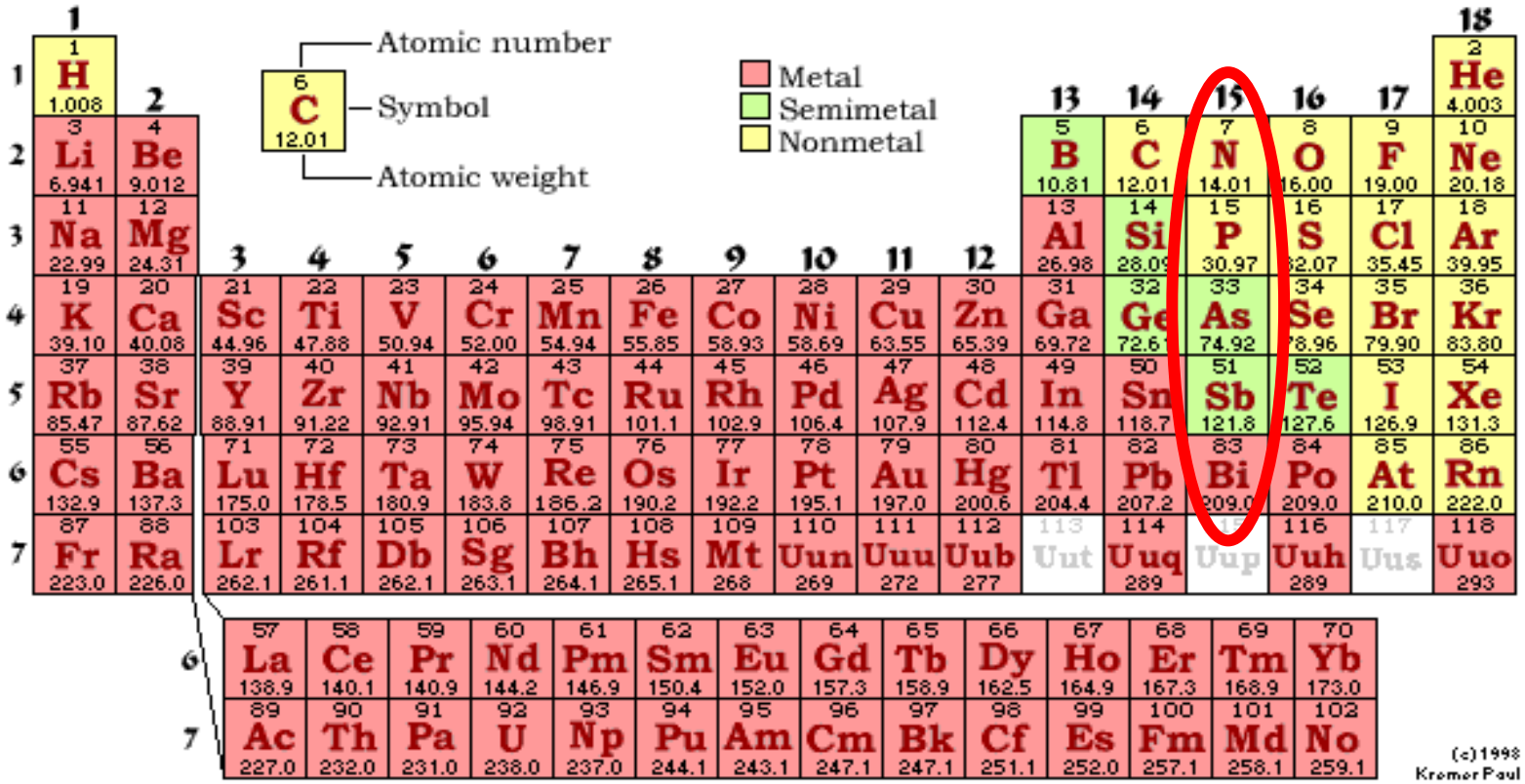
Think of the pnictide column.

Bi and Sb are great to work with and offer lots of neat compounds

As and P have manifest compelling physics in the Fe-based materials

What about N?????

WE WANT TO MAKE N-BASED MELTS!!



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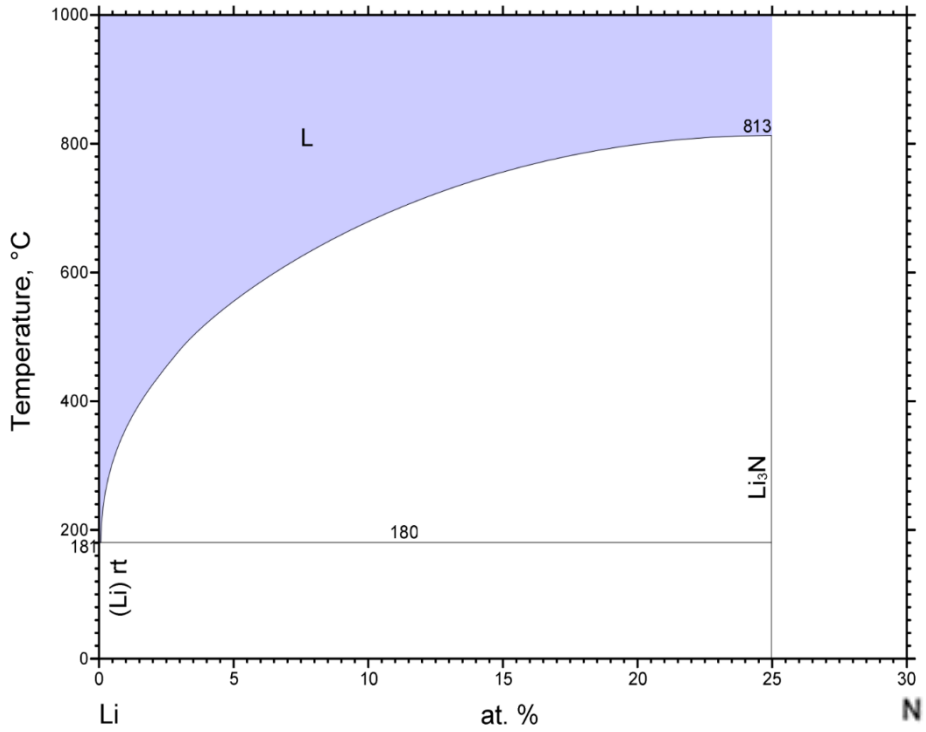

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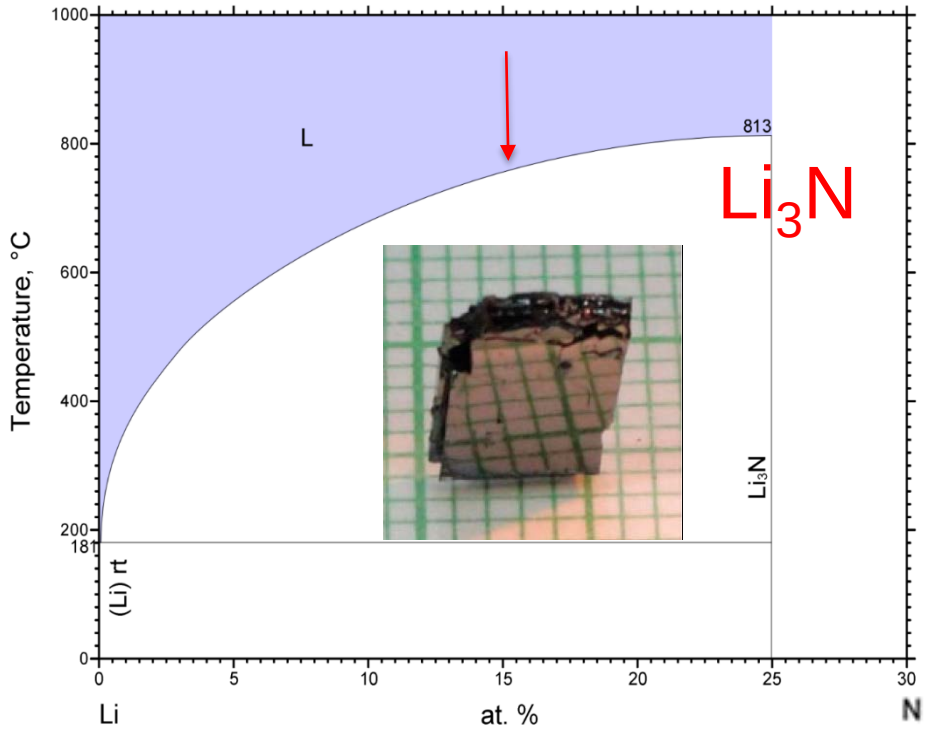

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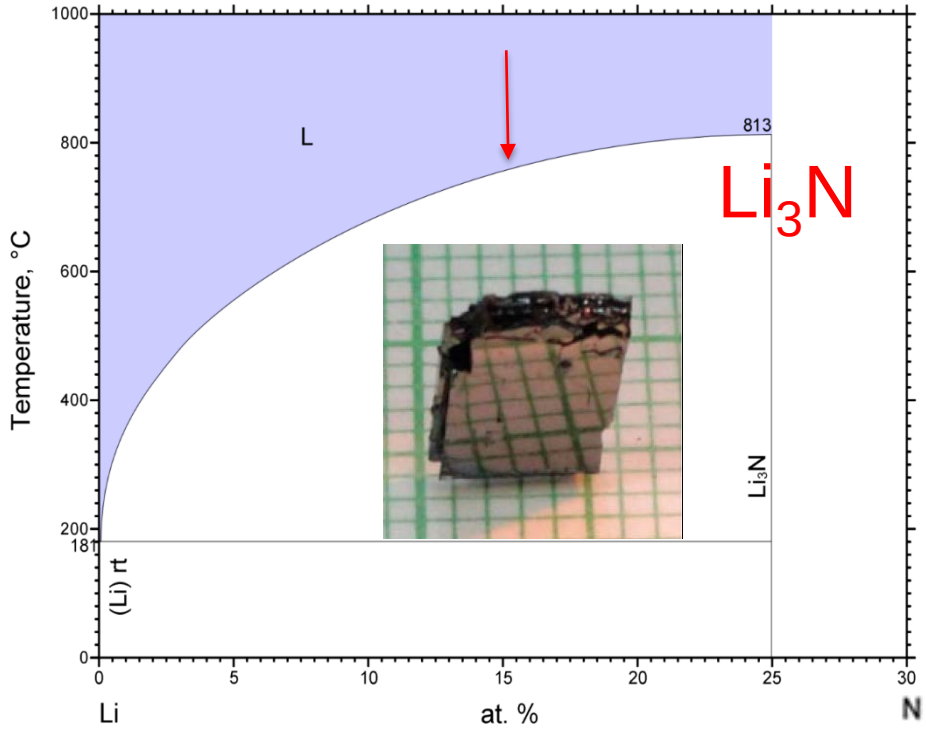
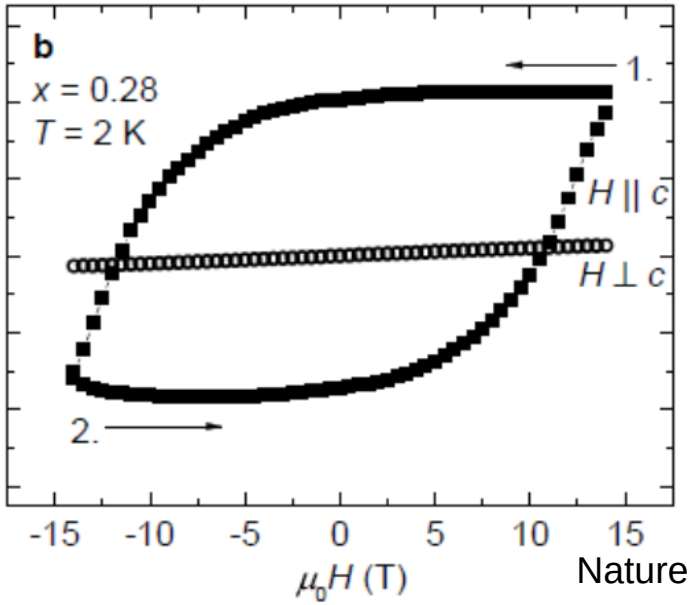
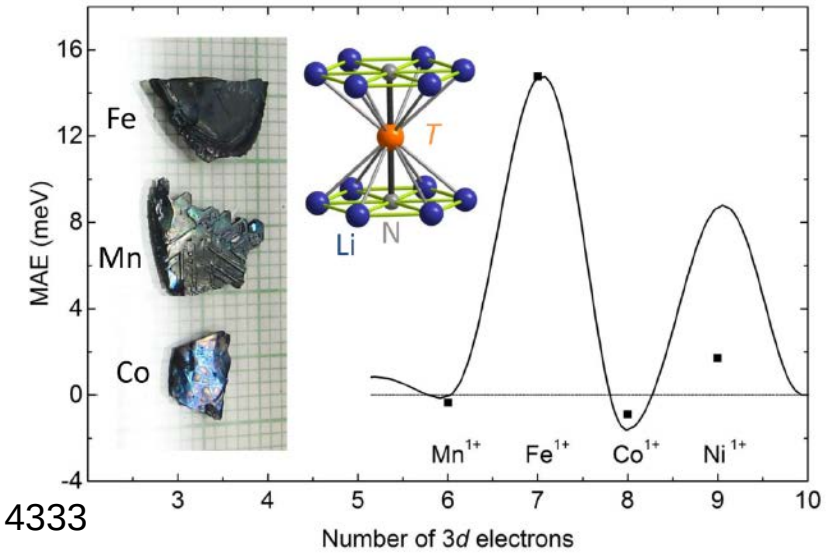


$Li_2(Li_{1-x}Fe_x)N$





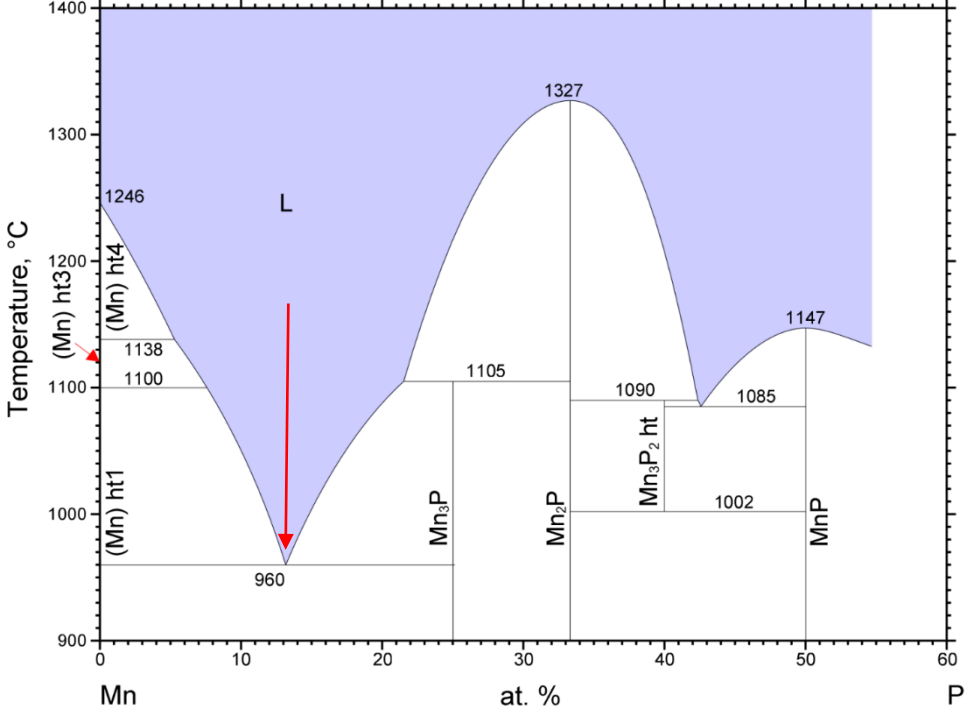
Nature Comm. 5 (2014) 4333

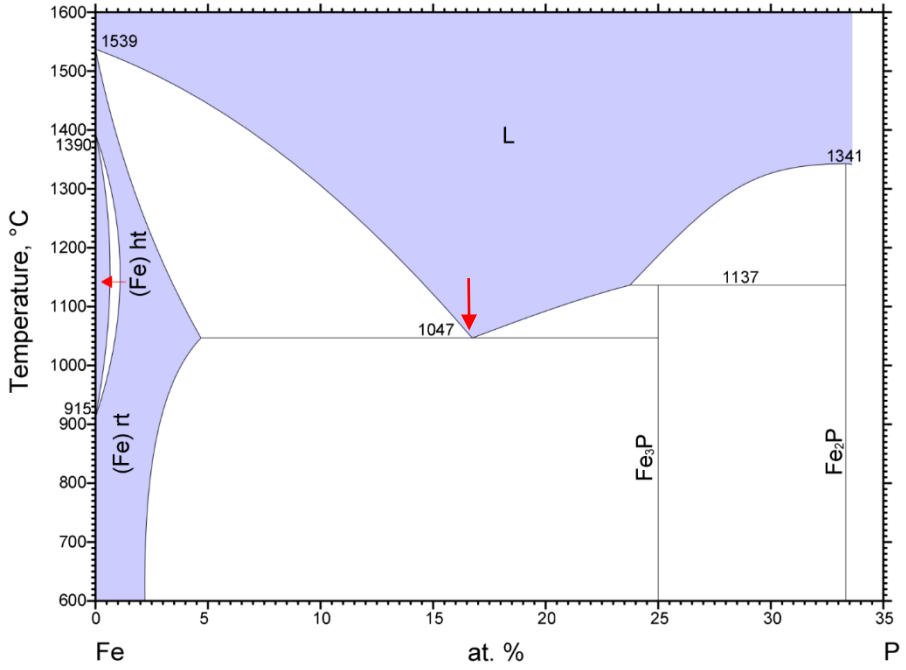
In a similar manner we have been mastering other transition metal – volatile eutectics so as to better explore transition metal rich ternary and higher melts new or poorly explored states

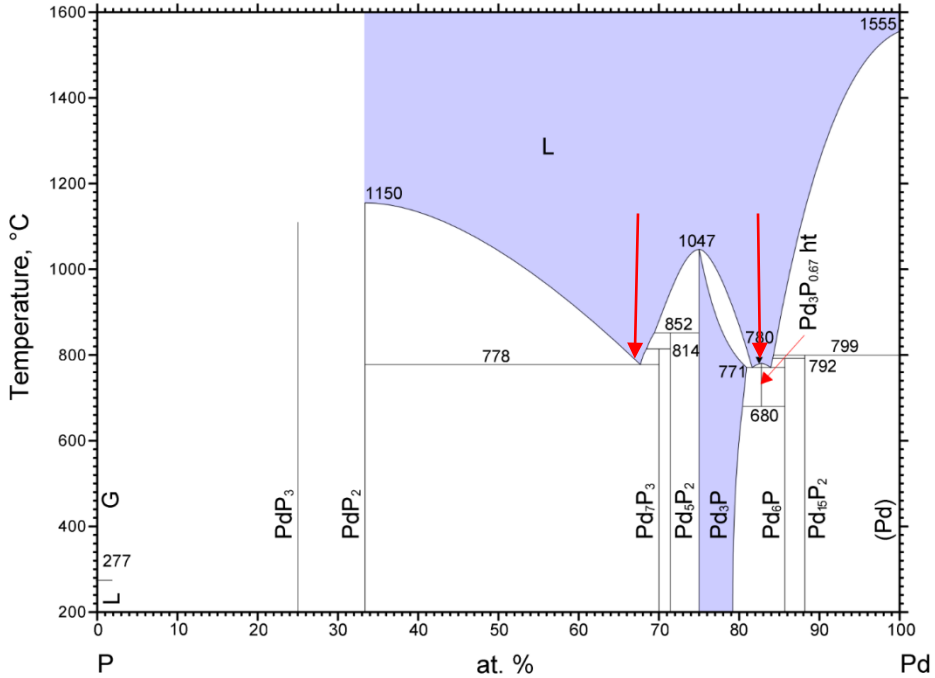
We find solutions

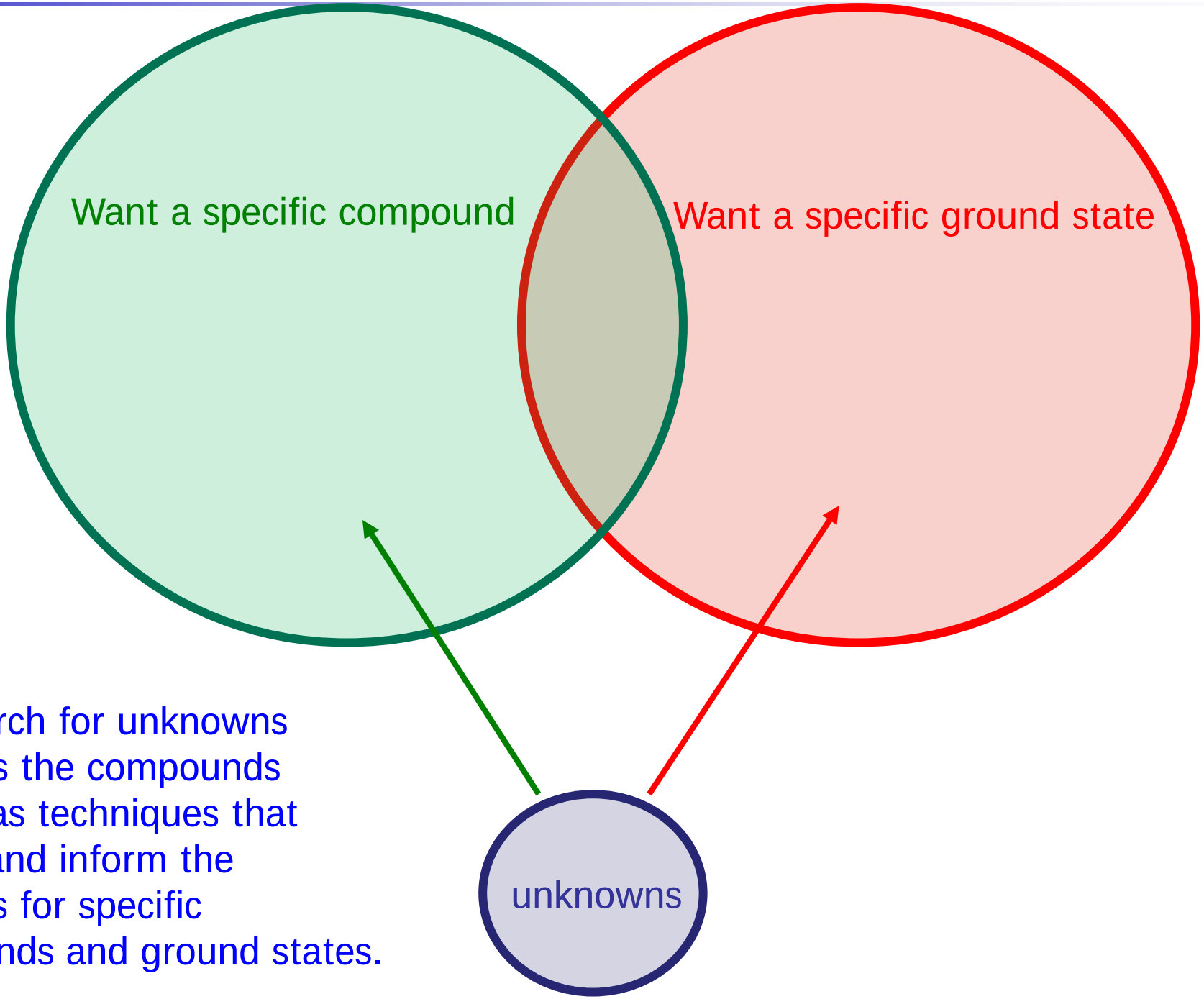
In a similar manner we have been mastering other transition metal – volatile eutectics so as to better explore transition metal rich ternary and higher melts new or poorly explored states

These are the starting points for searches for compounds ranging from hard ferromagnets to fragile antiferromagnets.



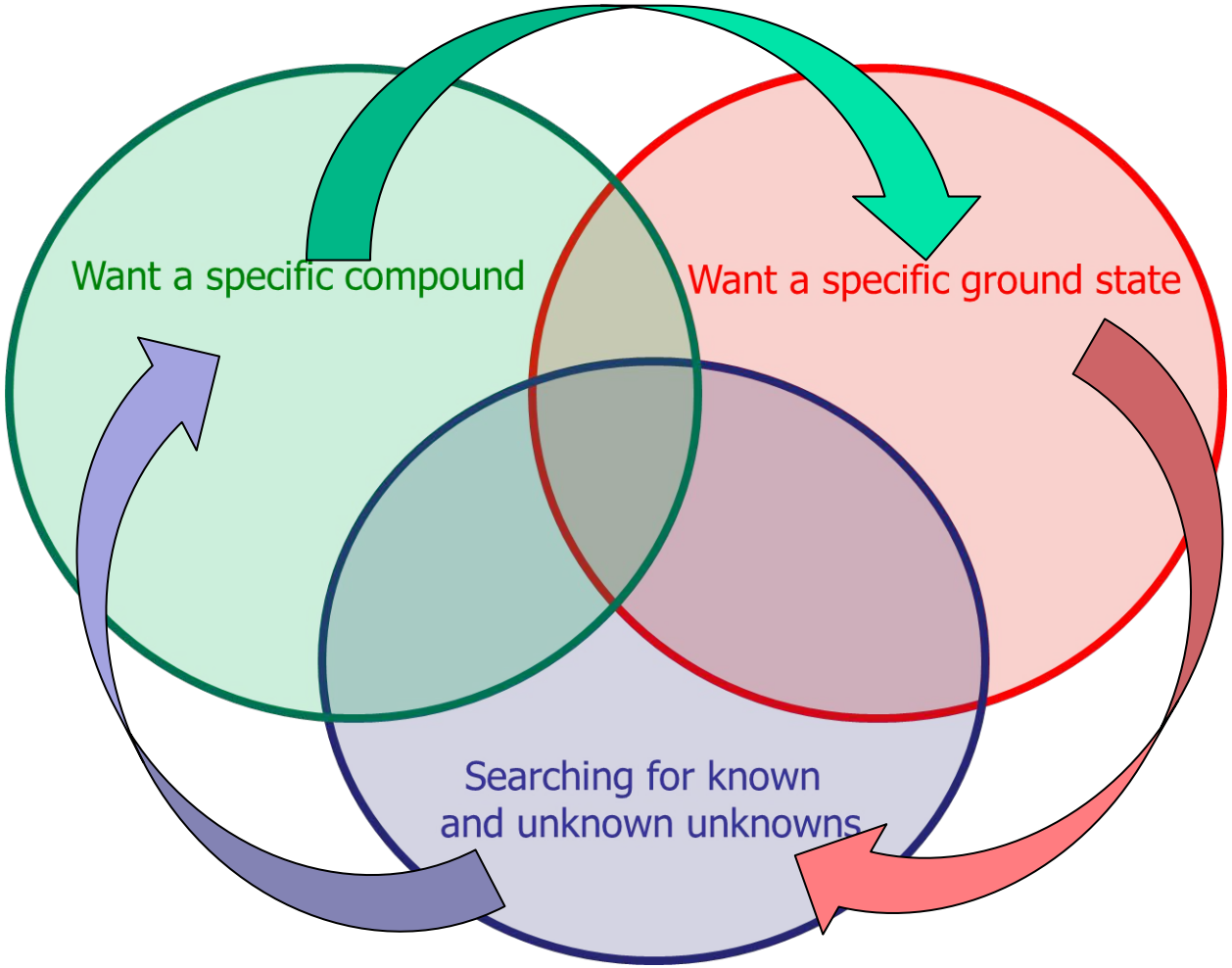






The search for unknowns develops the compounds as well as techniques that enable and inform the searches for specific compounds and ground states.

These basic motivations for making a growth feed into each other in every possible permutation

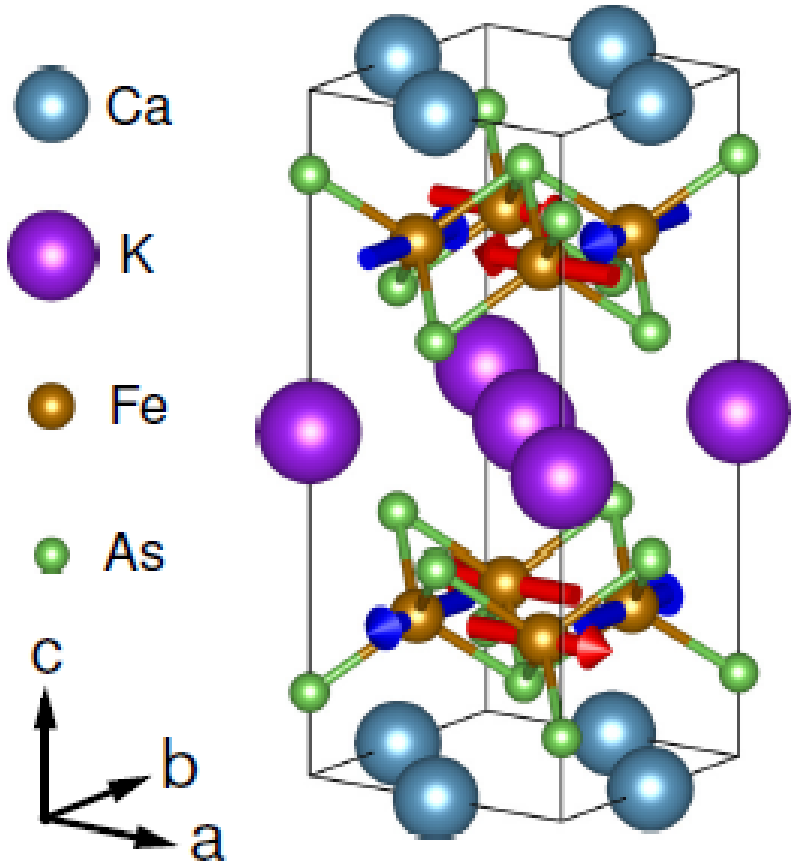


Let me end with a current, ongoing example: $CaKFe_4As_4$

Discovered in early 2016

A. Iyo, K. Kawashima, T. Kinjo, T. Nishio, S. Ishida, H. Fujihisa, Y. Gotoh, K. Kihou, H. Eisaki, and Y. Yoshida, J. Am. Chem. Soc. **138**, 3410 (2016).

This is a hybrid version of the 122 structure with alternating planes of Ca and K along the c-axis



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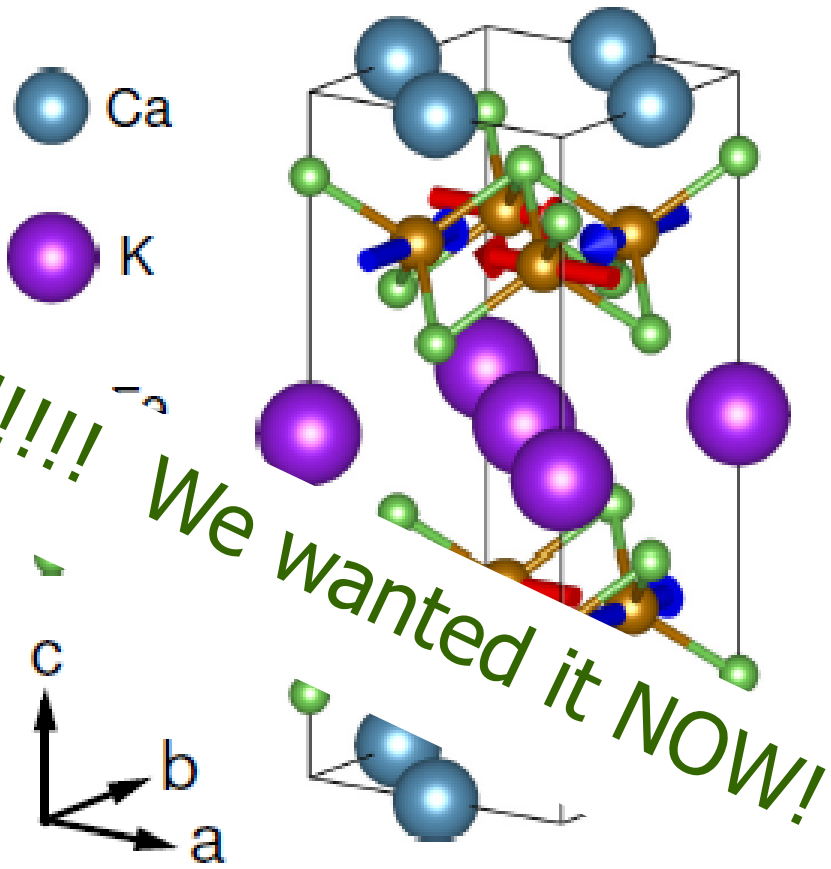
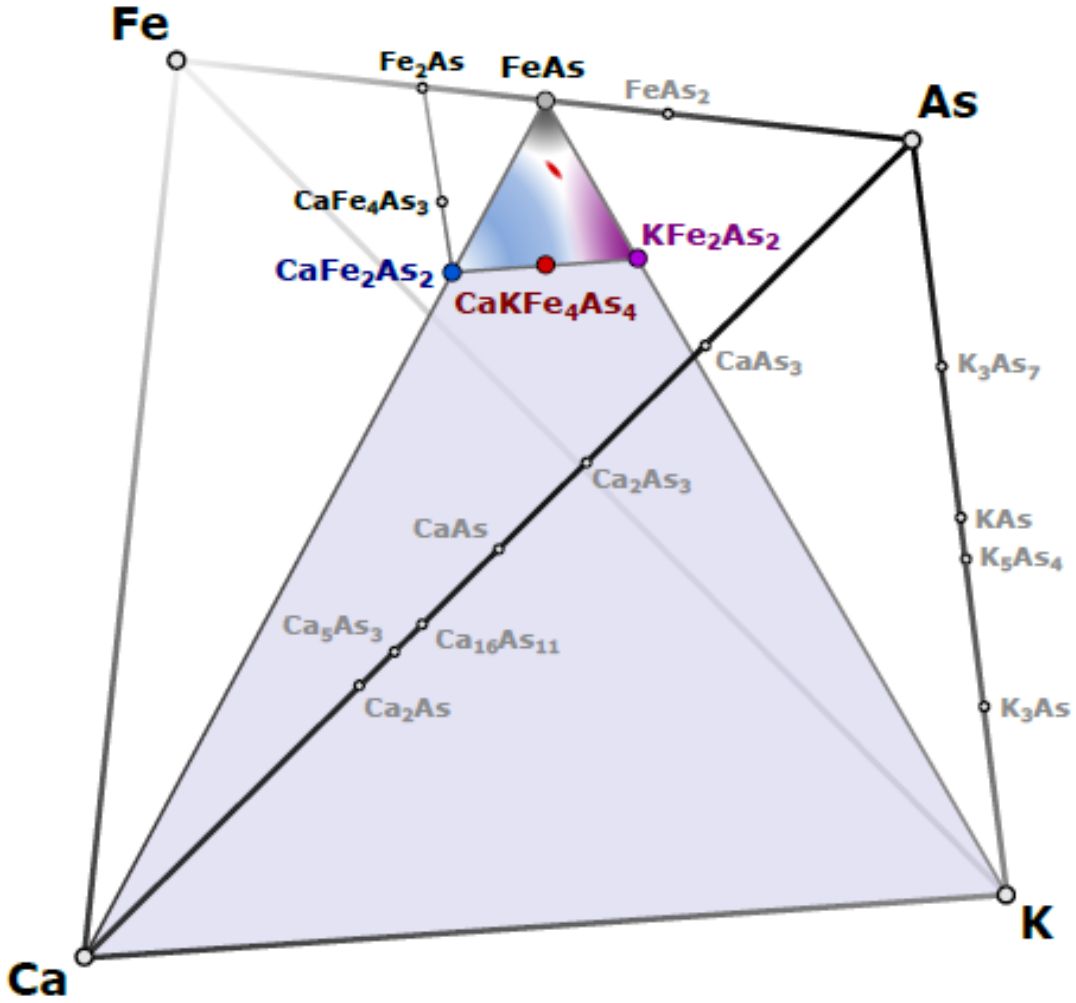
We wanted this specific compound!!!! We wanted it NOW!

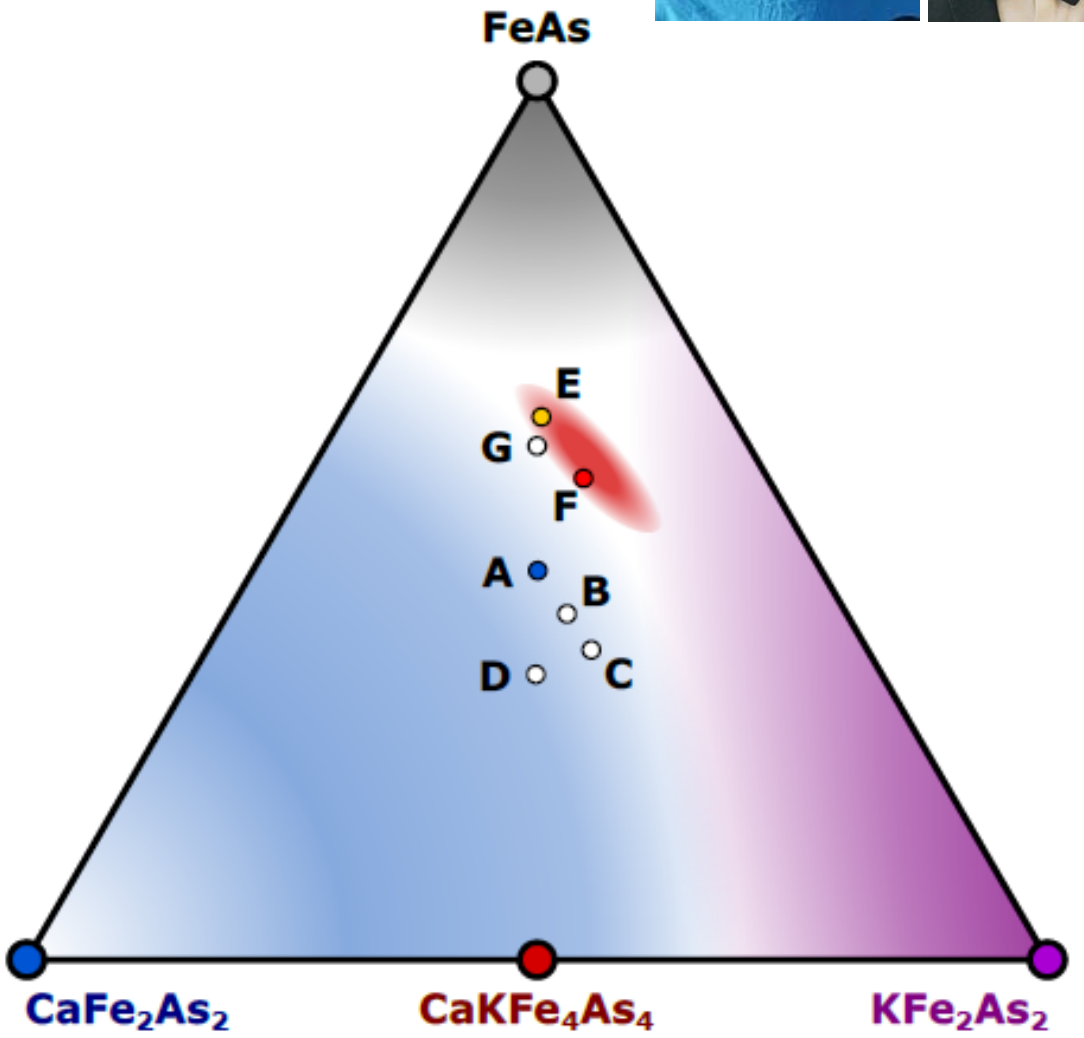
This is a hy… version of the 122 structure with alternating planes of Ca and K along the c-axis



This is a quaternary growth of toxic, reactive and volatile components.



(a)



(b)

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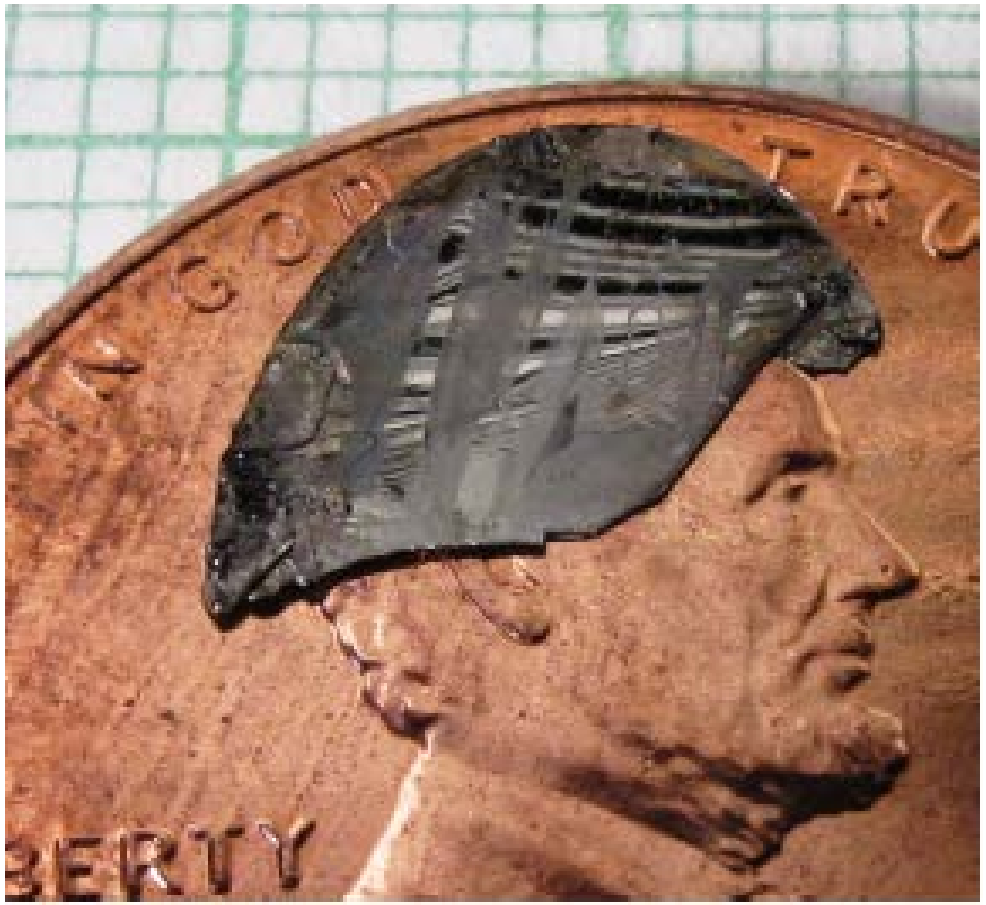

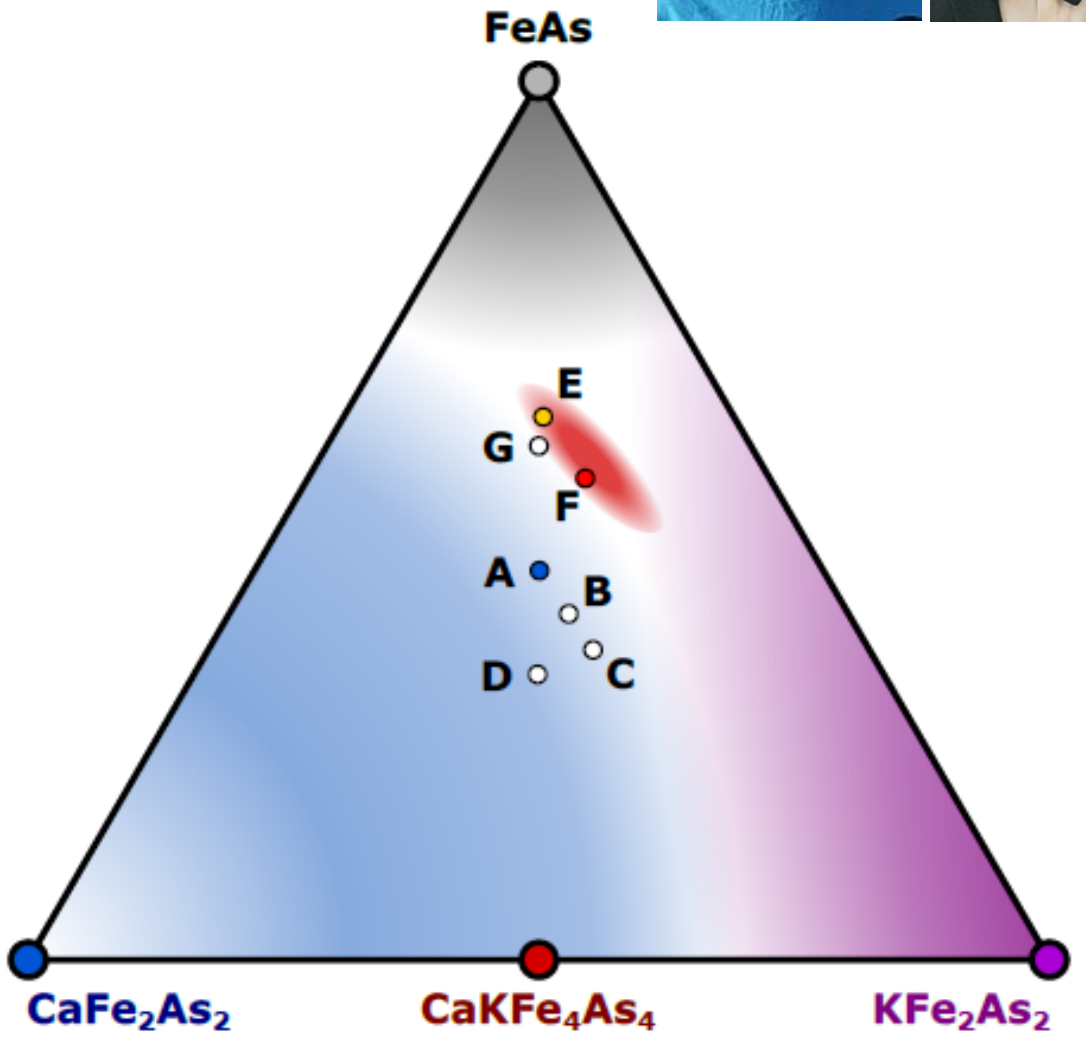

(b)

Within a few months we got it under control.

PHYSICAL REVIEW B **94**, 064501 (2016)

Anisotropic thermodynamic and transport properties of single-crystalline $CaKFe_4As_4$

W. R. Meier,[1,2] T. Kong,[1,2] U. S. Kaluarachchi,[1,2] V. Taufour,[1] N. H. Jo,[1,2] G. Drachuck,[1,2] A. E. Böhmer,[1] S. M. Saunders,[1,2] A. Sapkota,[1,2] A. Kreyssig,[1,2] M. A. Tanatar,[1,2] R. Prozorov,[1,2] A. I. Goldman,[1,2] Fedor F. Balakirev,[3] Alex Gurevich,[4] S. L. Bud'ko,[1,2] and P. C. Canfield[1,2,*]

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[3]*National High Magnetic Field Laboratory, Los Alamos National Laboratory, MS-E536, Los Alamos, New Mexico 87545, USA*

[4]*Department of Physics, Old Dominion University, Norfolk, Virginia 23529, USA*

(Received 18 May 2016; revised manuscript received 11 July 2016; published 1 August 2016)

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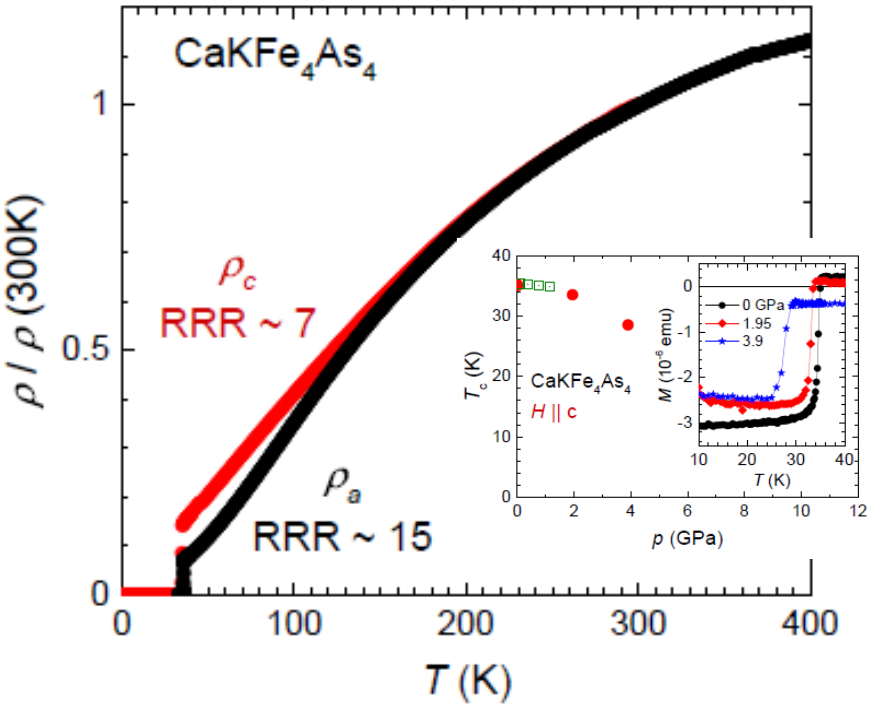

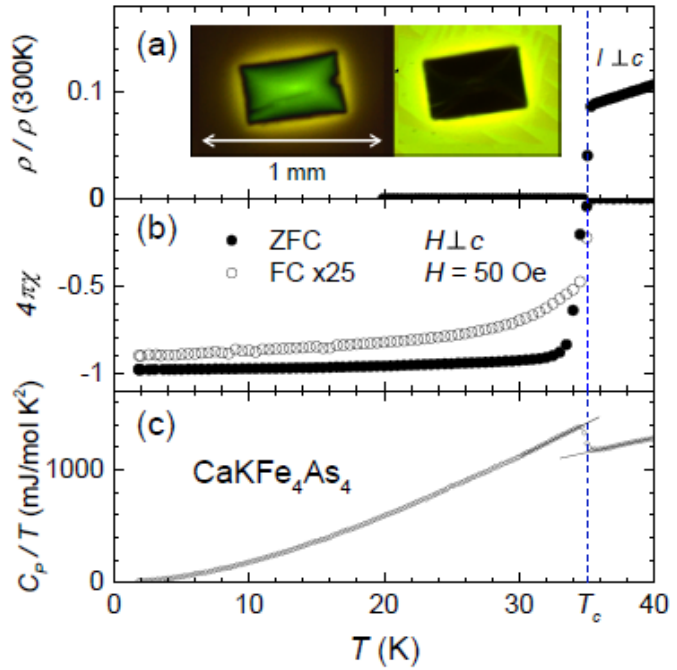

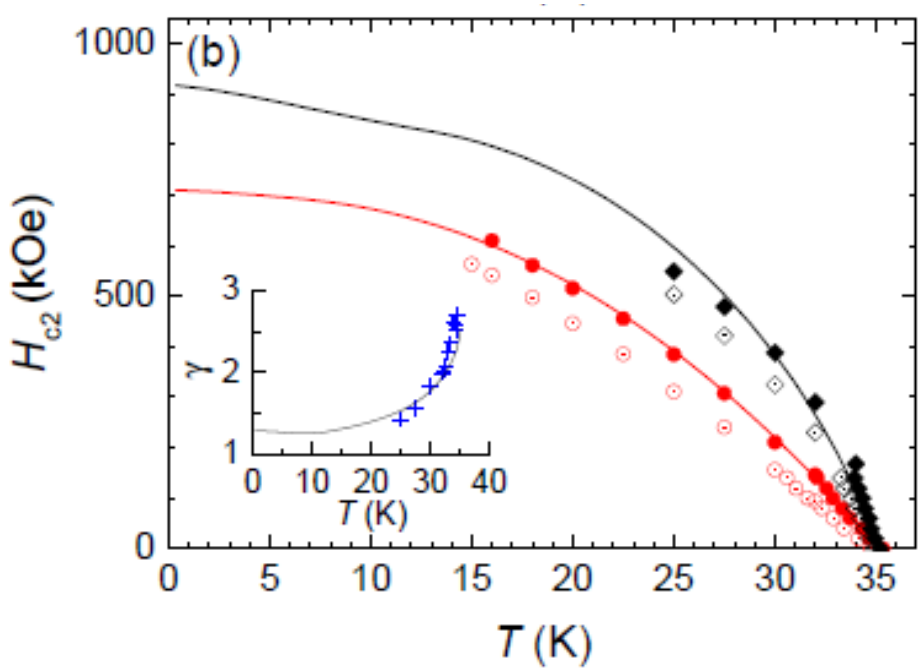

PHYSICAL REVIEW B **94**, 064501 (2016)

PHYSICAL REVIEW MATERIALS **1**, 013401 (2017)

Optimization of the crystal growth of the superconductor $CaKFe_4As_4$ from solution in the $FeAs$-$CaFe_2As_2$-KFe_2As_2 system

W. R. Meier, T. Kong,* S. L. Bud'ko, and P. C. Canfield†

Ames Laboratory US DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

(Received 28 April 2017; published 19 June 2017)

PHYSICAL REVIEW B **94**, 064501 (2016)

PHYSICAL REVIEW MATERIALS **1**, 013401 (2017)

PRL **117,** 277001 (2016) PHYSICAL REVIEW LETTERS week ending 30 DECEMBER 2016

Enhancement of the Superconducting Gap by Nesting in $CaKFe_4As_4$: A New High Temperature Superconductor

Daixiang Mou,[1,2] Tai Kong,[1,2] William R. Meier,[1,2] Felix Lochner,[3] Lin-Lin Wang,[1] Qisheng Lin,[1] Yun Wu,[1,2] S. L. Bud'ko,[1,2] Ilya Eremin,[3] D. D. Johnson,[1,2,4] P. C. Canfield,[1,2] and Adam Kaminski[1,2]

[1]*Division of Materials Science and Engineering, Ames Laboratory, Ames, Iowa 50011, USA*

[2]*Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

[3]*Institut fur Theoretische Physik III, Ruhr-Universitat Bochum, 44801 Bochum, Germany*

[4]*Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA*

(Received 17 June 2016; published 28 December 2016)

PHYSICAL REVIEW B **94**, 064501 (2016)

PHYSICAL REVIEW MATERIALS **1**, 013401 (2017)

PRL **117,** 277001 (2016) PHYSICAL REVIEW LETTERS week ending 30 DECEMBER 2016

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **95**, 100502(R) (2017)

Nodeless multiband superconductivity in stoichiometric single-crystalline $CaKFe_4As_4$

Kyuil Cho,[1] A. Fente,[2] S. Teknowijoyo,[1] M. A. Tanatar,[1] K. R. Joshi,[1] N. M. Nusran,[1] T. Kong,[1] W. R. Meier,[1] U. Kaluarachchi,[1] I. Guillamón,[2] H. Suderow,[2] S. L. Bud'ko,[1] P. C. Canfield,[1] and R. Prozorov[1,*]

[1]*Ames Laboratory, Ames and Department of Physics & Astronomy, Iowa State University, Ames, Iowa 50011, USA*

[2]*Laboratorio de Bajas Temperaturas, Unidad Asociada UAM CSIC, Departamento de Física de la Materia Condensada, Instituto Nicolás Cabrera and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

(Received 20 June 2016; revised manuscript received 30 November 2016; published 8 March 2017)

PHYSICAL REVIEW B **94**, 064501 (2016)

PHYSICAL REVIEW MATERIALS **1**, 013401 (2017)

PRL **117,** 277001 (2016) PHYSICAL REVIEW LETTERS week ending 30 DECEMBER 2016

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **95**, 100502(R) (2017)

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **96**, 140501(R) (2017)

Pressure-induced half-collapsed-tetragonal phase in $CaKFe_4As_4$

Udhara S. Kaluarachchi,[1,2] Valentin Taufour,[2,*] Aashish Sapkota,[1,2] Vladislav Borisov,[3] Tai Kong,[1,2,†] William R. Meier,[1,2] Karunakar Kothapalli,[2] Benjamin G. Ueland,[2] Andreas Kreyssig,[1,2] Roser Valentí,[3] Robert J. McQueeney,[1,2] Alan I. Goldman,[1,2] Sergey L. Bud'ko,[1,2] and Paul C. Canfield[1,2]

[1]*Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

[2]*Ames Laboratory, U.S. DOE, Iowa State University, Ames, Iowa 50011, USA*

[3]*Institute of Theoretical Physics, Goethe University Frankfurt am Main, D-60438 Frankfurt am Main, Germany*

(Received 21 February 2017; revised manuscript received 20 June 2017; published 2 October 2017)

PHYSICAL REVIEW B **94**, 064501 (2016)

PHYSICAL REVIEW MATERIALS **1**, 013401 (2017)

PRL **117,** 277001 (2016) PHYSICAL REVIEW LETTERS week ending 30 DECEMBER 2016

RAPID COMMUNICATIONS

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RAPID COMMUNICATIONS

PHYSICAL REVIEW B **96**, 140501(R) (2017)

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PHYSICAL REVIEW B **96**, 104512 (2017)

Magnetic fluctuations and superconducting properties of $CaKFe_4As_4$ studied by ^{75}As NMR

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RAPID COMMUNICATIONS

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arXiv:1608.00605v1 [cond-mat.supr-con] 1 Aug 2016

Vortices in two-effective-band, stoichiometric high T_c $CaKFe_4As_4$ superconductor

Antón Fente,[1] William R. Meier,[2,3] Tai Kong,[2,3] Vladimir G. Kogan,[2]
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VOL. 97, NO. 29, 2689–2703
https://doi.org/10.1080/14786435.2017.1347726

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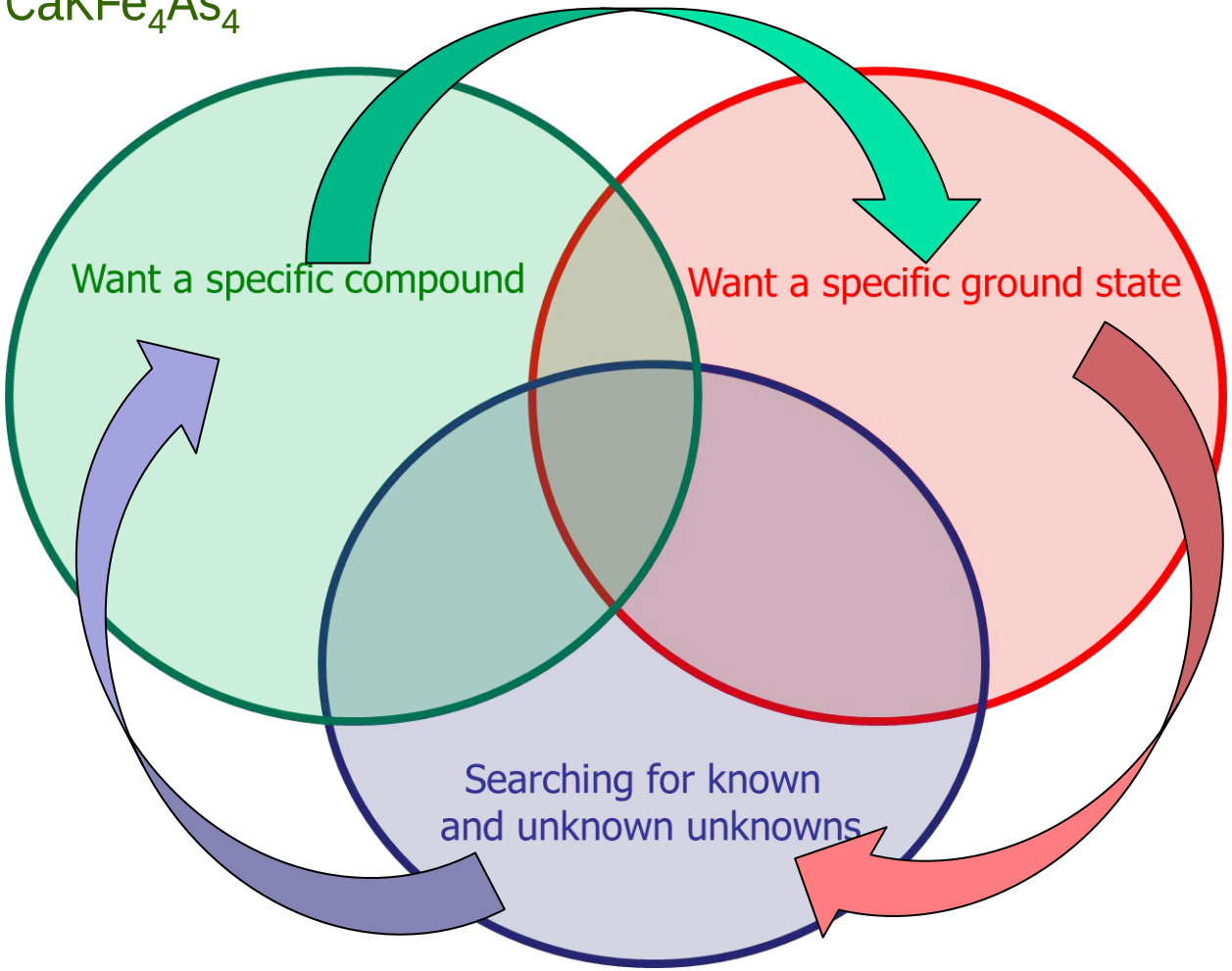
^{57}Fe Mössbauer study of stoichiometric iron-based superconductor $CaKFe_4As_4$: a comparison to KFe_2As_2 and $CaFe_2As_2$

Sergey L. Bud'ko[a], Tai Kong[a,d], William R. Meier[a], Xiaoming Ma[b,c] and Paul C. Canfield[a]

Really wanted
$CaKFe_4As_4$



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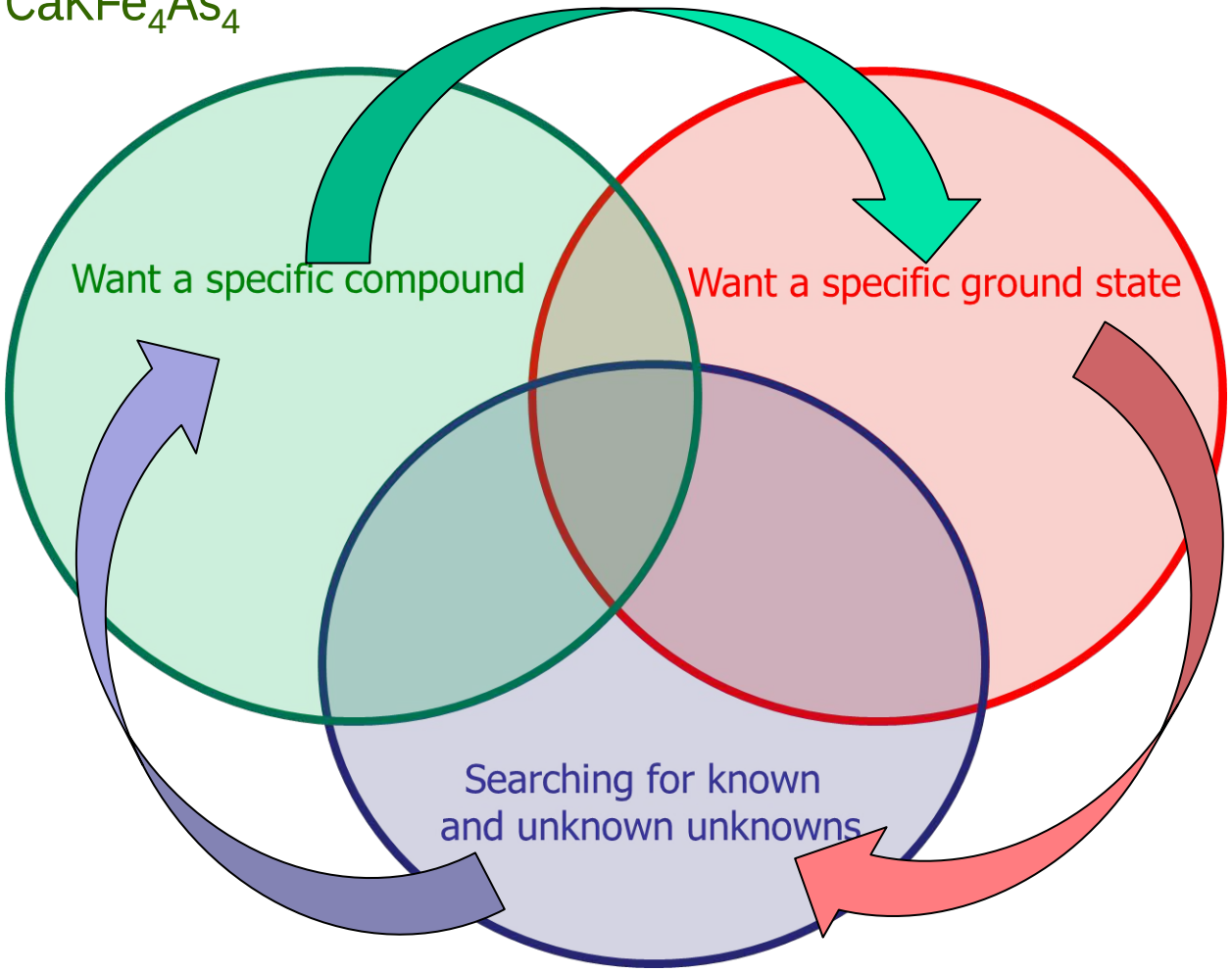

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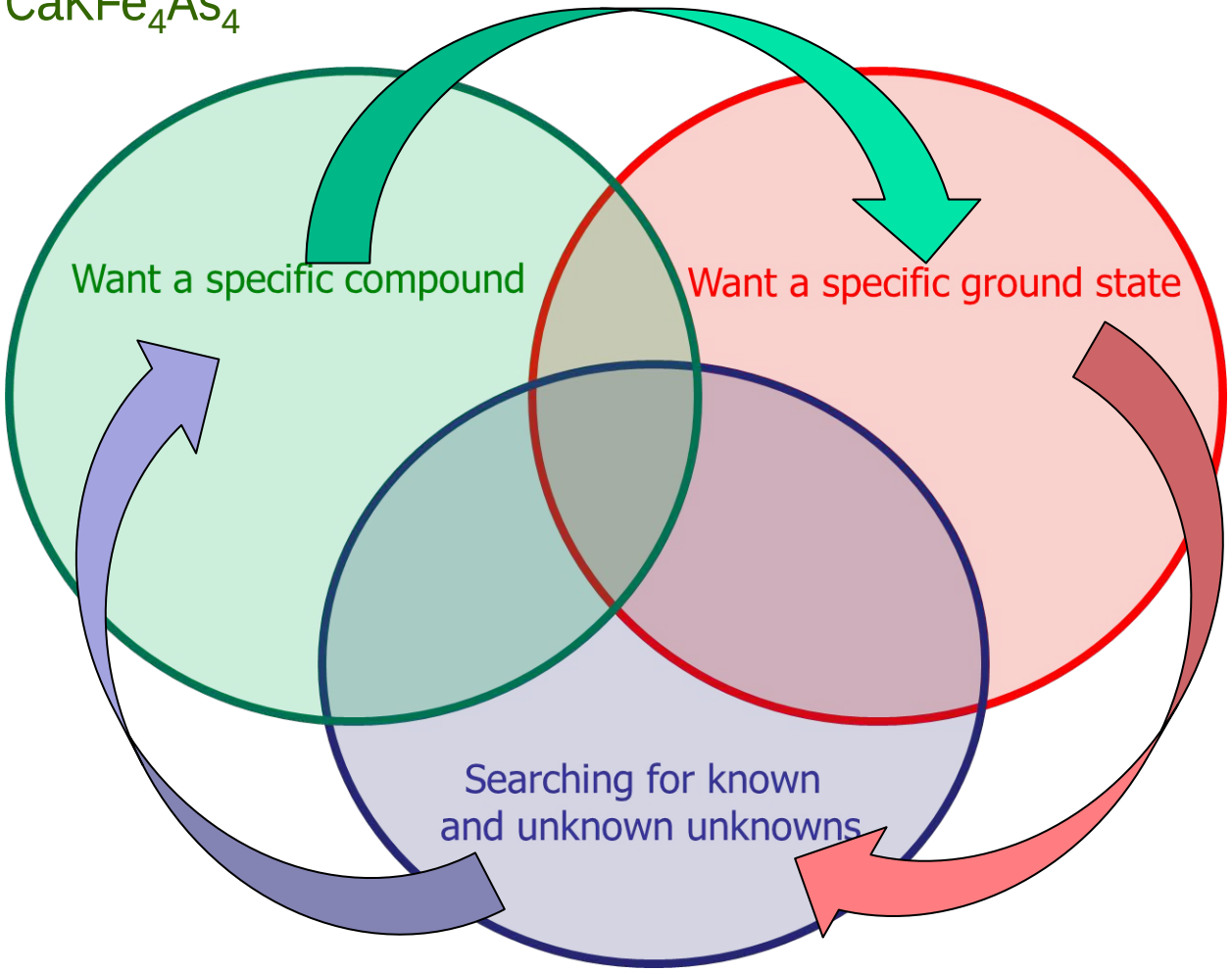

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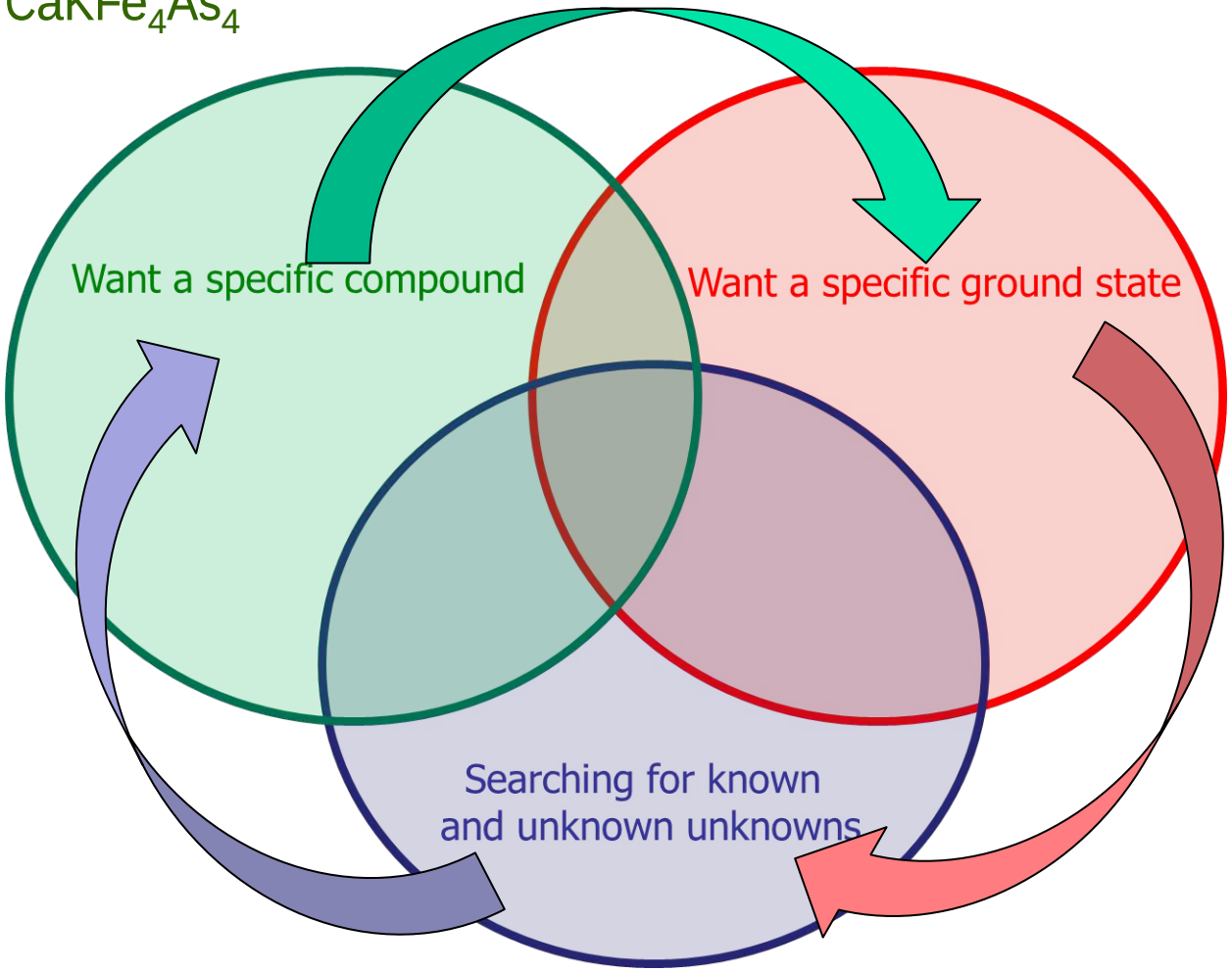

Now, really want specific variants of $CaKFe_4As_4$ ....

for example, induce magnetism

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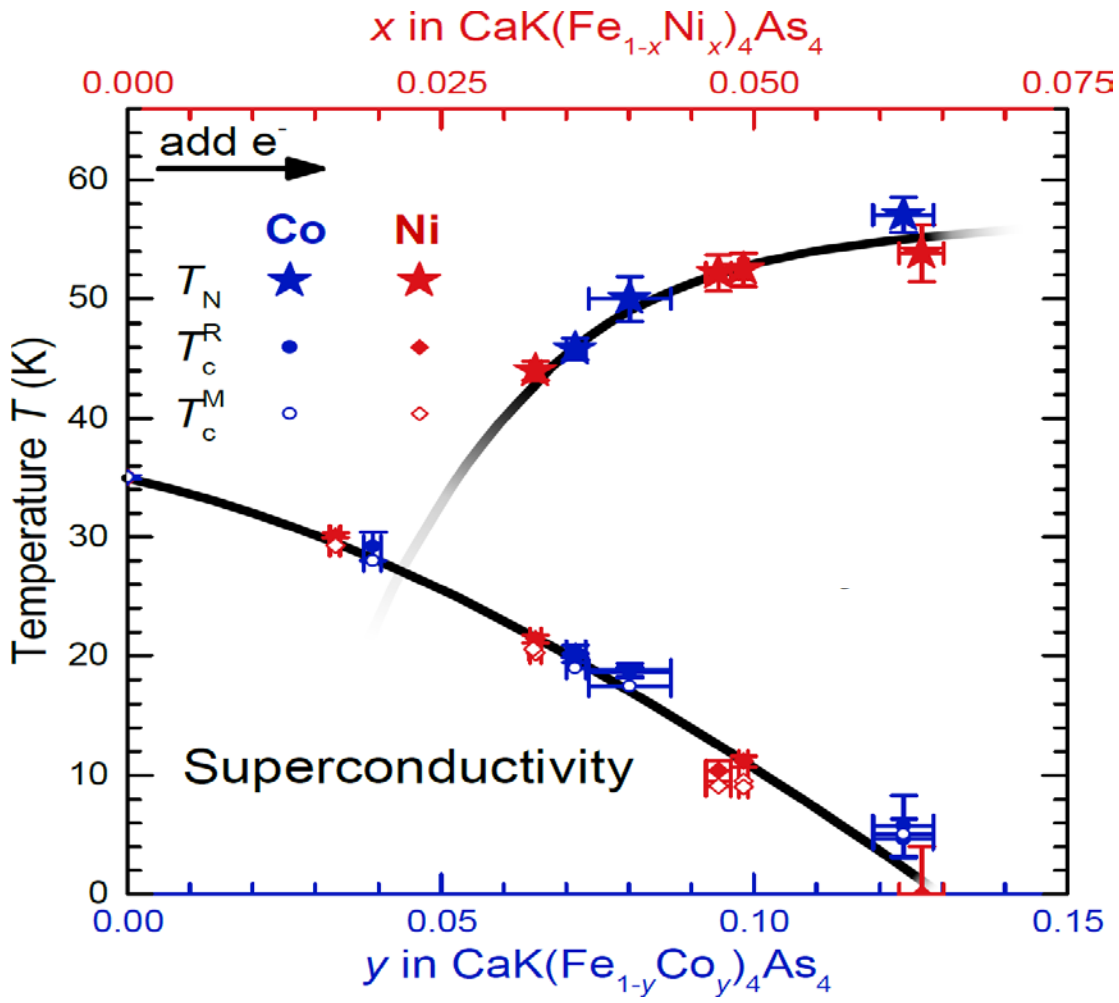
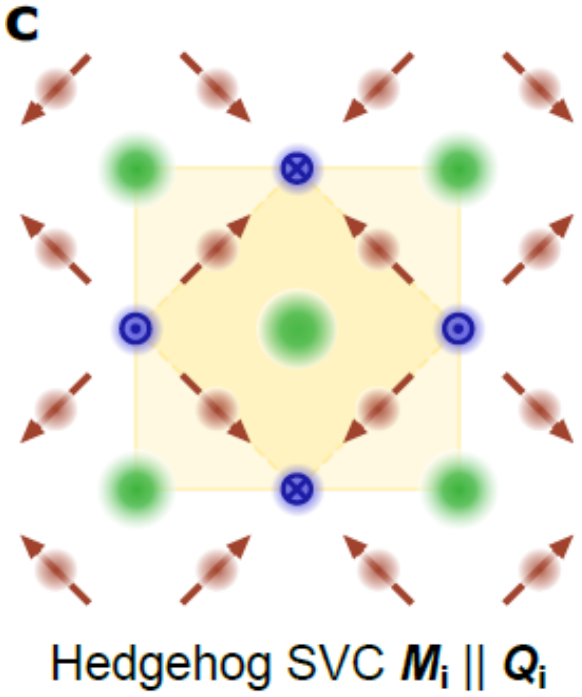
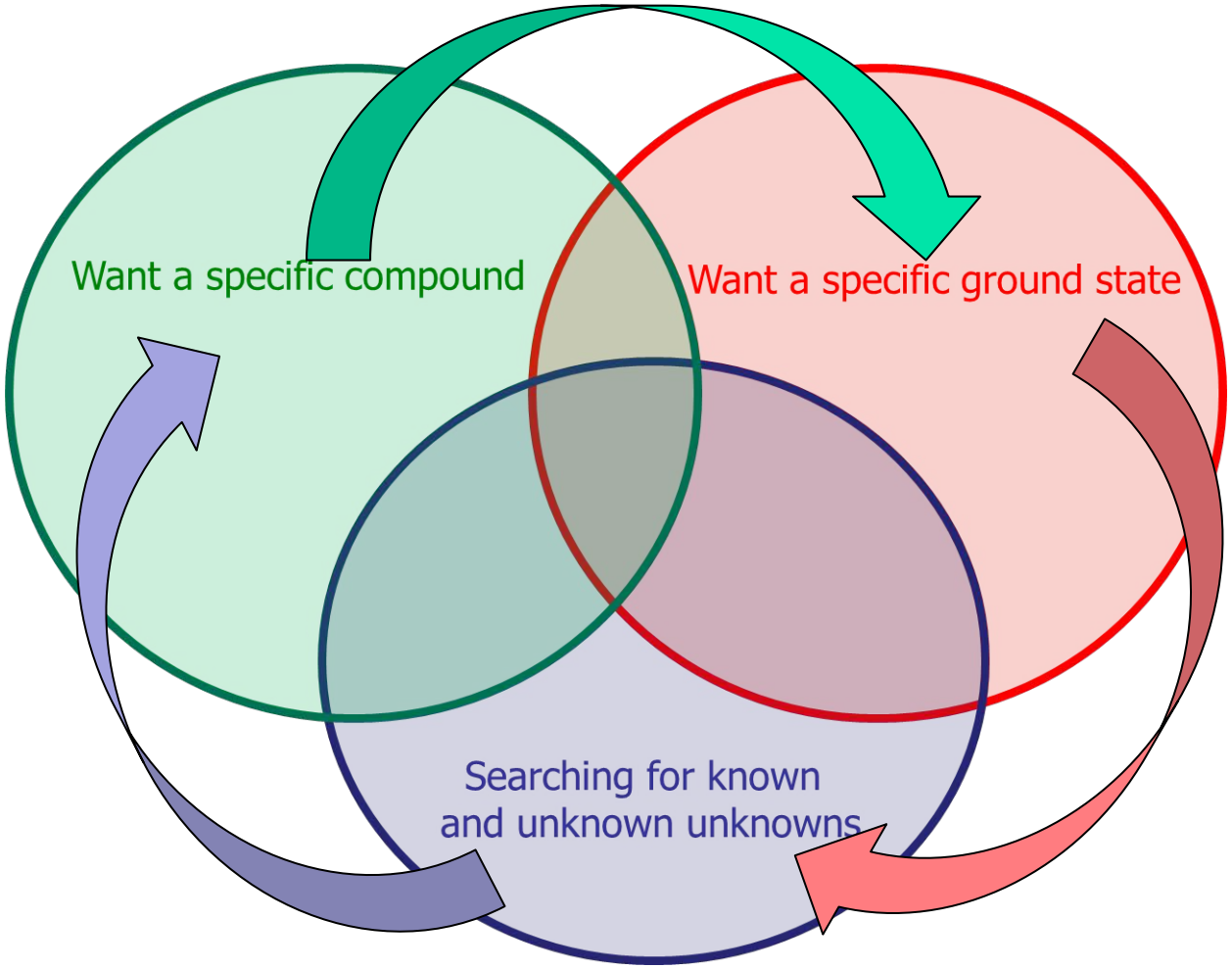
Discovery of spin-vortex-crystal magnetic order in Ni- and Co- doped $CaKFe_4As_4$





arXiv:1706.01067v1 [cond-mat.supr-con] 4 Jun 2017
npj Quantum Materials (2018)3:5 ; doi:10.1038/s41535-017-0076-x

These basic motivations for making a growth feed into each other in every possible permutation



Advances in one often inspire new endeavors in another.

An adequately broad research focus is imperative to allow for such a symbiotic interaction between these three modes of research.

DOE/BES has been the premier funding agency to support such long-term, broad exploratory synthesis efforts. Its long term support has preserved and fostered new materials discover over the past scores of years.

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The Gordon and Betty Moore Foundation has, over the past 4 years, become a key source of new materials research support through its Moore Materials Synthesis Investigators program.

Let’s end with conclusions:

The design, discovery and growth of novel materials is the heart and soul of New Materials Physics.

Synthesis combined with broad characterization tools and an eclectic interest in novel states of matter is the wellspring from which the solutions of humanity’s pressing problems will emerge.

Our charge it to refine and utilize this powerful tool as efficiently as possible and teach its multifaceted use to as many researchers as possible.

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We need to be both humble and ambitious as we go forward.

Humble in recognizing that there are many unknown that can only be discovered by broad, discovery oriented synthetic programs.

Ambitious in striving to make these discoveries more frequent by taking advantage of any and all new experimental, computational and theoretical advances.

Questions?