The Design, Discovery, Growth and Physical Properties of Novel Intermetallic Compounds

SUPERCONDUCTIVITY

Paul C. Canfield

Distinguished Professor,

Department of Physics

Senior Physicist, Ames Laboratory

Iowa State University

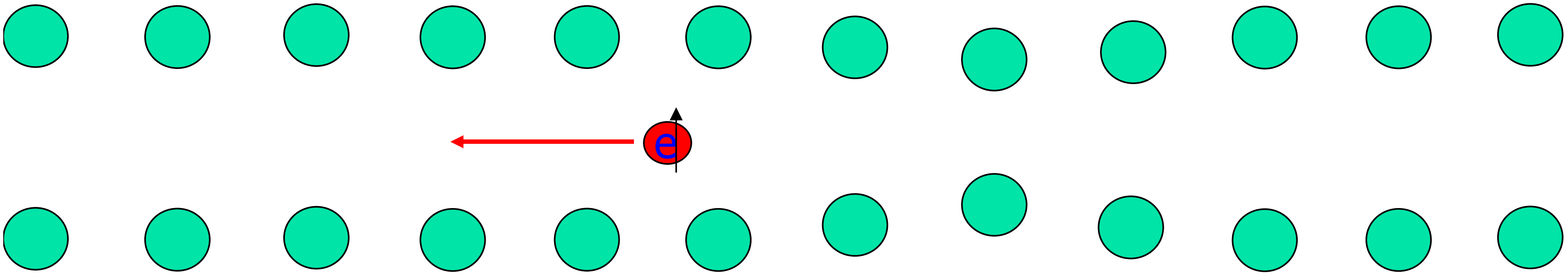
2nd European School in Material Science,

May 21-26 2007   Ljubljana, Slovenia

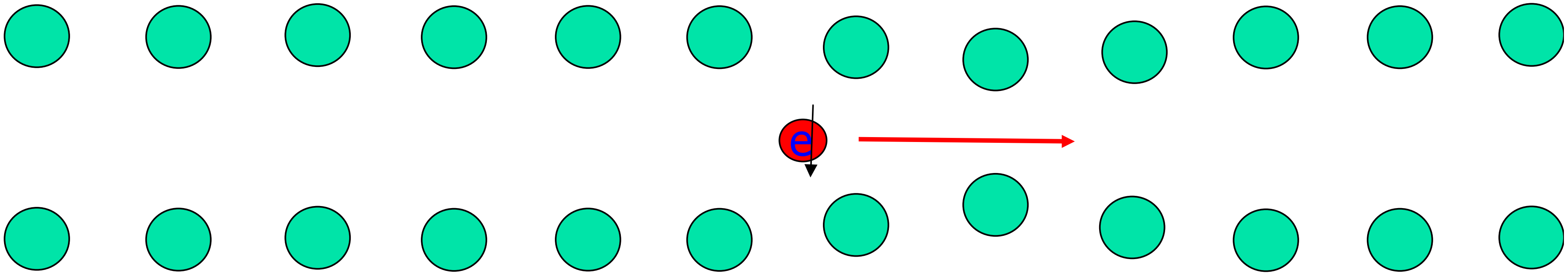
Physics among light-weights: Superconductivity in MgB_2 and other borides

Or, superconductivity from RNi_2B_2C to MgB_2

The key idea in BCS superconductivity is the interaction between electrons and phonons



An electron moving through the lattice leaves a distortion in its wake. The net, positive charge on this distortion attracts a second electron, briefly forming a Cooper pair.



This interaction clearly depends on electons, phonons, and their coupling….

BCS Superconductivity: 3 parameters (+ some prejudices)

$$k_B T_C = 1.13\hbar\omega_D e^{-1/VN(E_F)}$$

1) Electrons pair via exchange of a phonon (lattice vibration). ω_D is the characteristic frequency of the lattice. For a simple mass/spring system $\omega = \sqrt{k/m}$ → lighter m → higher T_C

Prejudice: higher T_C values can be found in compounds with light mass elements

2) V ≡ electron-phonon coupling strength.

Higher V → Higher T_C, BUT too large of a V leads to distortions (e.g. CDW)

Prejudice: higher T_C values can be found close to structural phase transitions

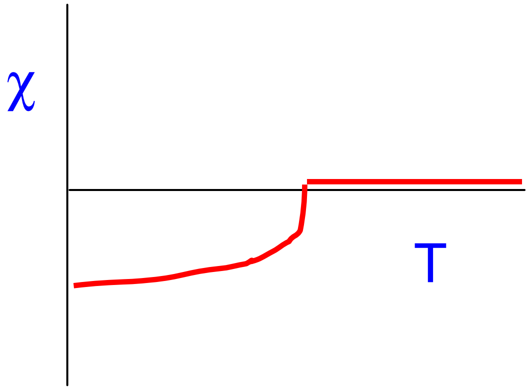
3) $N(E_F)$ = Density of states at the Fermi surface. This is basically a caliper of the number of electrons that can participate in the superconducting ground state. (Note that d-levels generally have higher $N(E_F)$ than p-levels or s-levels.

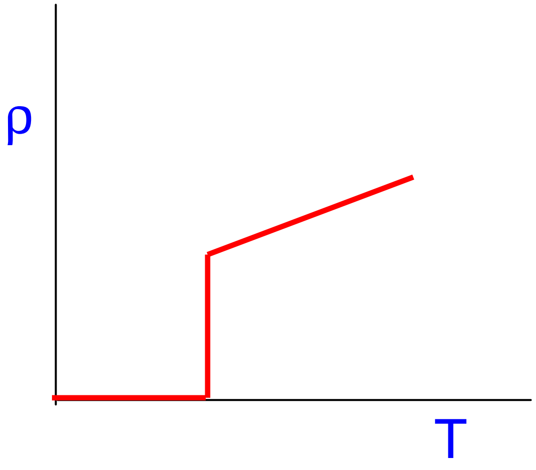
Prejudice: For high T_C values there has to be a transition metal element (with its d-levels) so as to pump up the $N(E_F)$

Superconductivity: a recent history.

In the 1950's, 1960's and even 1970's there was a large-scale hunt for higher T_c superconductors (intermetallics since they were *the only* place to expect such phenomena). In the U.S., these took place in Bell Labs, GE, UCSD, etc.

Binary compounds were made (often by arcmelting) and tested for superconductivity, usually by quick $\rho(T)$ or $\chi(T)$ measurements at low-T.





These were exciting times! You could make a sample in the morning and discovery a new superconductor by afternoon coffee.

For decades T_c was stuck at ~ 20 K. (Theories were written why B.C.S. could not support T_c > 30 K while others predicted T_c up to ~ 100 K.)

Then came the copper oxides….T_c > 120 K

Pleasure

Pain

Complex materials problems

?Mechanisms?

Hard to work with

But even during these exciting times, intermetallics remained interesting….

The past thirteen years have been an exciting time for boride based superconductors..

1994: RNi_2B_2C and YPd_2B_2C

2001: MgB_2

These two classes of compounds have pushed our understanding of superconductivity in intermetallic compounds, extending the range over which superconductivity is know to exist: to higher temperatures and new extremes of interaction with local moments as well as with the underlying lattice.

Based the three prejudices, what you want is the following:

Light atoms / high characteristic frequencies
Strong electron phonon coupling, but no structural transition
Good $N(E_F)$, probably coming (in part) from transition metal

RNi_2B_2C series as well as YPd_2B_2C are perfect!!

$LuNi_2B_2C$: $T_C \sim 17$ K
$N(E_F)$ large with significant Ni contribution
Very close to a structural phase transition
Large Debye temperature (high characteristic frequency)

YPd_2B_2C: $T_C \sim 23$ K
Metastable….If annealed loses structure---basically “just beyond” a structural phase transition, but, like diamond, can be trapped into structurally metastable state.

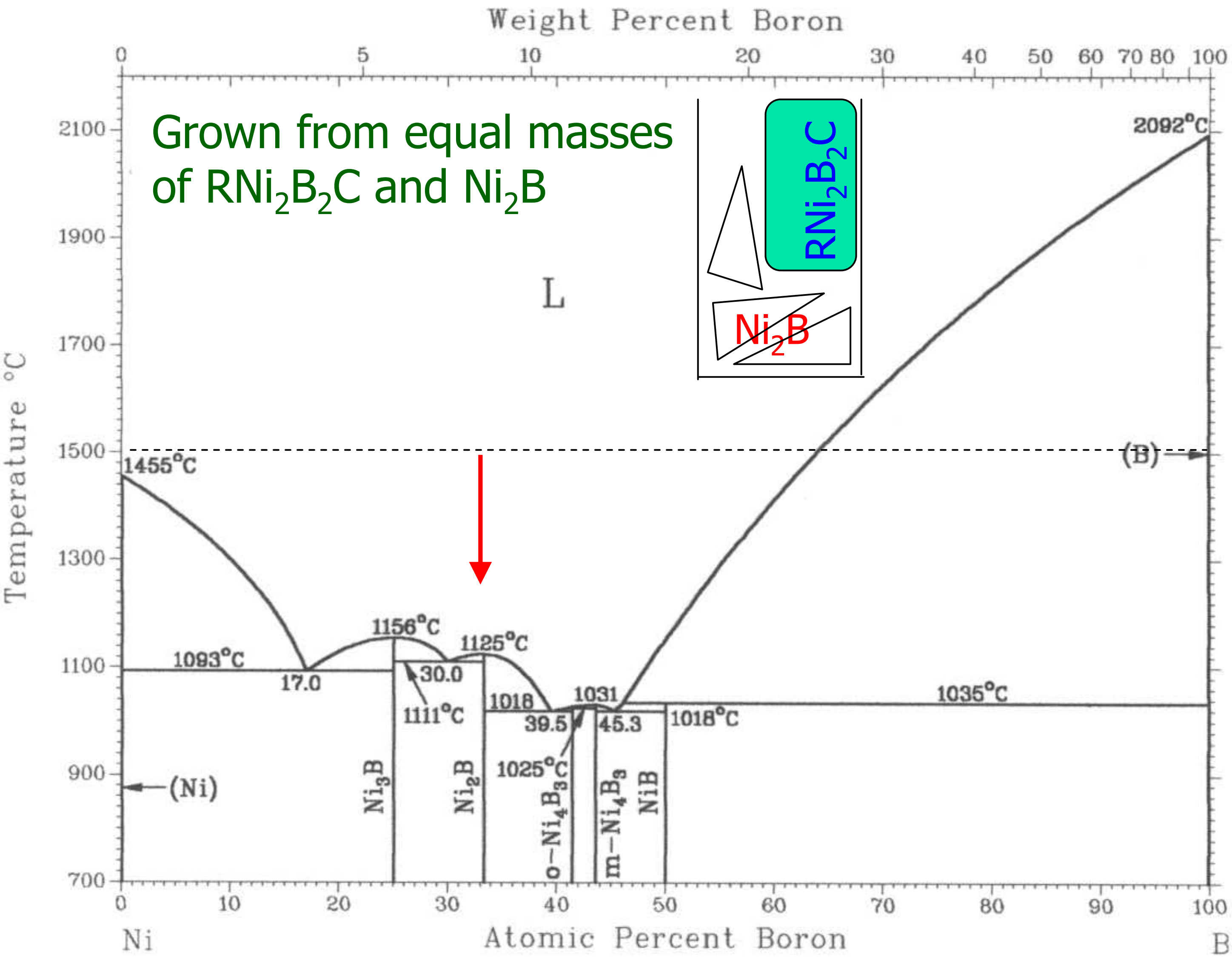
RNi_2B_2C growth

Within a couple of months of their discovery (in Tata institute and Bell Labs) we devised a method for single crystal growth.

This is a two step growth:

1) Under protective atmosphere heat to 1500 and cool slowly to 1200 and quench.

2) Seal in silica, reheat to 1200, soak and then decant.

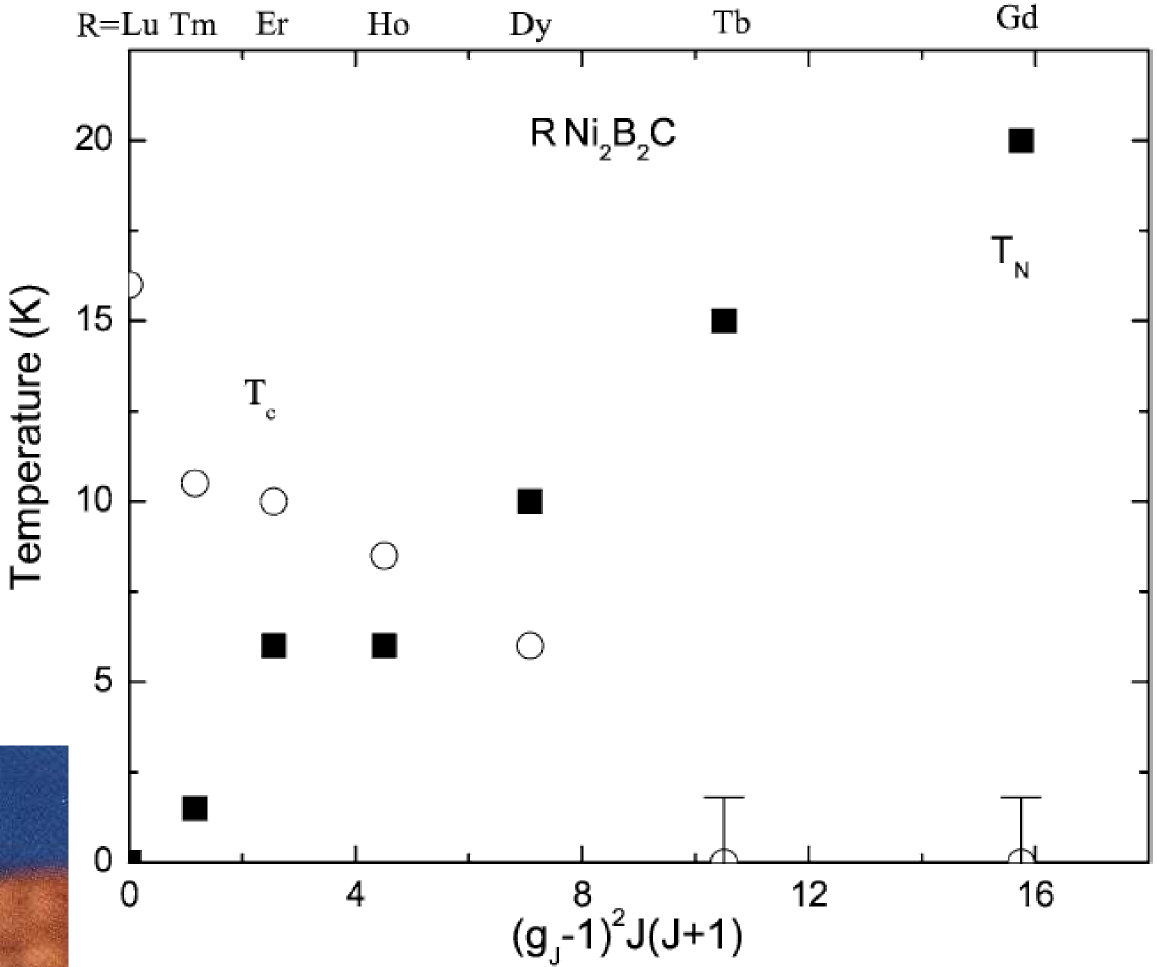


Grown from equal masses of RNi_2B_2C and Ni_2B

RNi_2B_2C family

R = Gd – Lu, Y

P. C. Canfield et al.
Physics Today Oct. 1998

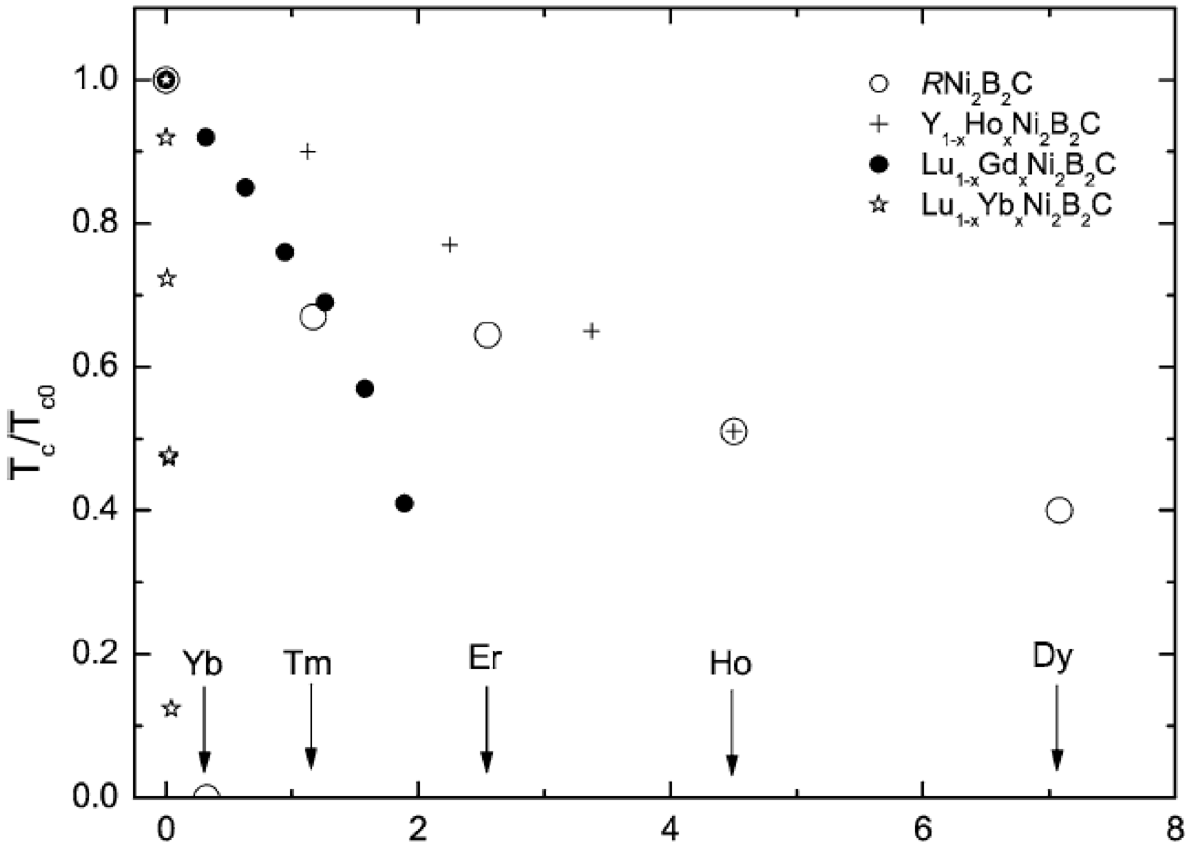


Superconducting for R = Dy, Ho, Er, Tm, Lu, Y
T_C values ranging from 17 K – 6 K

Magnetic order for R = Gd, Tb, Dy, Ho, Er, Tm
T_N values ranging from 20 K to 1.5 K

The suppression of T_c with increasingly magnetic rare earth is due to the fact that the Cooper pairs are spin up, spin down pairs. The interaction between the electrons and local moments involves a spin flip, thereby acting as a pair breaker.

This pair breaking is one of the reasons why magnetic superconductors are so interesting: they allow the study of competing effects.



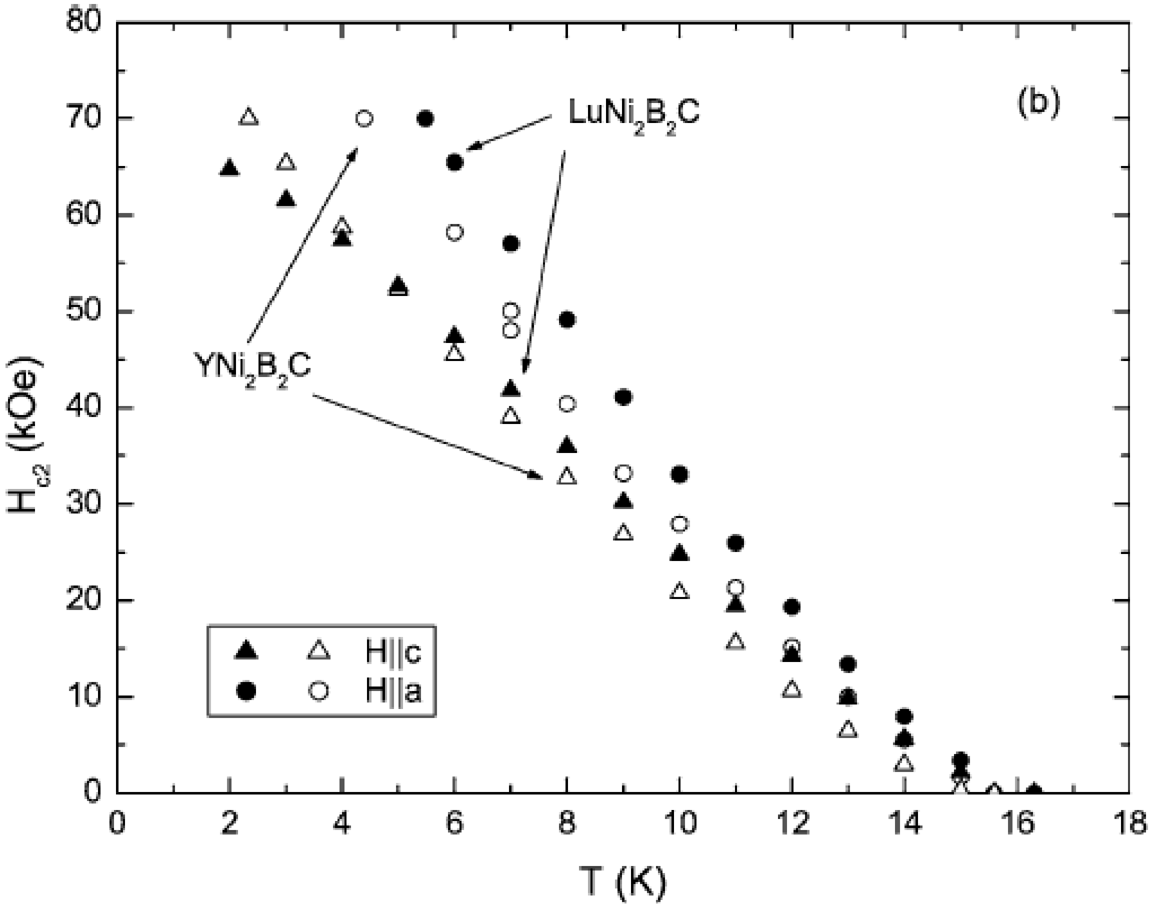
S.L. Bud'ko, P.C. Canfield / C. R. Physique 7 (2006) 56–67

This interplay between superconductivity and local moment magnetism manifests itself most clearly as anomalies in T_c and $H_{c2}(T)$.

Let's start by looking at $H_{c2}(T)$

Since Lu and Y are non-moment bearing rare earths, both $LuNi_2B_2C$ and YNi_2B_2C serve as examples of what superconductivity in these compounds looks like when there is no 4f-based, local moment magnetism present.

Both manifest relatively high T_c values and minor $H_{c2}(T)$ anisotropy.



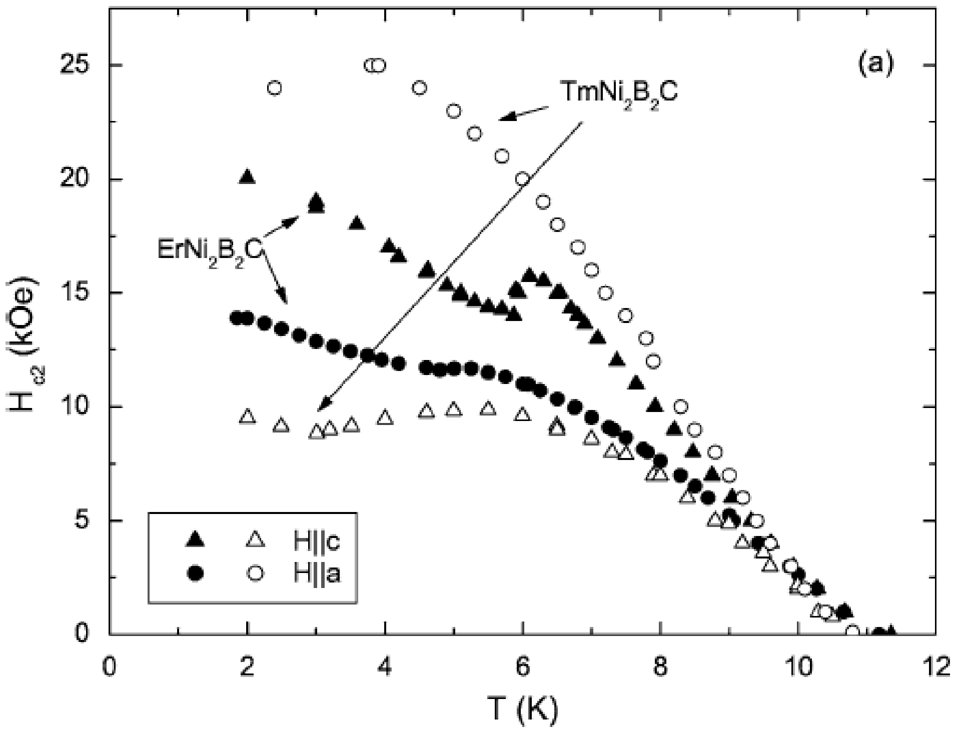
S. L. Bud'ko, V. G. Kogan, and P. C. Canfield PHYSICAL REVIEW B, VOLUME 64, 180506(R) 12 October 2001

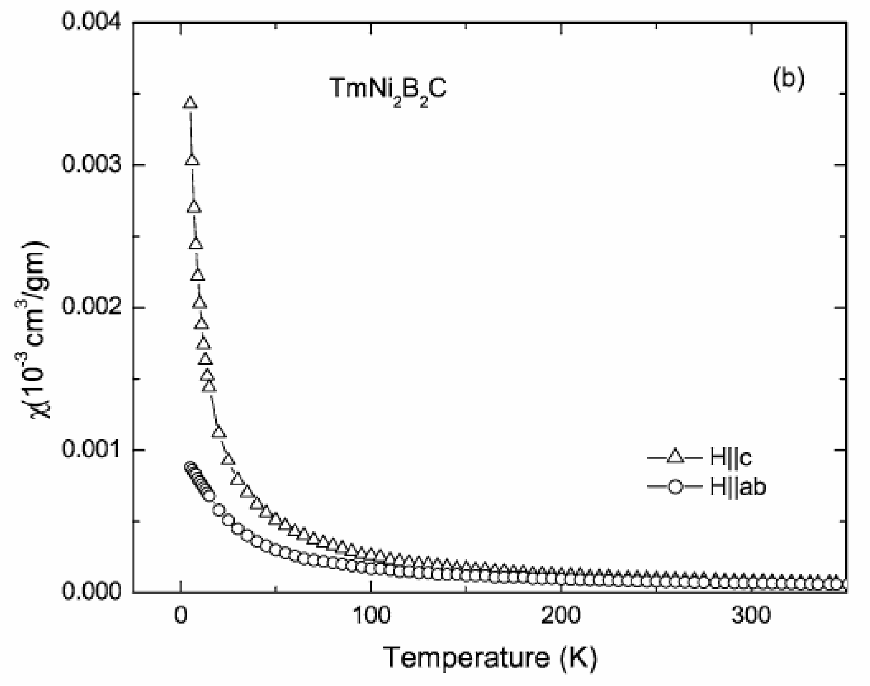
S.L. Bud'ko, P.C. Canfield / C. R. Physique 7 (2006) 56–67

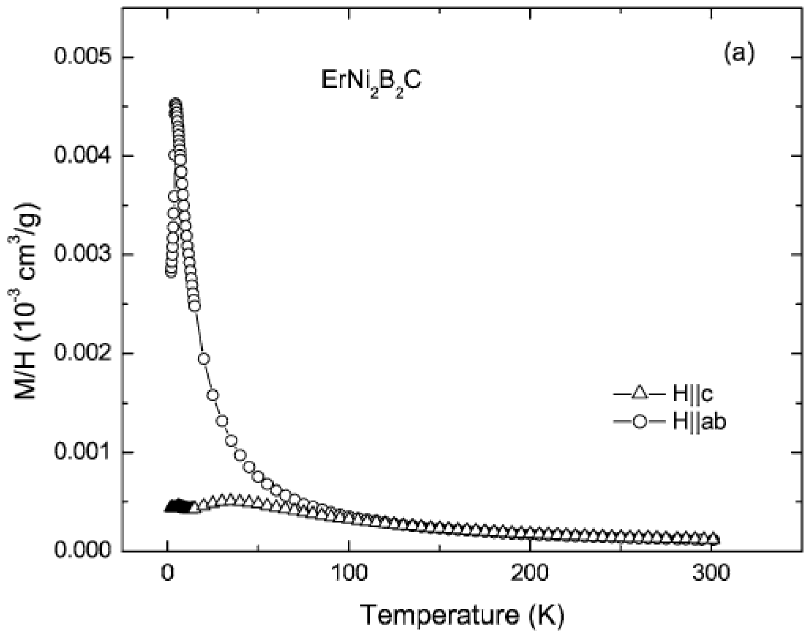
One effect of local moment magnetism is immediately clear from the correlations between the anisotropy of χ and $H_{c2}(T)$: larger χ leads to smaller $H_{c2}(T)$. This is due to the internal field suppressing superconductivity.

P. C. Canfield et al. Physics Today Oct. 1998

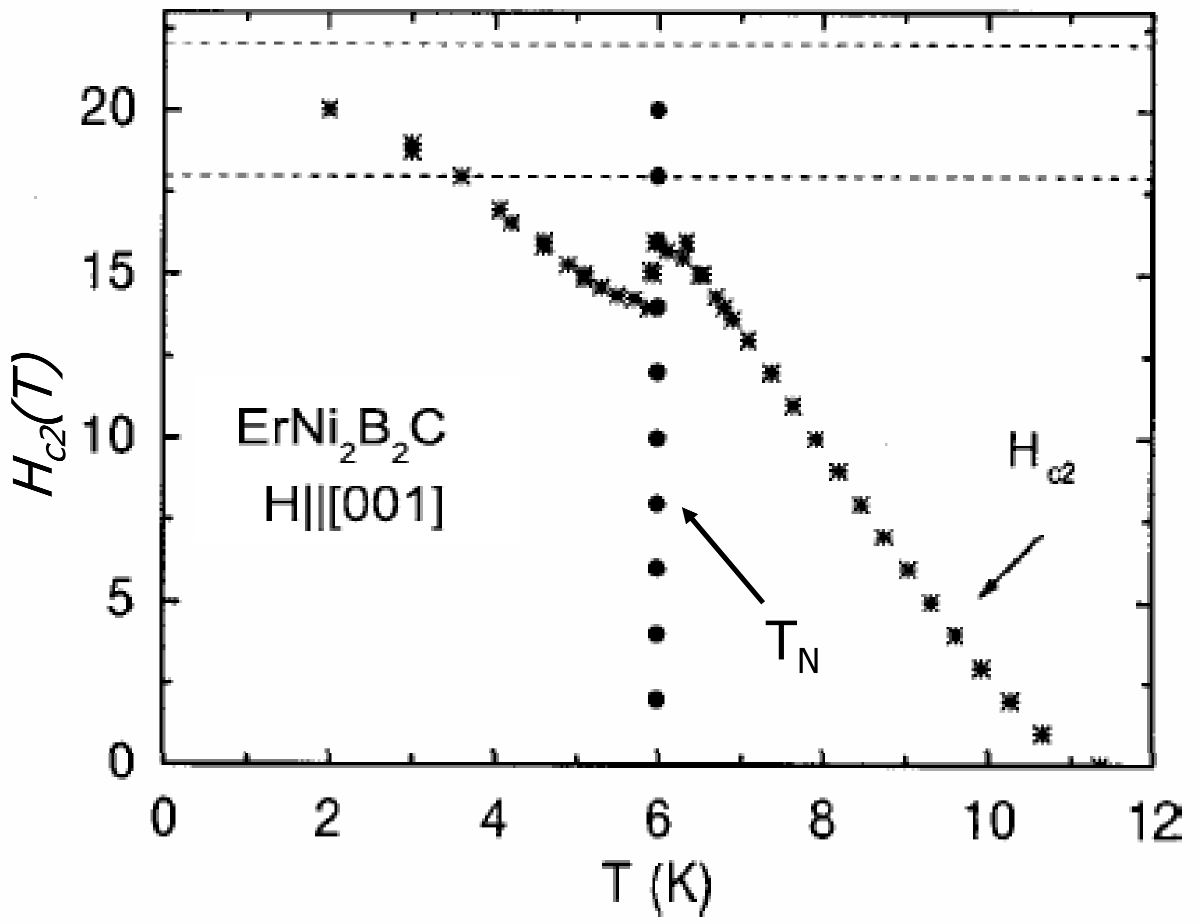
S.L. Bud'ko, P.C. Canfield / C. R. Physique 7 (2006) 56–67







In addition: sharp features in $H_{c2}(T)$ are due to the local moment ordering:

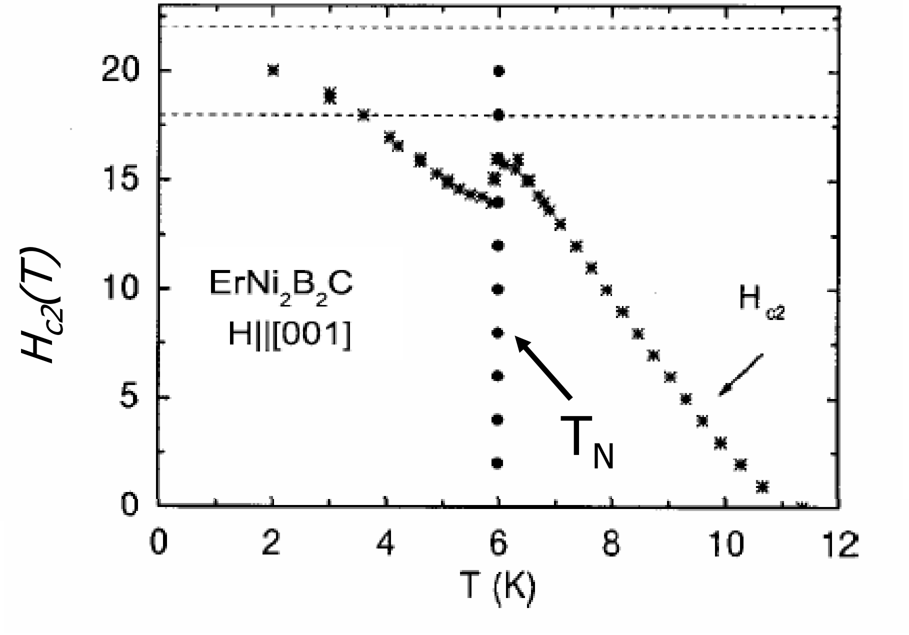


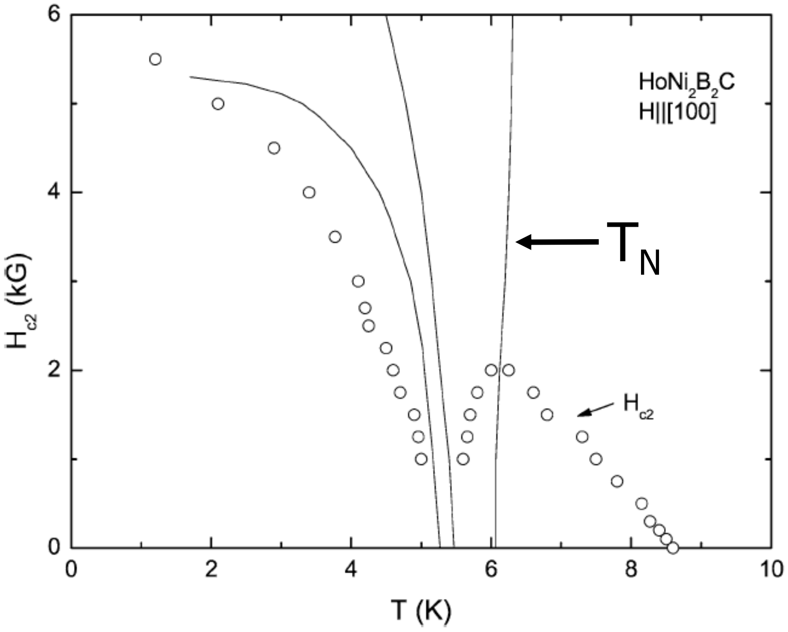
SERGEY L. BUD'KO AND PAUL C. CANFIELD PRB 61 R14 932 1 JUNE 2000-II

The other conspicuous feature in the $H_{c2}(T)$ data is the sharp decrease in $H_{c2}(T)$ when the sample crosses from the paramagnetic to antiferromagnetically ordered state. This can be seen most clearly by creating a composite H-T phase diagram that shows phase lines for both superconductivity as well as local moment order.

This suppression in $H_{c2}(T)$ has been the focus of intense research and debate. It has been associated with the onset of long range magnetic order that has an ordering wavevector that is determined by Fermi surface nesting (i.e. details of the conduction electron bands).

This goes well beyond the scope of an introductory lecture, but is clearly revealed by the simple construction of composite H-T phase diagrams.





S.L. Bud'ko, P.C. Canfield / C. R. Physique 7 (2006) 56–67

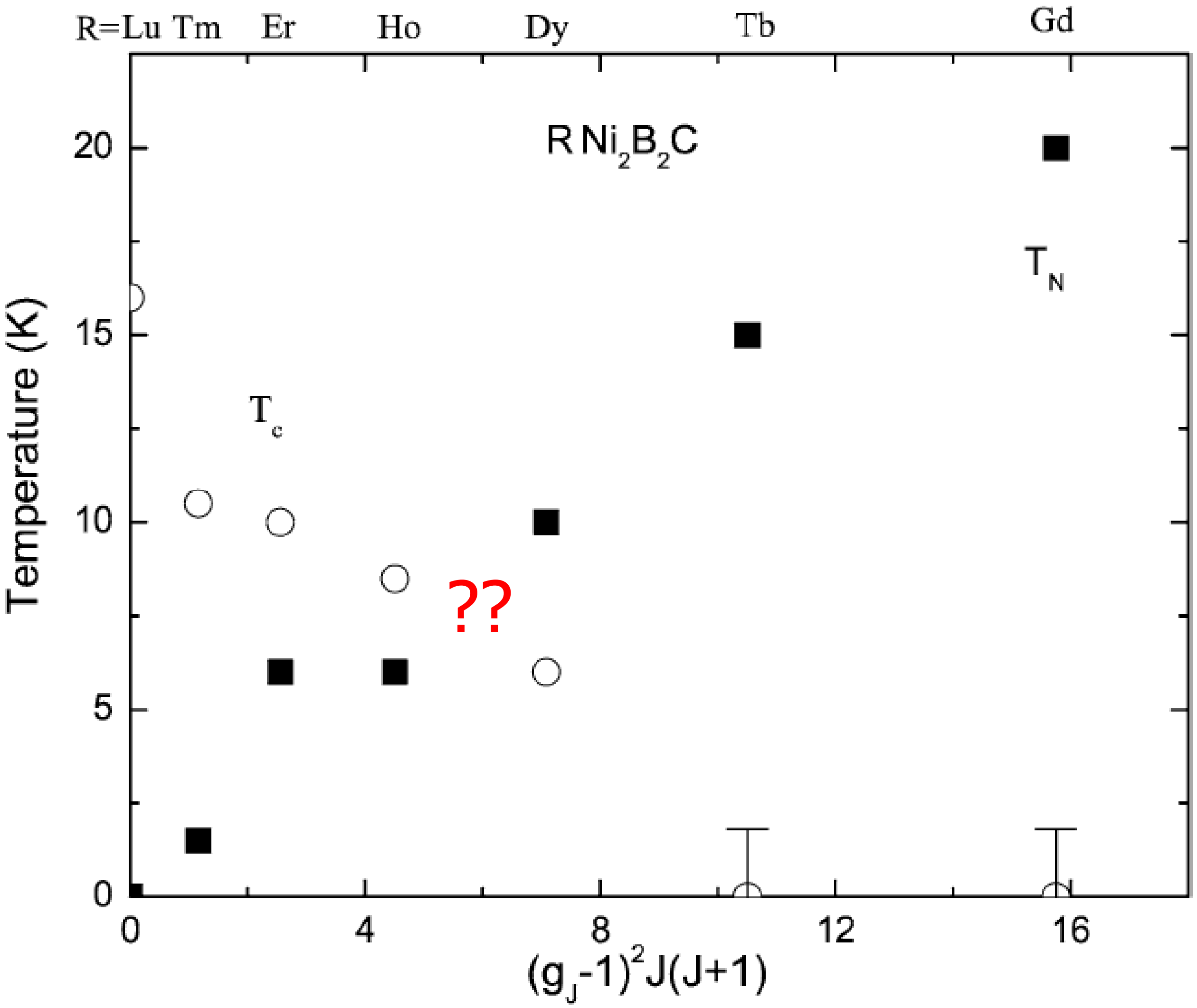
SERGEY L. BUD'KO AND PAUL C. CANFIELD PRB 61 R14 932 1 JUNE 2000-II

Rathnayaka et al. PRB 53 (1996) 5688

The T_c versus Rare Earth (or de Gennes factor) plot also brings up what can be called "a clever monkey" question: What happens as we make T_c cross T_N?

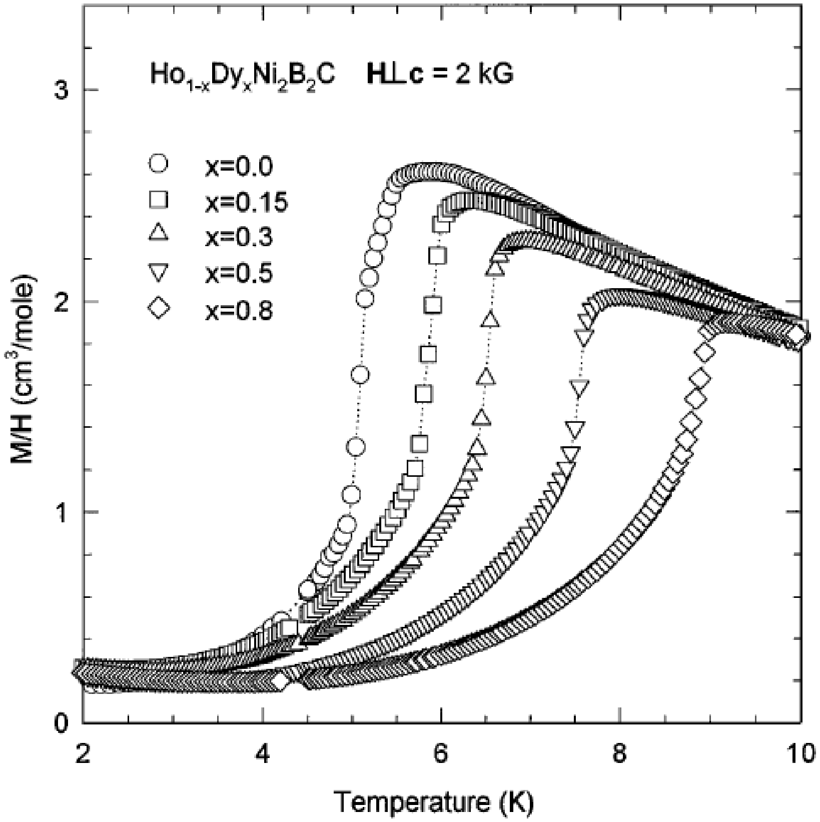
In order to address this question we need to grow a specific series of compounds:

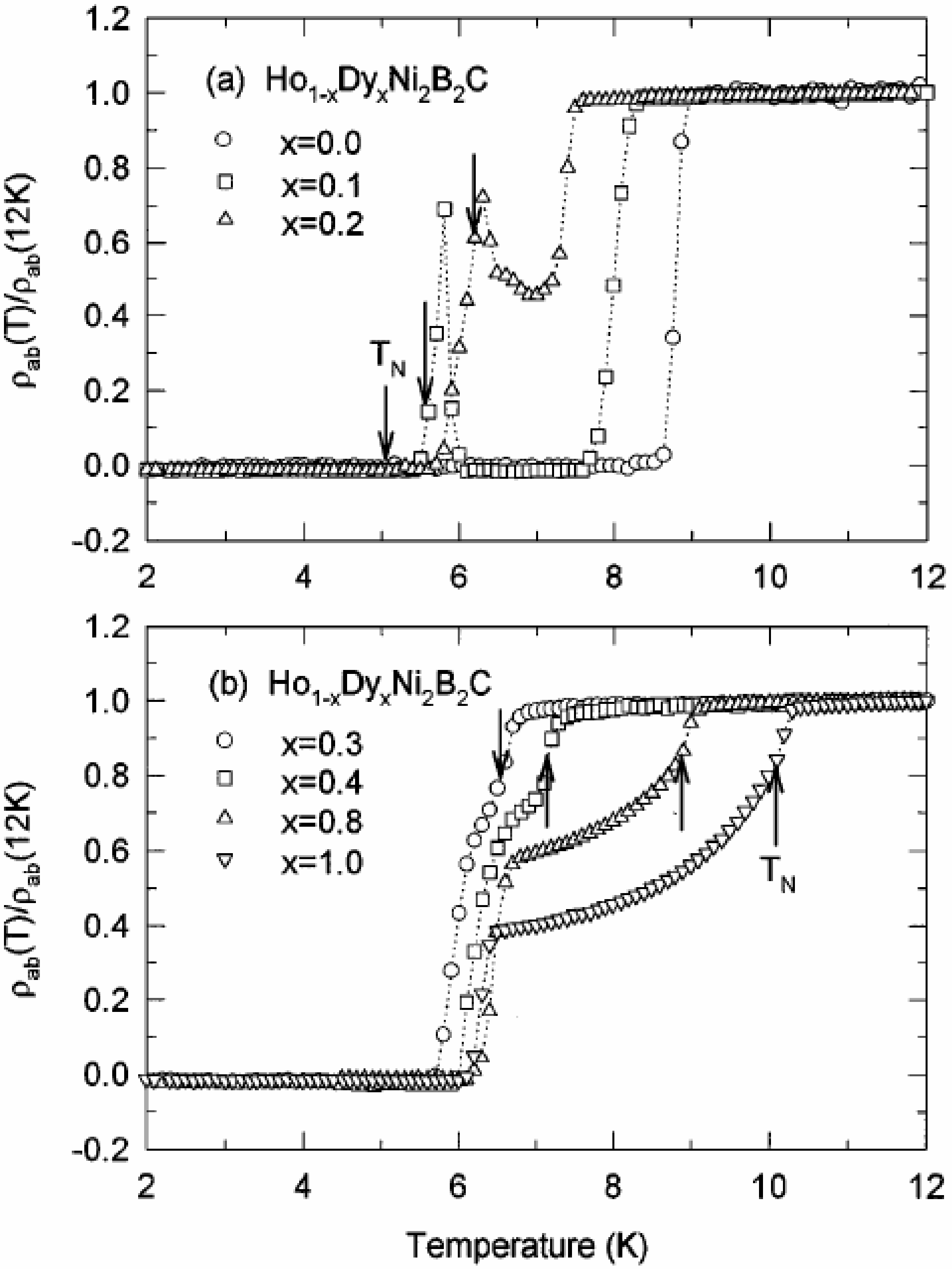
$(Ho_{1-x}Dy_x)Ni_2B_2C$



P. C. Canfield et al. Physics Today Oct. 1998 S.L. Bud'ko, P.C. Canfield / C. R. Physique 7 (2006) 56–67

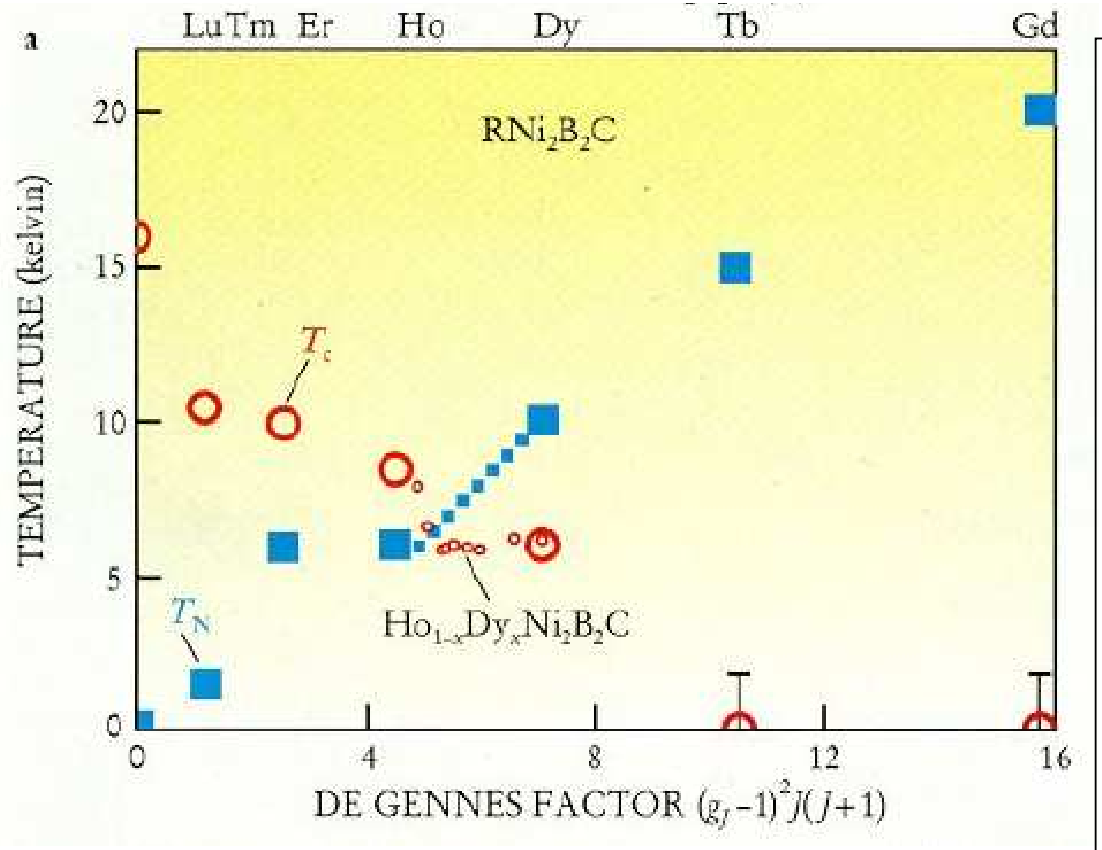
As we discussed last lecture, both T_c and T_N can be tracked via χ as well as ρ.





B. K. Cho,* P. C. Canfield, and D. C. Johnston PHYSICAL REVIEW LETTEI VOLUME 77, 1996 163

We find that something remarkable happens: Whereas T_N continues to change in a linear manner, T_c essentially becomes independent of dG factor when $T_c < T_N$.



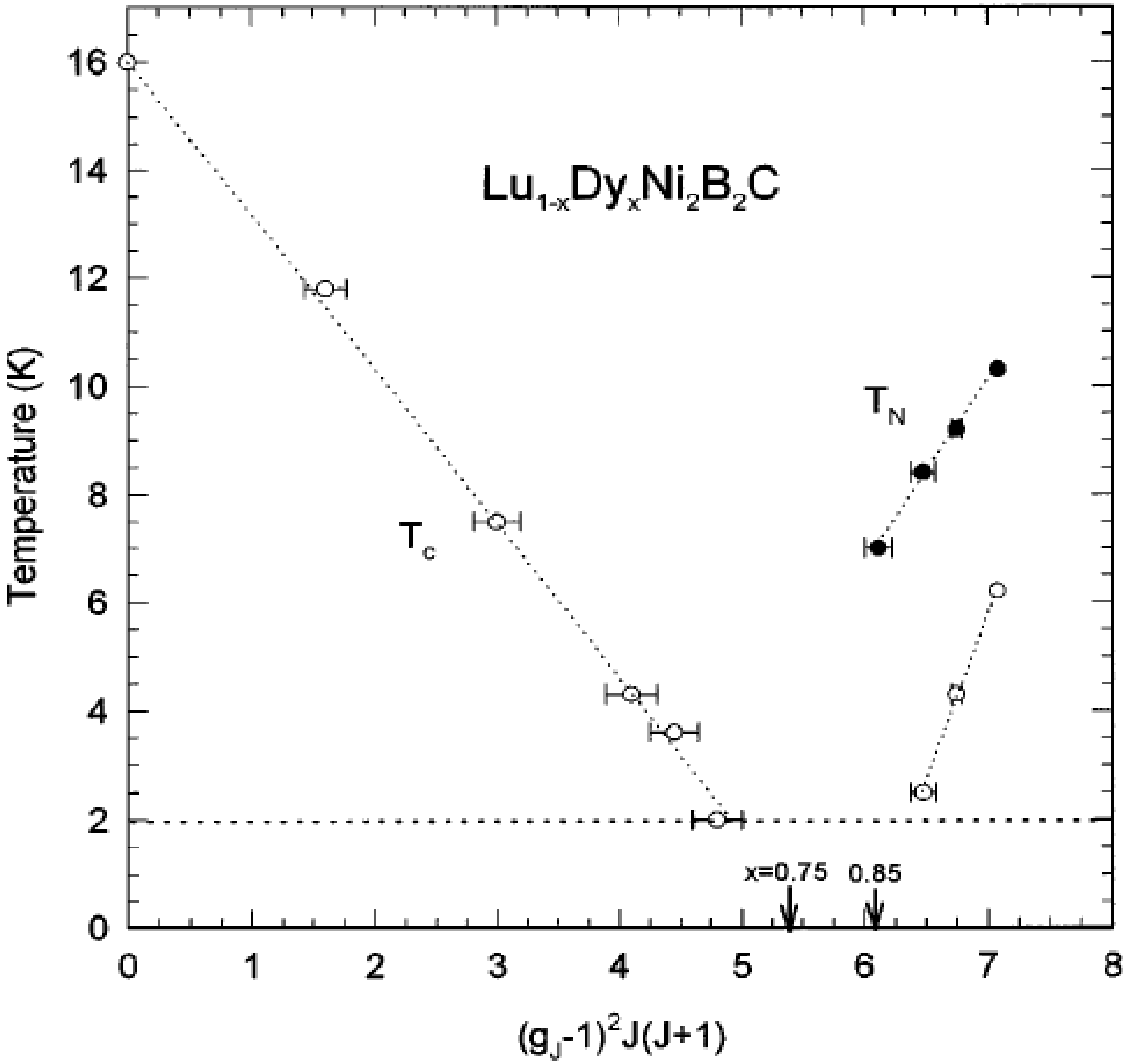
P. C. Canfield et al. Physics Today Oct. 1998

B. K. Cho,* P. C. Canfield, and D. C. Johnston PHYSICAL REVIEW LETTEI VOLUME 77, 1996 163

In order to get a better idea of what was going on, we retreated to what we thought would be a simpler system: $Lu_{1-x}Dy_xNi_2B_2C$.

We found that $DyNi_2B_2C$ was actually a very rare beast indeed: a system that is superconducting only because there is a higher temperature antiferromagnetic transition.

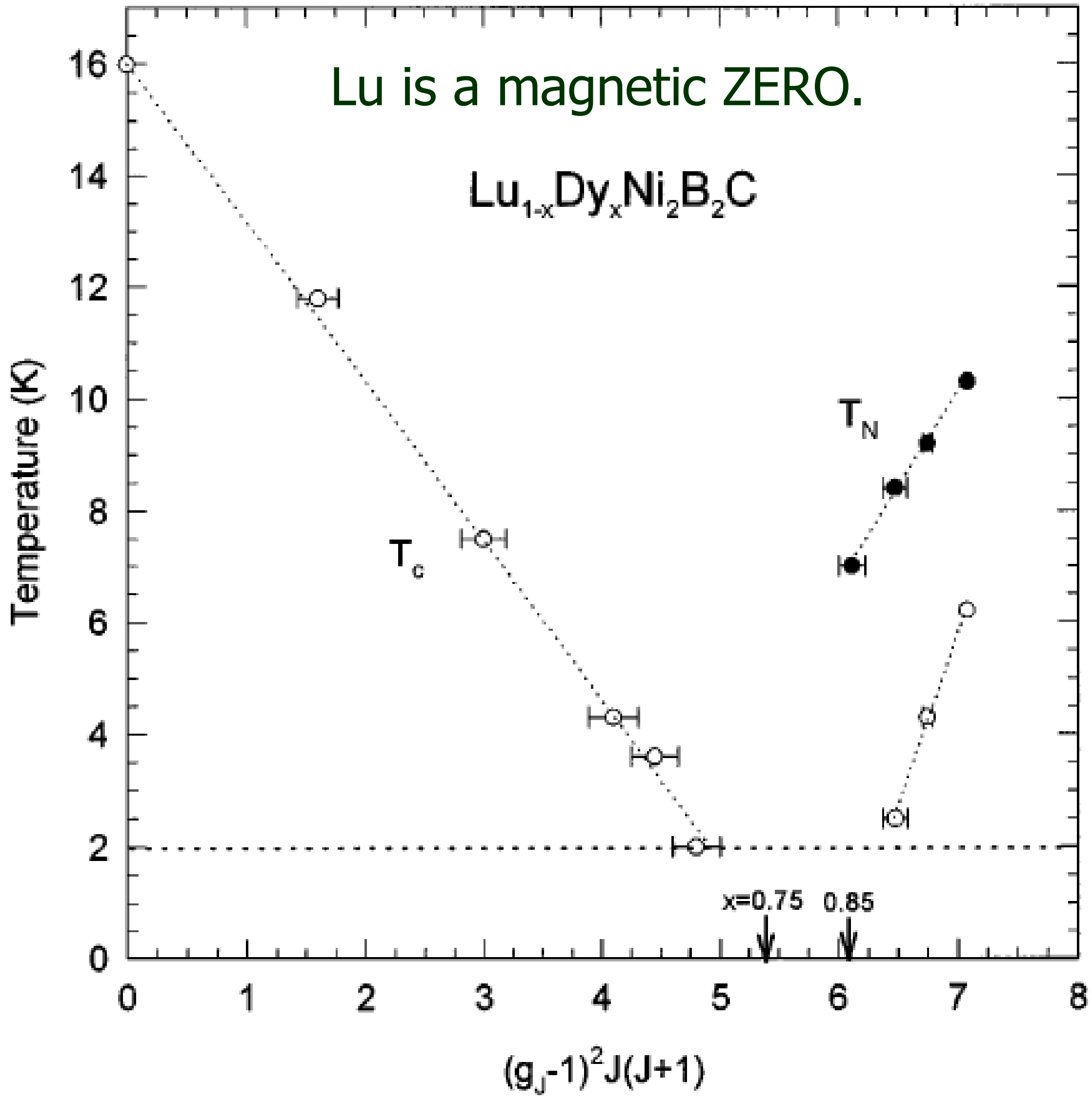
If $DyNi_2B_2C$ remained paramagnetic, it would never superconduct.



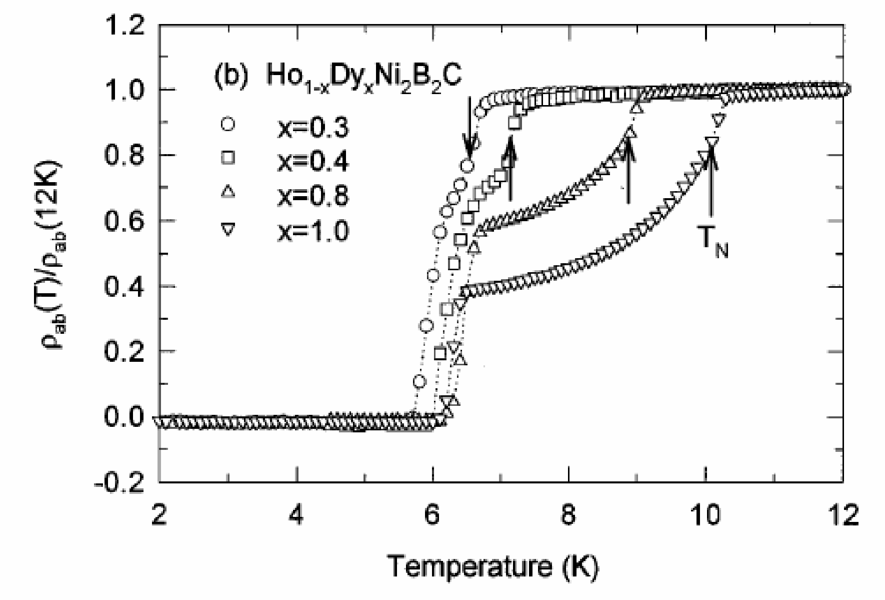
B. K. Cho,* P. C. Canfield, and D. C. Johnston PHYSICAL REVIEW LETTEI VOLUME 77, 1996 163

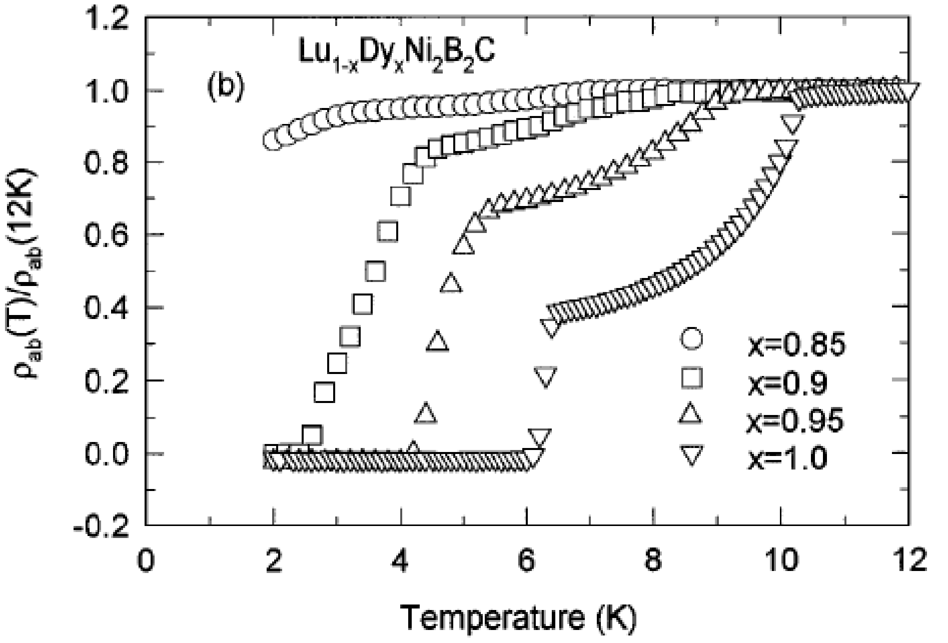
In order to understand this conclusion we need to note that in the ordered state pair breaking is *NOT* from isolated spin flip scattering. The Cooper pair has to interact with magnetic excitations.

Ho and Dy are very similar, especially in the RNi_2B_2C compounds.


Lu is a magnetic ZERO.

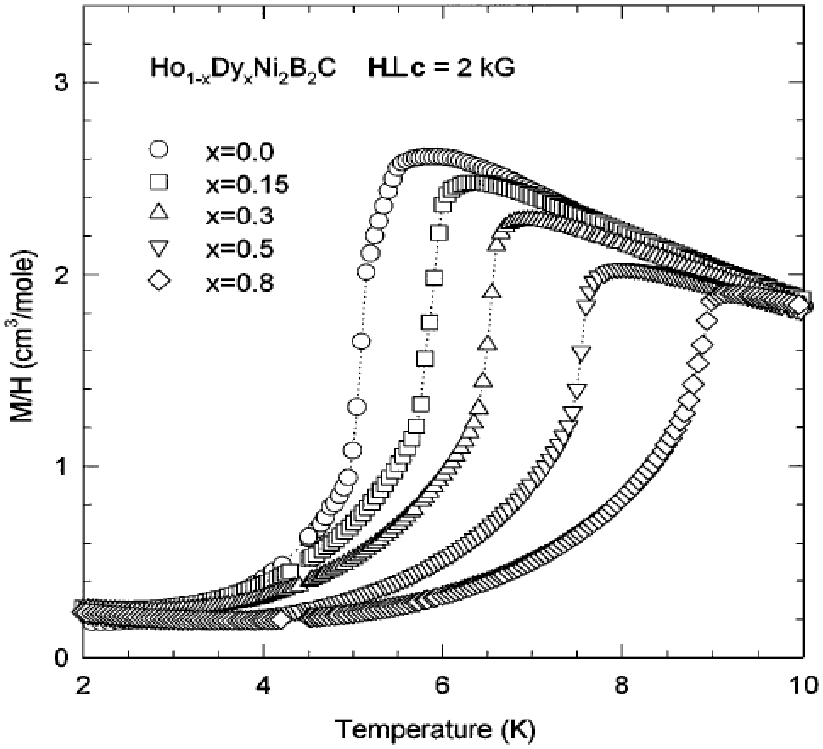
The effects of this can be seen in the $T < T_N$ resistivity. As Lu is added to $(Lu_{1-x}Dy_x)Ni_2B_2C$ the “loss of spin-disorder scattering” decreases dramatically and rapidly. This is consistent with having the Lu not only suppress T_N, but also soften the magnetic lattice, allowing many more, low temperature excitations.

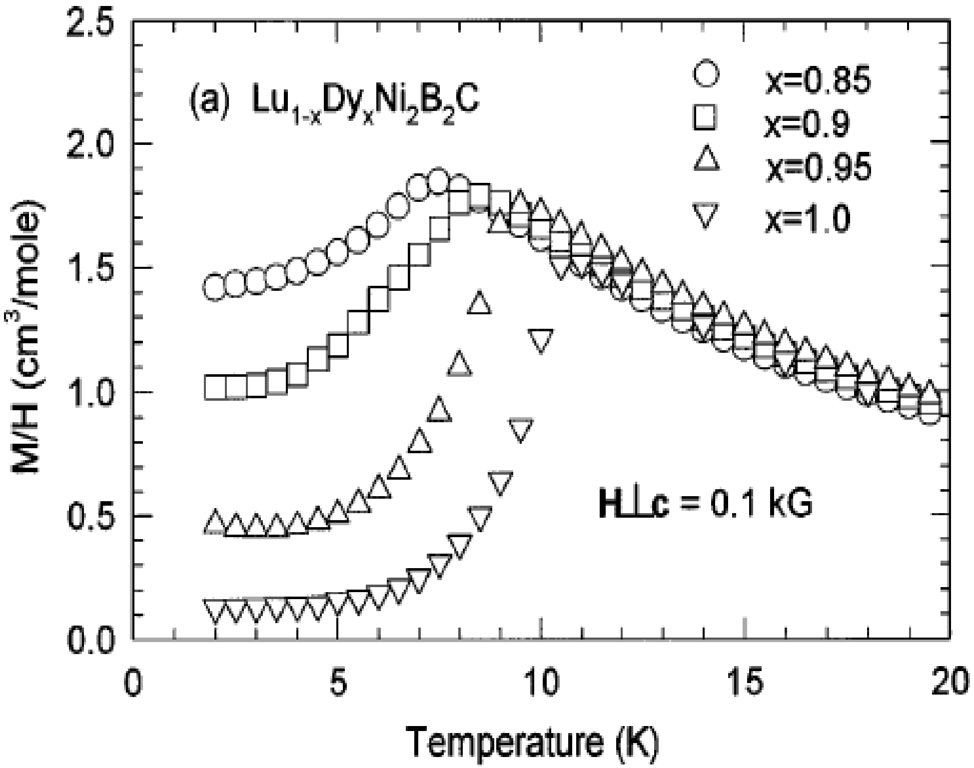




B. K. Cho,* P. C. Canfield, and D. C. Johnston PHYSICAL REVIEW LETTEI VOLUME 77, 1996 163

The increase of magnetic excitations with the addition of Lu is further confirmed by comparisons of the magnetic susceptibilities of $(Lu_{1-x}Dy_x)Ni_2B_2C$ and $(Ho_{1-x}Dy_x)Ni_2B_2C$. Whereas the $\chi(T < T_N)$ remains low for the Ho substitution, it rises rapidly for the Lu substitution.



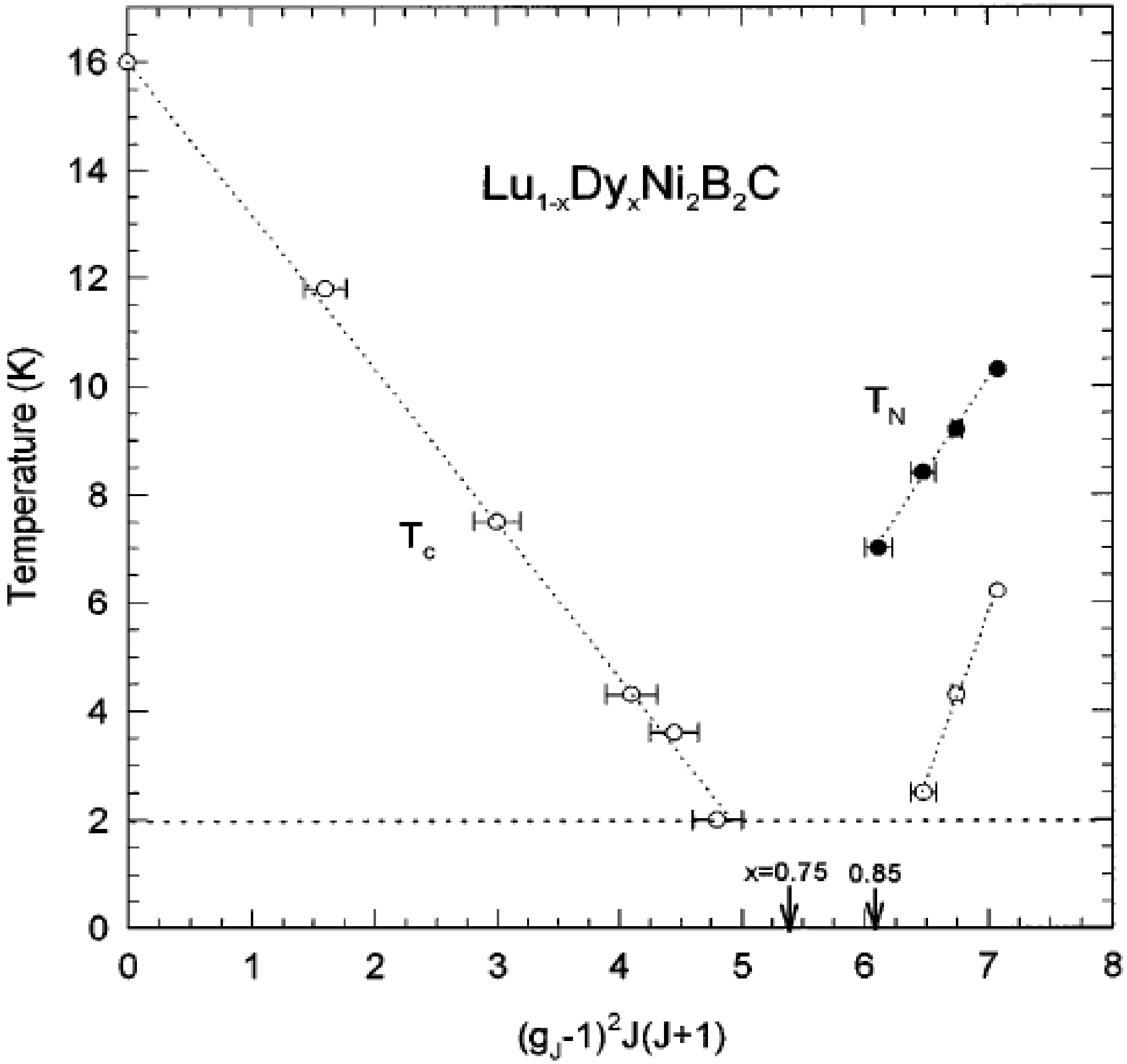


B. K. Cho,* P. C. Canfield, and D. C. Johnston PHYSICAL REVIEW LETTEIVOLUME 77,; 1996 163

We can look at the T-x phase diagram of $Lu_{1-x}Dy_xNi_2B_2C$ from both ends. As we add Dy to $LuNi_2B_2C$ we suppress T_c via the paramagnetic Dy breaking Cooper pairs.

On the other hand, as we add Lu to $DyNi_2B_2C$ T_N is suppressed rapidly and pair breaking from low-energy excitations is enhanced dramatically.

If $DyNi_2B_2C$ only superconducts because it is antiferromagnetic, then any degradation of the antiferromagnetic state is very bad for the superconductivity.



B. K. Cho,* P. C. Canfield, and D. C. Johnston PHYSICAL REVIEW LETTEIVOLUME 77,; 1996 163

In addition to the interplay between superconductivity and local moment magnetism, the RNi_2B_2C series has:

Heavy Fermion for $YbNi_2B_2C$
$T_K \sim 10$ K; $T_{\Delta CEF} \sim 100$ K; T_C, $T_N < 100$ mK (possibly 0 K)

Flux Line Lattice phase transitions

Great tunability: T_N, H_{C2}, ℓ, ξ_0, H_2….

This series offers a wonderful playground for the study of the interactions between conduction electrons (normal or superconducting) and 4f-electrons (localized or itinerant).

But for this lecture, let’s return to some of the old prejudices:
remember #2, highest T_c near a structural phase transition.

LuNi$_2$B$_2$C (and YNi$_2$B$_2$C) are about as close to a CDW transition as they can be….Electron-phonon coupling is nearly optimized.

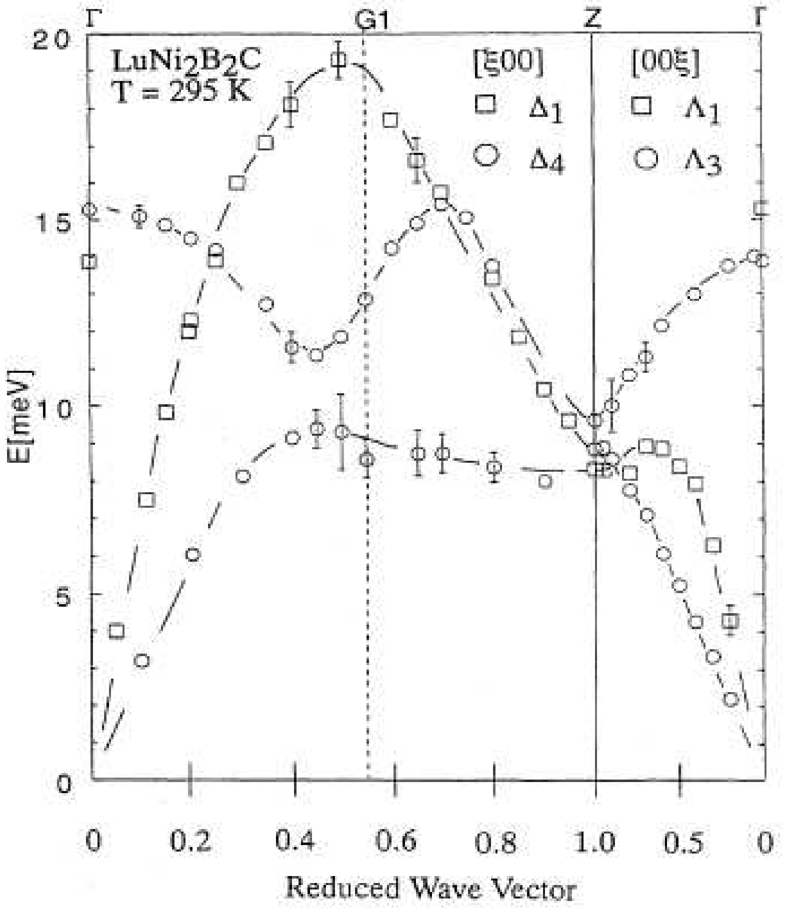


FIG. 1. Room-temperature acoustic and lowest-lying optical phonon dispersion curves of LuNi$_2$B$_2$C along the [ξ00] and [00ξ] symmetry directions. The lines are intended as guides to the eye. The size of the symbols is a measure of the estimated uncertainties in the measured frequencies.

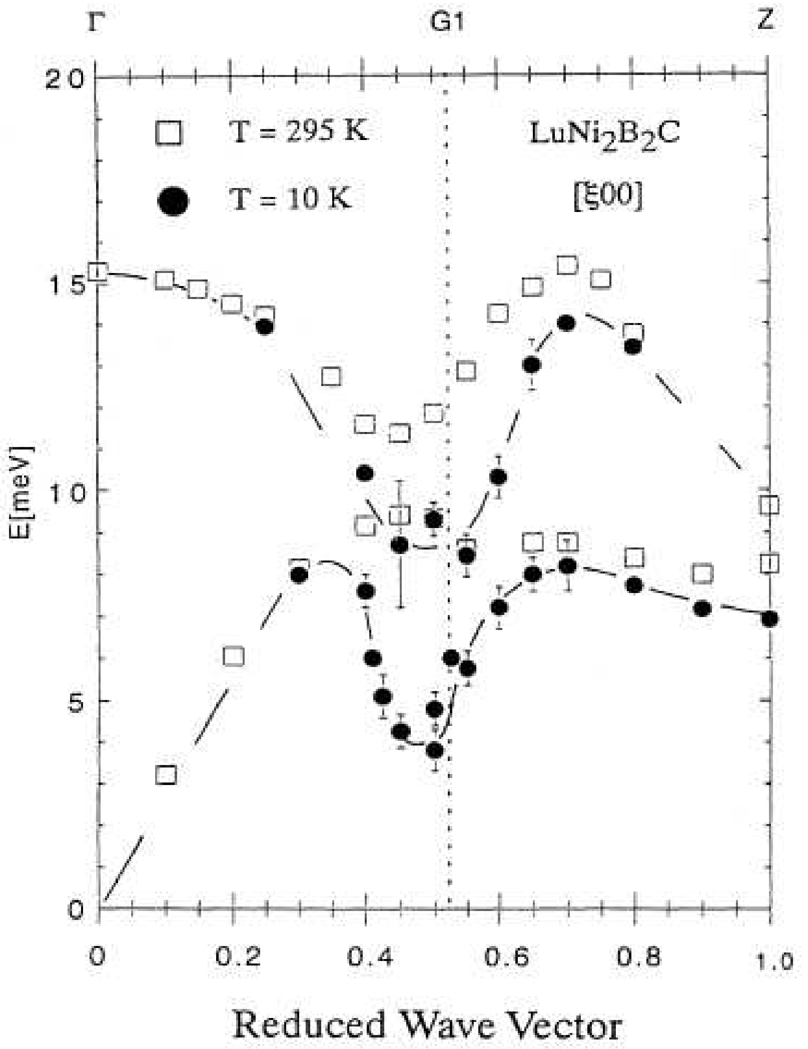


FIG. 2. The Δ_4 [ξ00] branches at 295 and 10 K. The lines through the 10 K points are intended as guides to the eye.

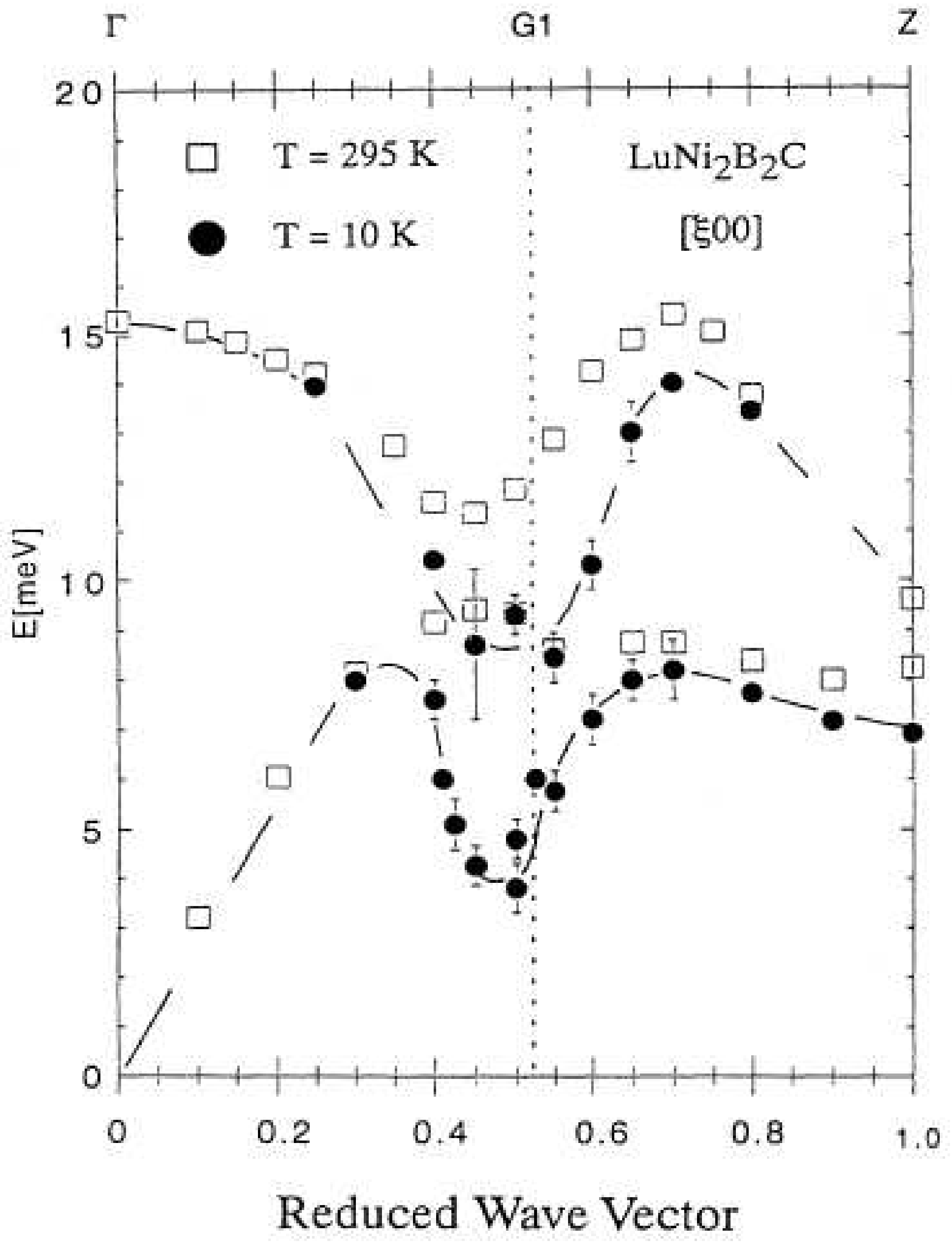
Dervenagas et al. PRB **52** (1995) 9839

Near the end of what

$k_B T_C = 1.13\hbar\omega_D e^{-1/VN(E_F)}$

has to offer.

If the electron phonon coupling were increased further, then the phonon would soften further and there would be a structural phase transition…. This is consistent with the higher T_c and metastability of YPd_2B_2C .



Dervenagas et al. PRB **52** (1995) 9839

In the late 1990’s the question arose:

So, what to do next?

Based on the wealth of physics, as well as the high T_C values, found in the RNi_2B_2C family many groups decided to look for other intermetallics with light elements and see if similar (or even higher) T_C values could be found.

Several groups (including my own) were examining compounds with combinations of Li, Be, B, C, Mg, Al, Si and other (often transition metal) elements.

In late 2000 the group lead by Prof. J. Akimitsu examined the Ti-Mg-B ternary *(Ti because we got to have those 3-d electrons)* and found…a binary: MgB_2.

In mid-January, 2001 Prof. Akimitsu announced an ~40 K T_C in MgB_2 as part of a passing reference in a talk at a meeting….

In mid-January, 2001 my group heard rumors of this announcement: i.e. that there may be superconductivity in MgB_2.

Immediately there were four basic questions.

Can we make it?

Can we confirm T_C?

Can we address the mechanism of superconductivity?

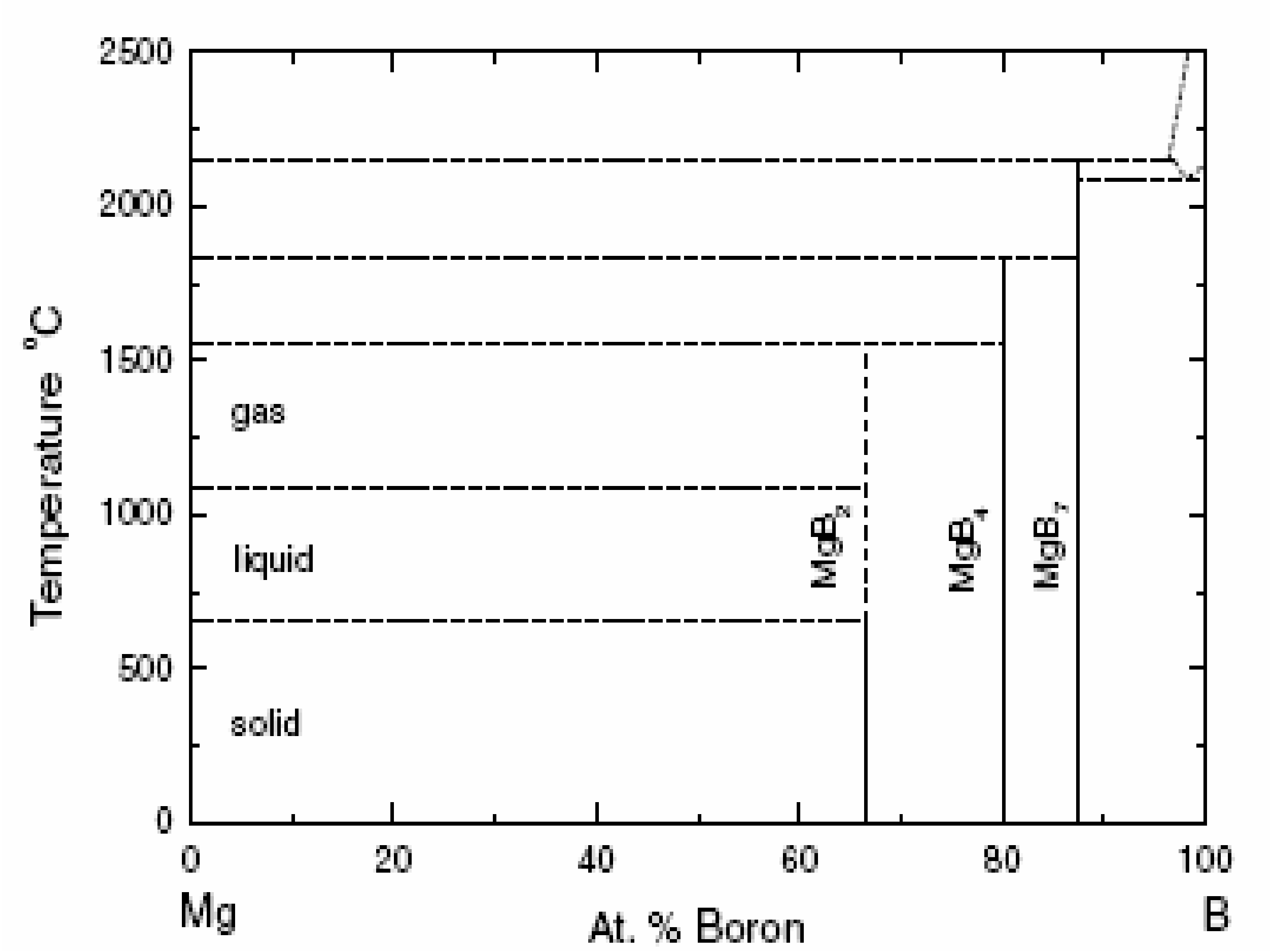
Can we delineate its basic properties?

MgB_2:

Can we make it?

This is a very inauspicious phase diagram. There is no exposed liquid–solidus line at all.

This is not promising for crystal growth.



Since the Department of Physics at Iowa State University is in the College of Liberal Arts and Sciences, we teach the classics of philosophy: Socrates and Aristotle, Freud and Jung, etc. In the words of Mick and Keith, Since the Department of Physics at Iowa State University is in the College of Liberal Arts and Sciences, we teach the classics of philosophy: Socrates and Aristotle, Freud and Jung, etc. In the words of Mick and Keith,

You can't always get what you want

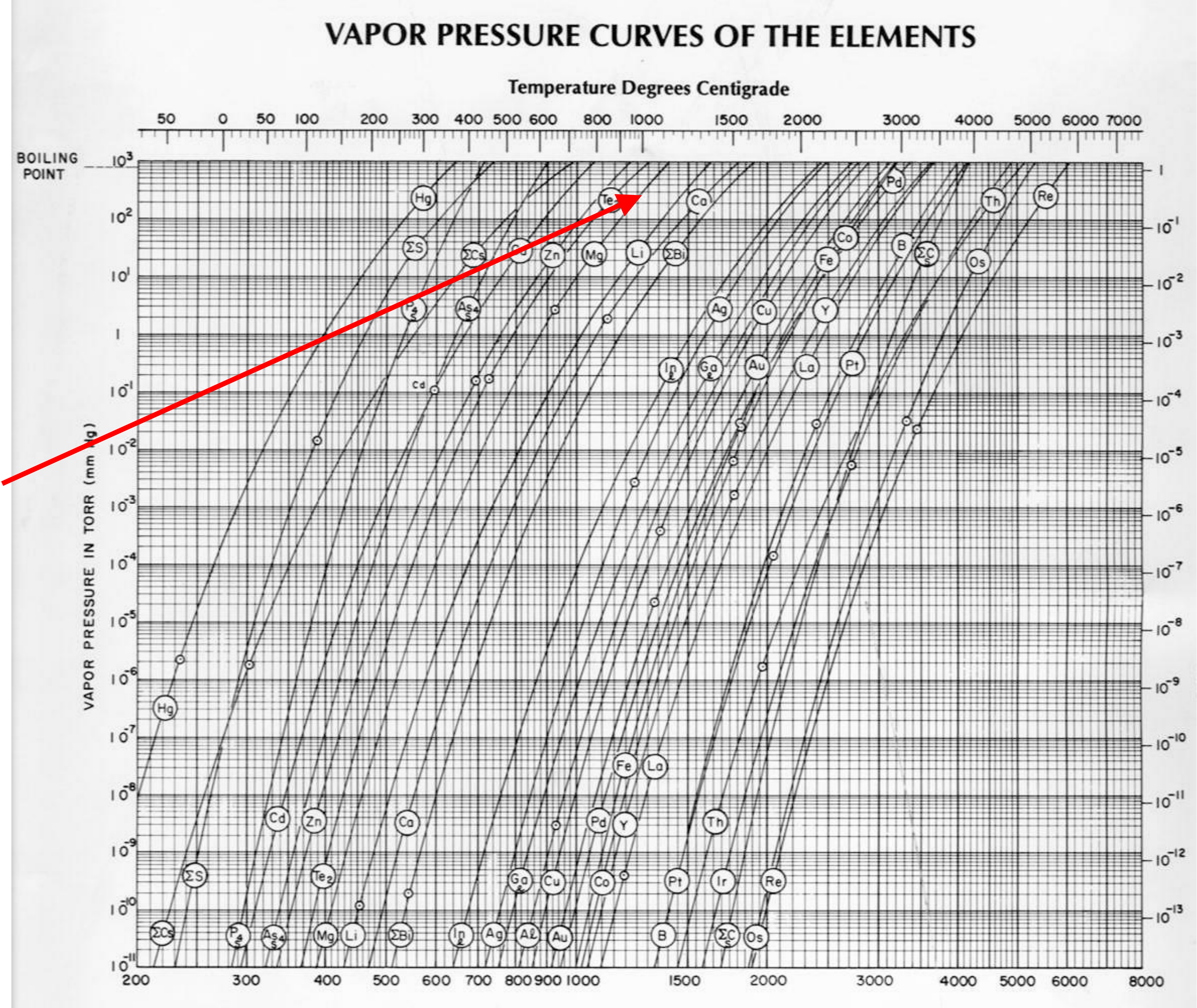
But sometimes you get what you need

Even though, as a group, we specialize in making measurements on single crystals, we found a lot of good work could be done of very high purity polycrystalline samples….

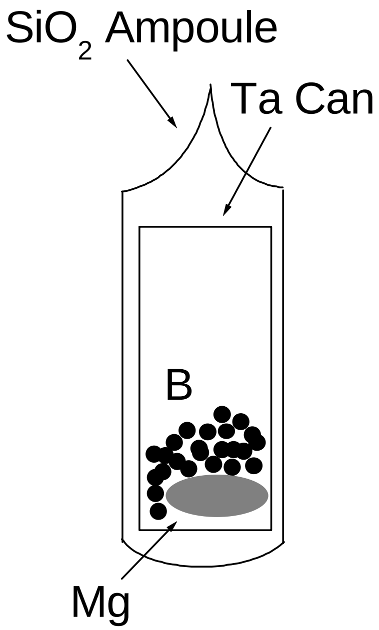
Often vapor pressure is a problem

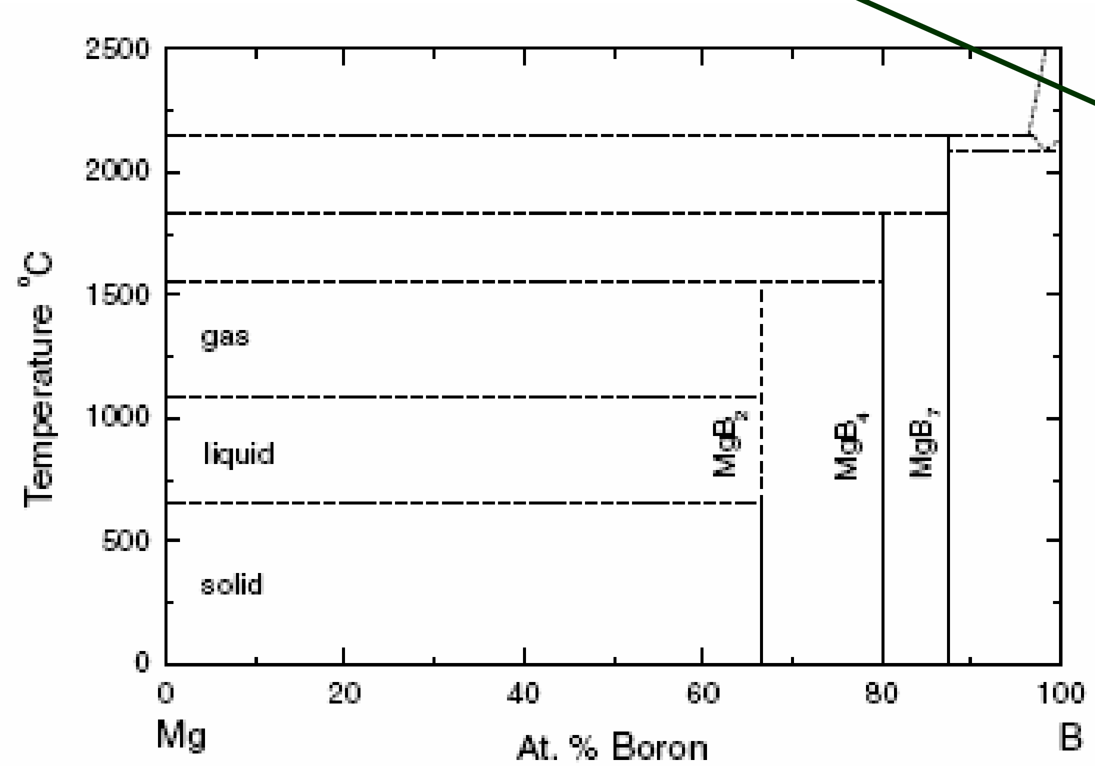
At 950 C Mg has ~ 1/3 atm vapor pressure

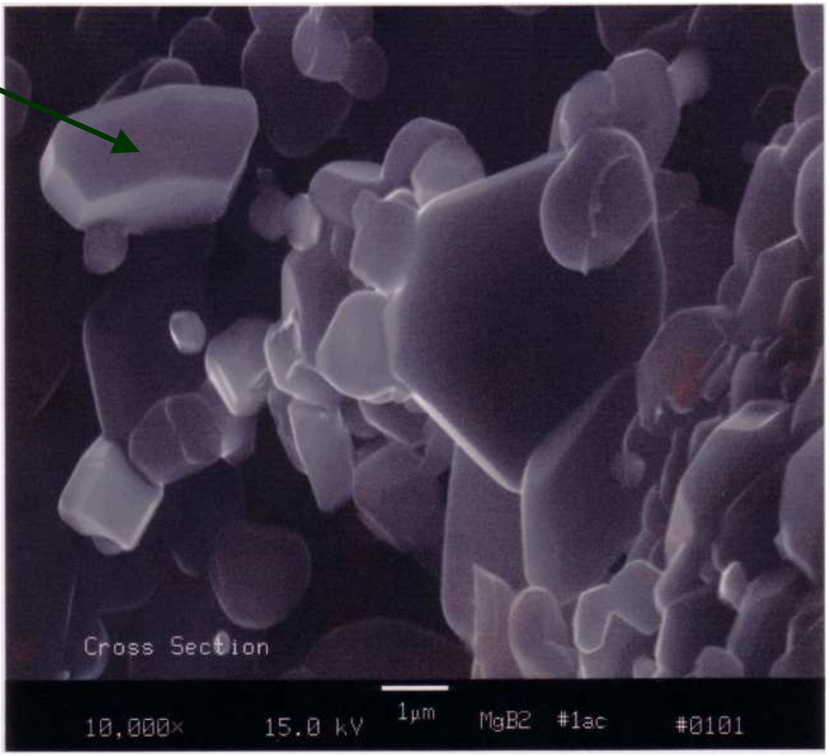
This time we use it to our advantage!



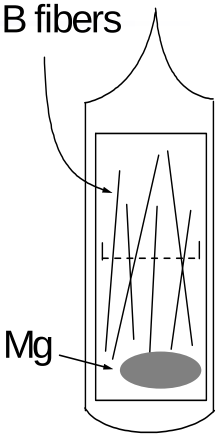
At 950 C the B powder is no where close to melting, but we found that it will react with Mg vapor (~1/3 atm. at 950 C) to form MgB_2 *within as little as 2 hours.*



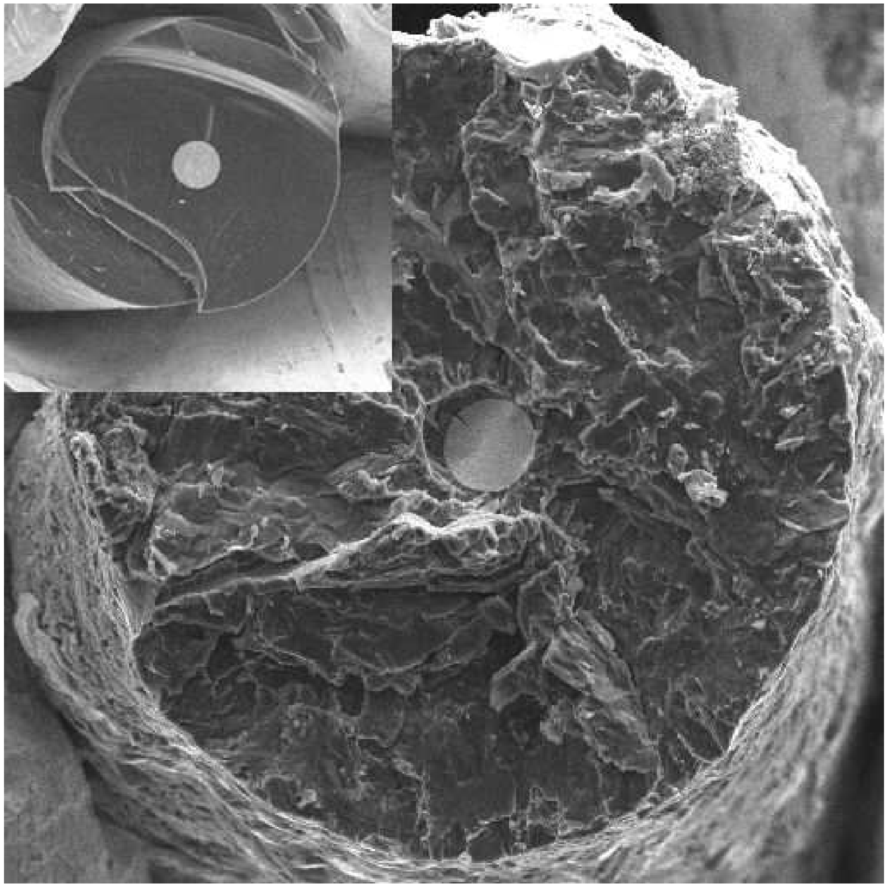




Boron comes in many form. MgB_2 can be made as sintered pellets, thin films and…

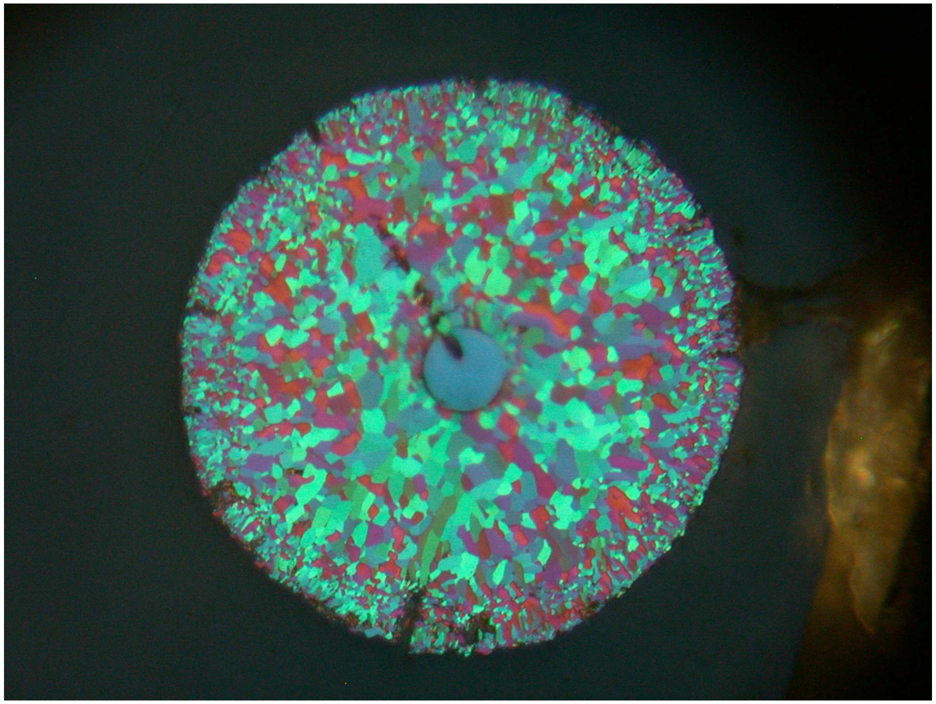


Dense MgB_2 Wires



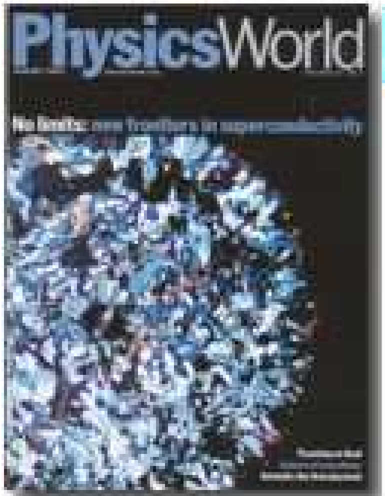
MgB_2 from boron filament

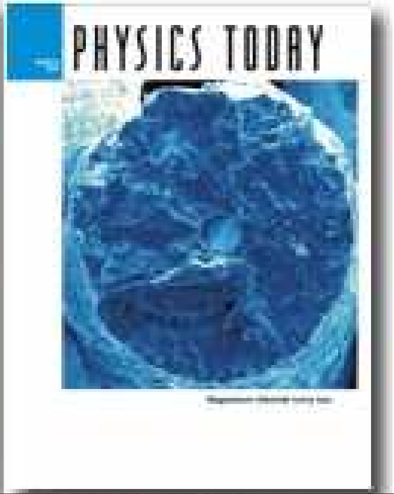
Canfield et al., PRL 86 (2001) 2423



MgB_2 grains illuminate under polarized light.

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

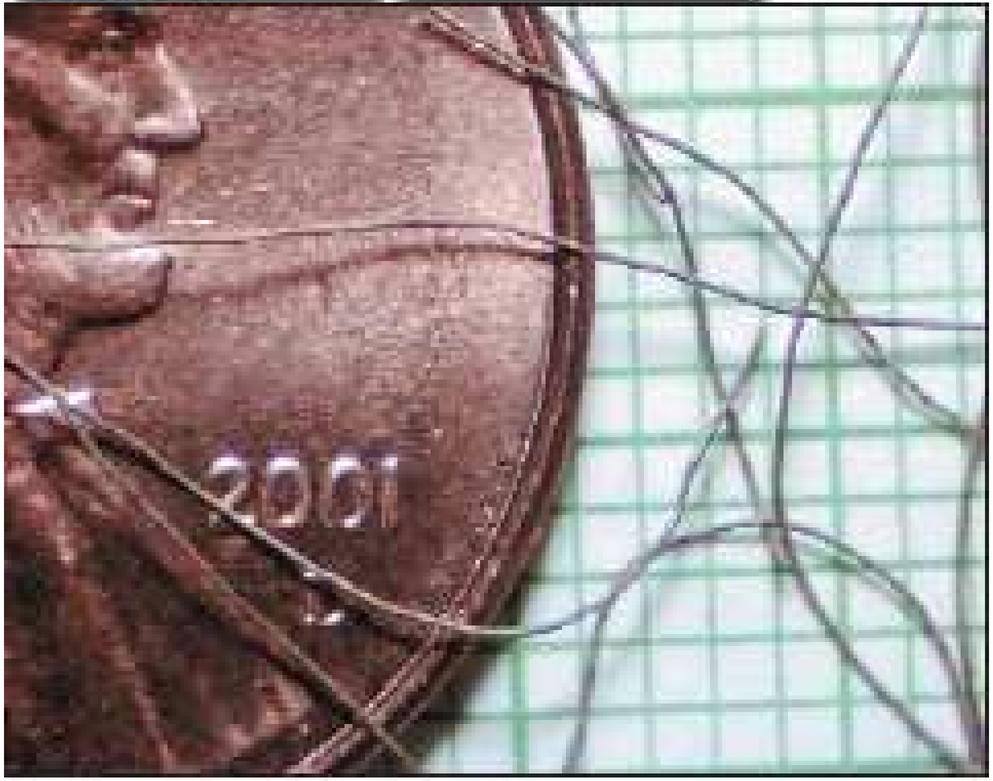
Thermodynamic and Transport Properties of Superconducting $Mg^{10}B_2$

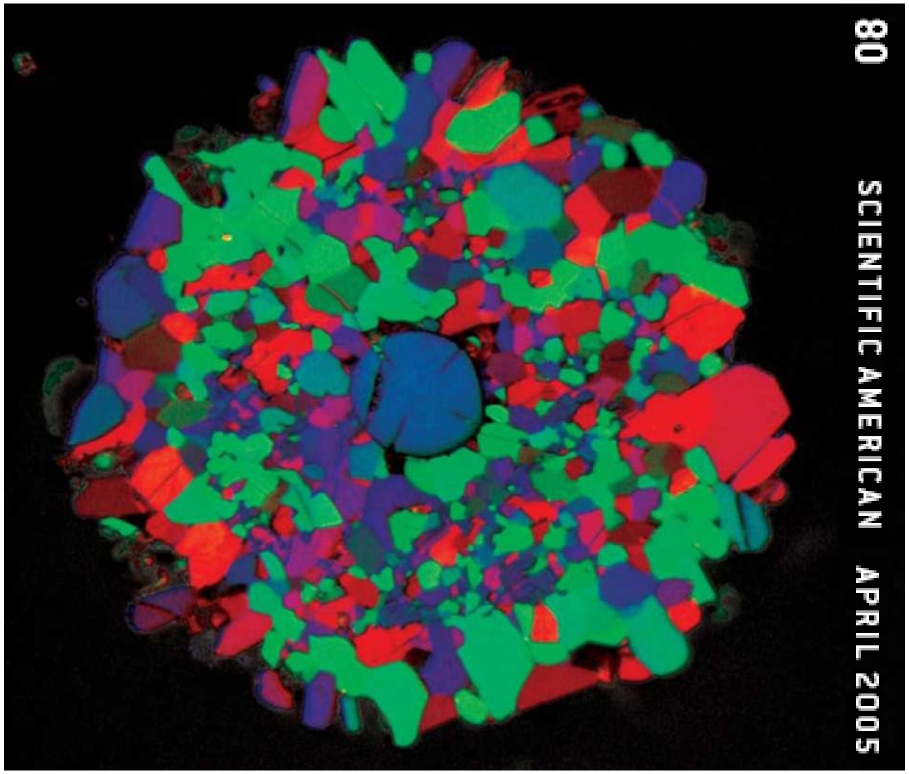
Volume 86, Number 11 PHYSICAL REVIEW LETTERS 12 March 2001

Superconductivity in Dense MgB_2 Wires

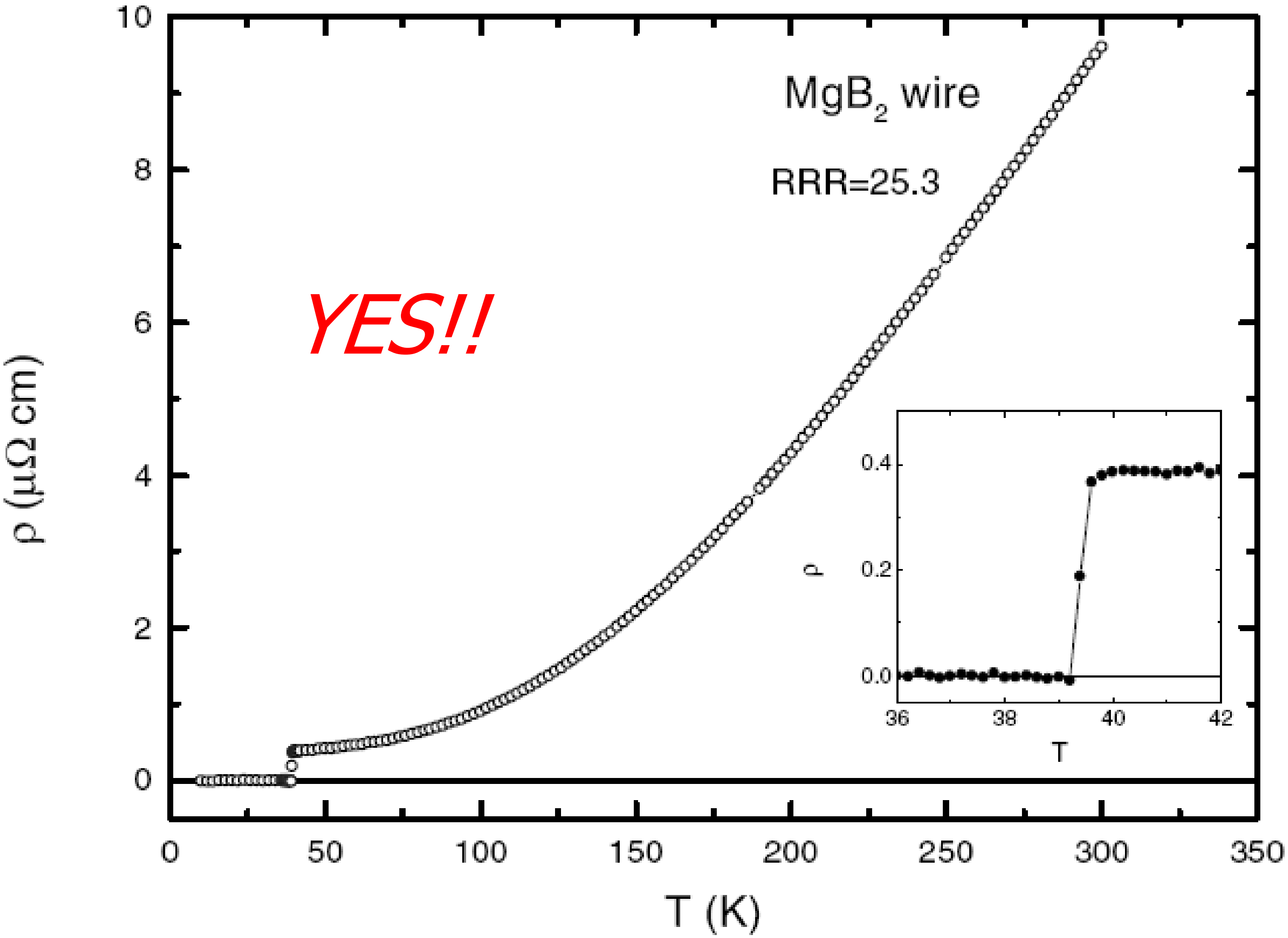
Volume 87, Number 4 PHYSICAL REVIEW LETTERS 23 July 2001

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





Can we confirm T_C?



YES!!

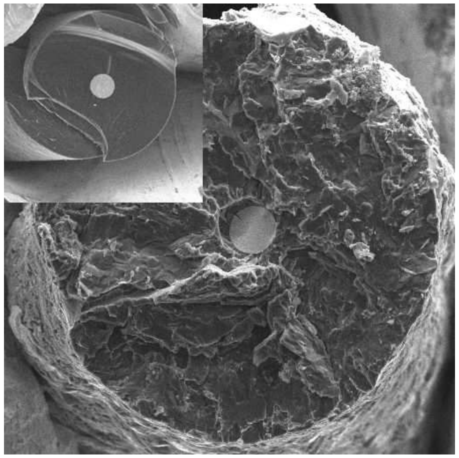
P. C. Canfield, D. K. Finnemore, S. L. Bud'ko, J. E. Ostenson, G. Lapertot,* C. E. Cunningham,† and C. Petrovic

PHYSICAL REVIEW LETTERS VOLUME 86, NUMBER 11 2423 12 MARCH 2001

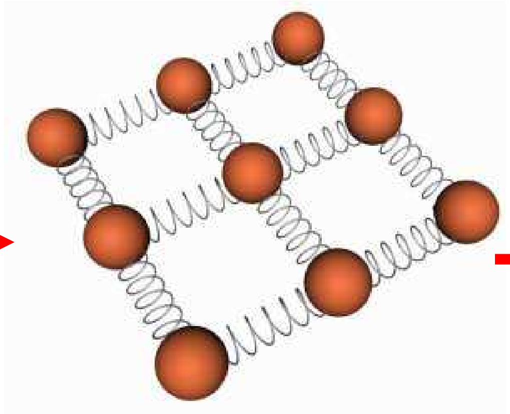
Can we address the mechanism of superconductivity?

If we start with the BCS equation for T_C: $k_B T_C = 1.13\hbar\omega_D e^{-1/VN(E_F)}$
we can see that T_C is directly proportional to ω_D.

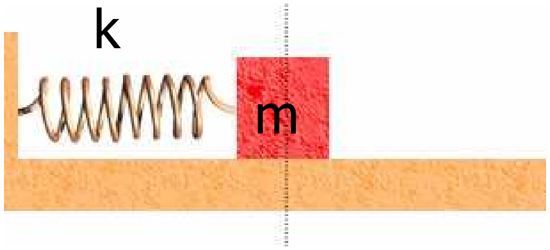
Real sample



Ball-spring model
of lattice



Single mass
and spring



$$\omega = \sqrt{k/m}$$

So, within this cascade of gross assumptions,
T_C should vary as $1/\sqrt{m}$

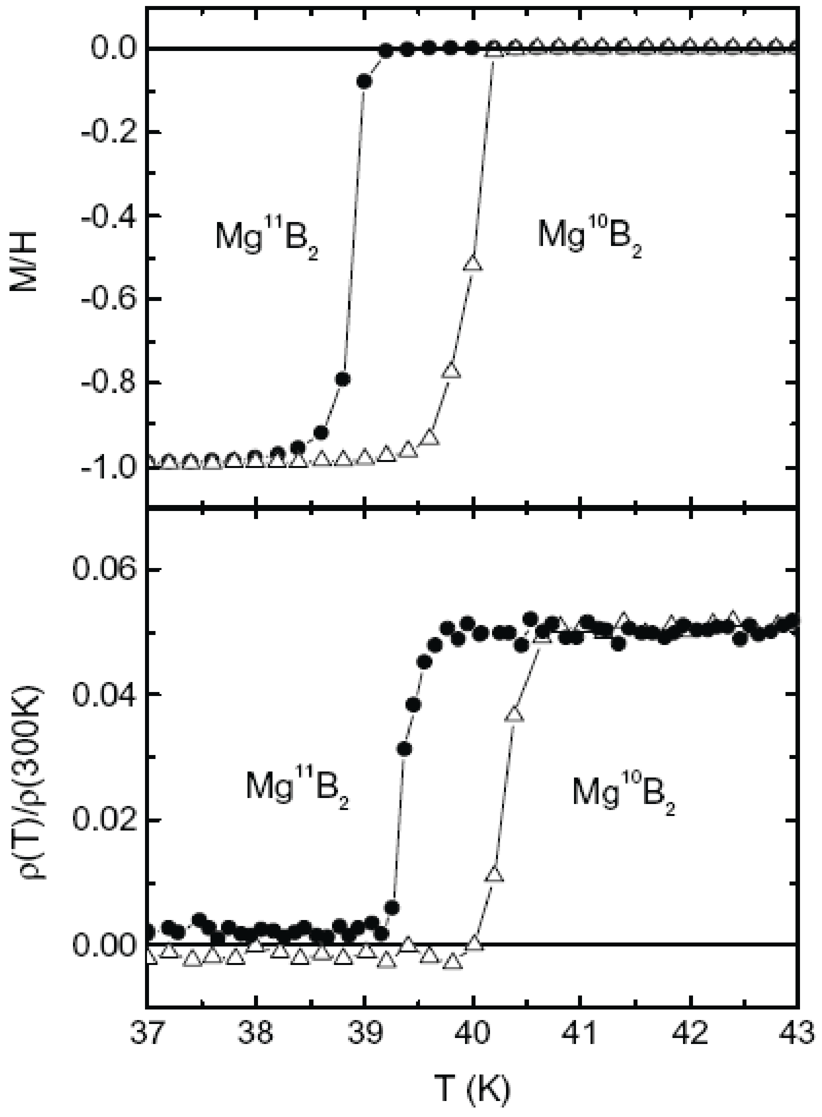
Boron Isotope Experiment

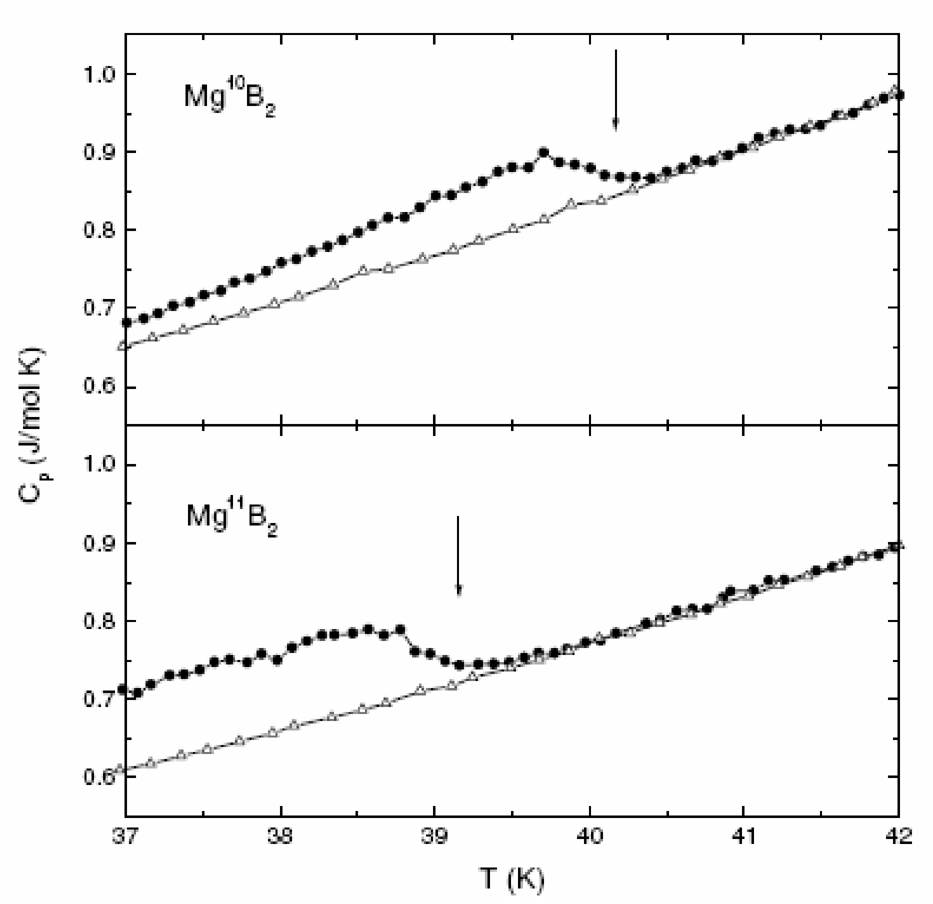
$\Delta T = 1.0$ K

(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.





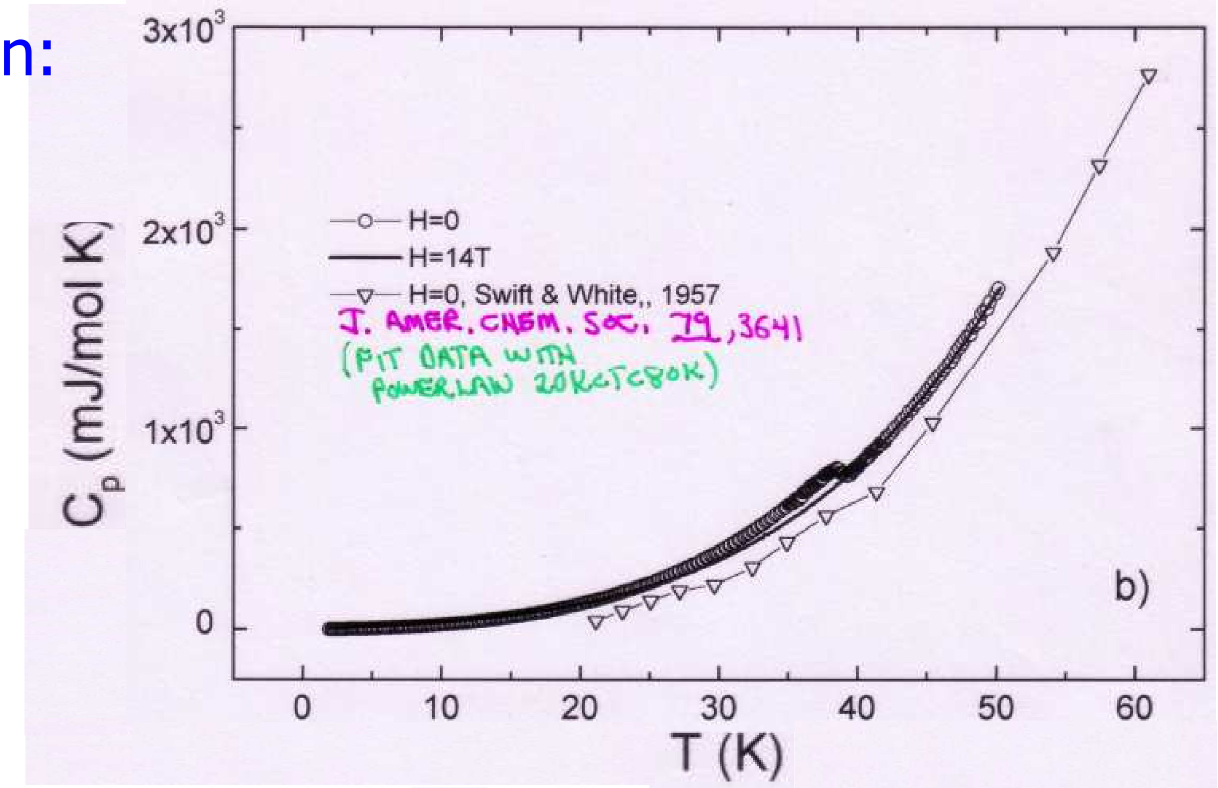
From $C_p(T)$ data we learn:

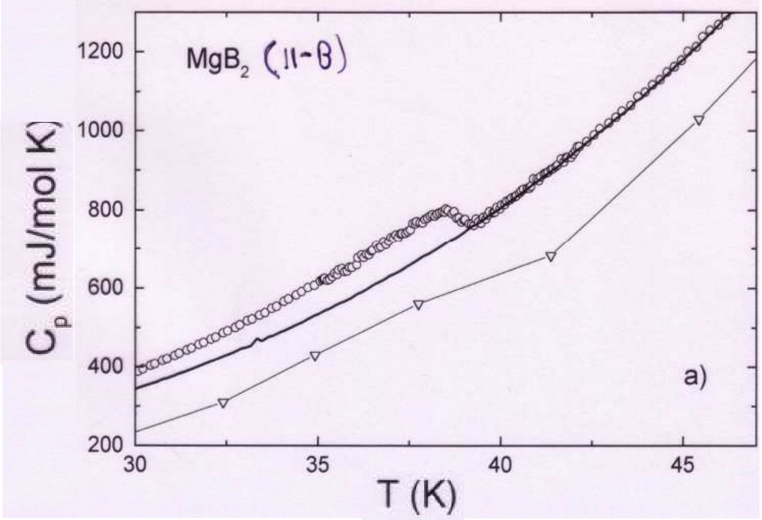
	θ_D
For MgB_2	~ 750 K
For Mg	~ 320 K
For Si	~ 625 K
For Diamond	~1860 K

(high ω_D for MgB_2)

$\gamma \sim 2.5 \pm 0.75$ mJ/mole-K^2

(small γ means small $N(E_F)$)





But we should not forget the triangles….

How was superconductivity in MgB_2 missed?

Hard to make by simple methods (cannot arc-melt it)

Did not fit prejudice (no d-shell electrons to boost $N(E_F)$)

….(Old data did not show superconductivity)….

MgB_2 forces a shift in emphasis when looking for other higher T_C compounds

$$k_B T_C = 1.13\hbar\omega_D e^{-1/VN(E_F)}$$

Old prejudice: Need to have large ω_D and large $N(E_F)$ and hope for good V

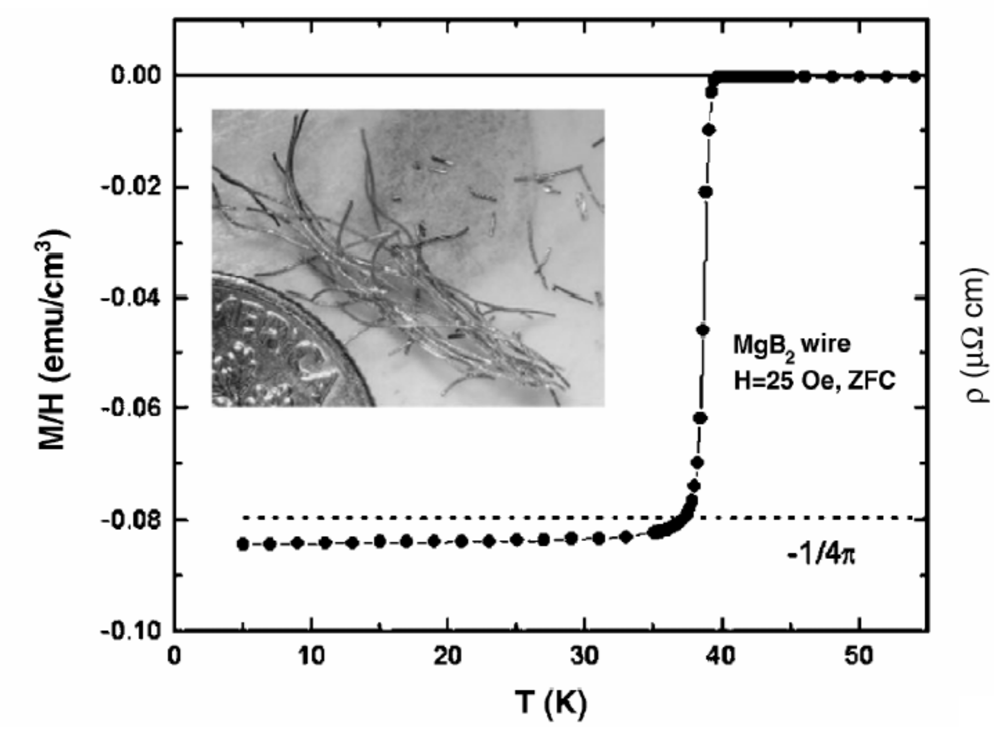
But MgB_2 has a very small $N(E_F)$ ($\gamma \sim 2.5$ mJ/mole-K^2)

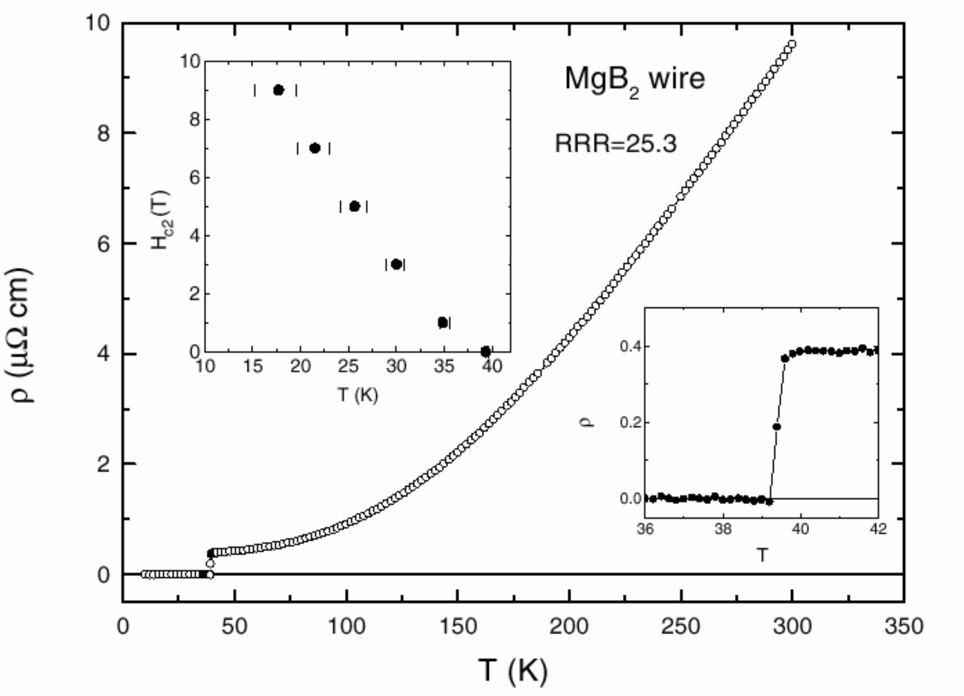
So, MgB_2 is a low $N(E_F)$ superconductor

For searches for MgB_2 like compounds we should look for large ω_D and large V and not obsess about $N(E_F)$ so much….

This is a much harder search algorithm.

Superconducting Properties



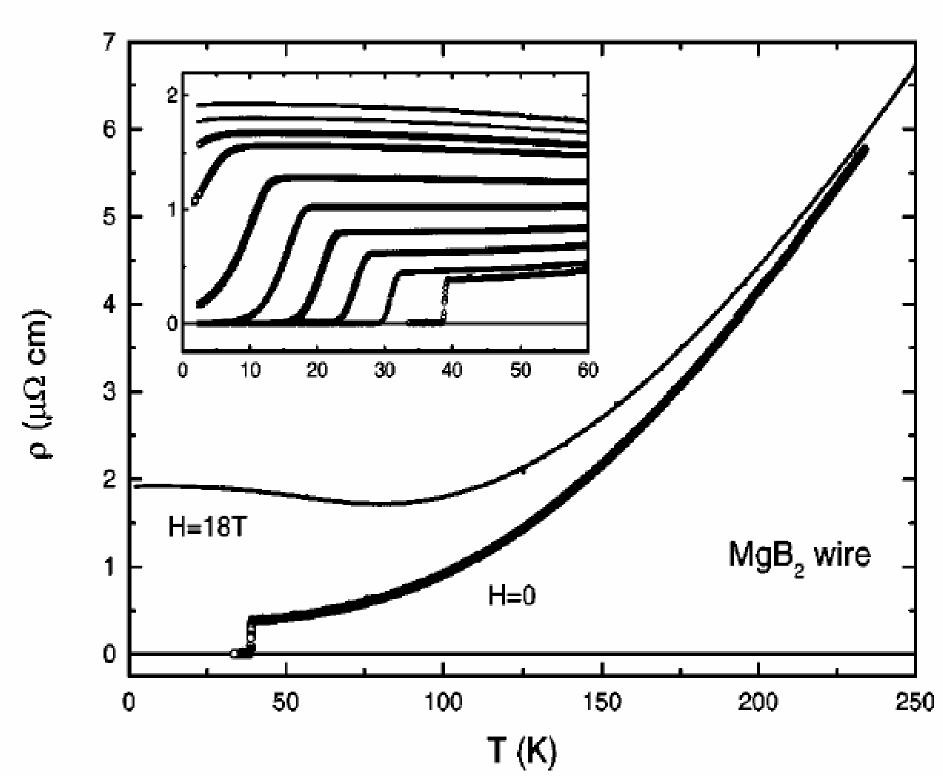


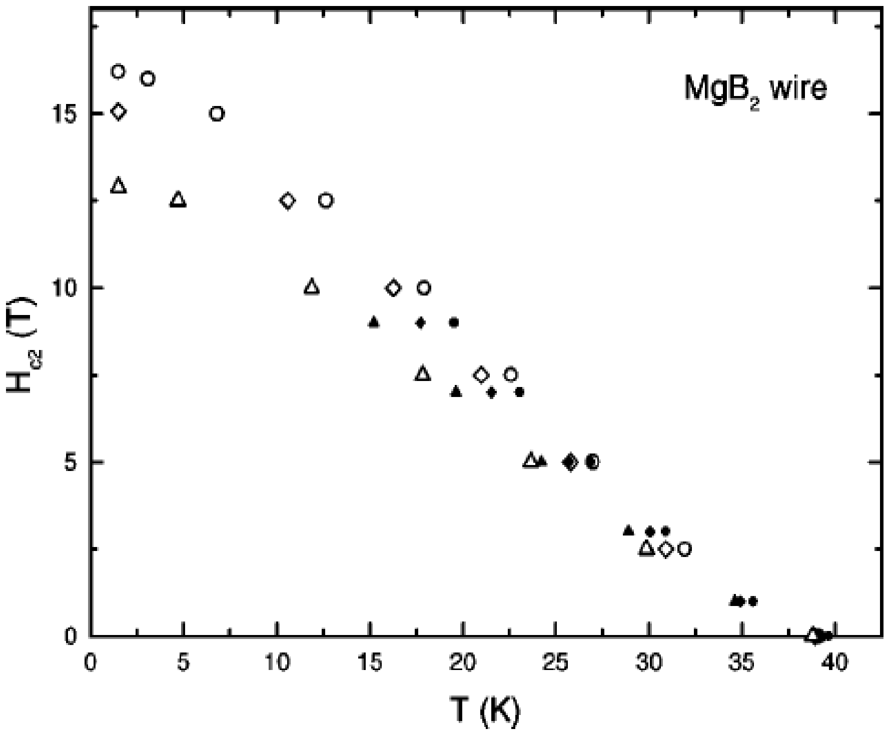
Canfield et al., PRL 86 (2001) 2423

- Over 90% dense => good grain to grain coupling.
- T_c above 39K
- Full diamagnetic screening.
- Low normal state resistivity.

H_{c2} of MgB_2

Using resistivity data we can determine H_{c2} of the polycrystalline sample.



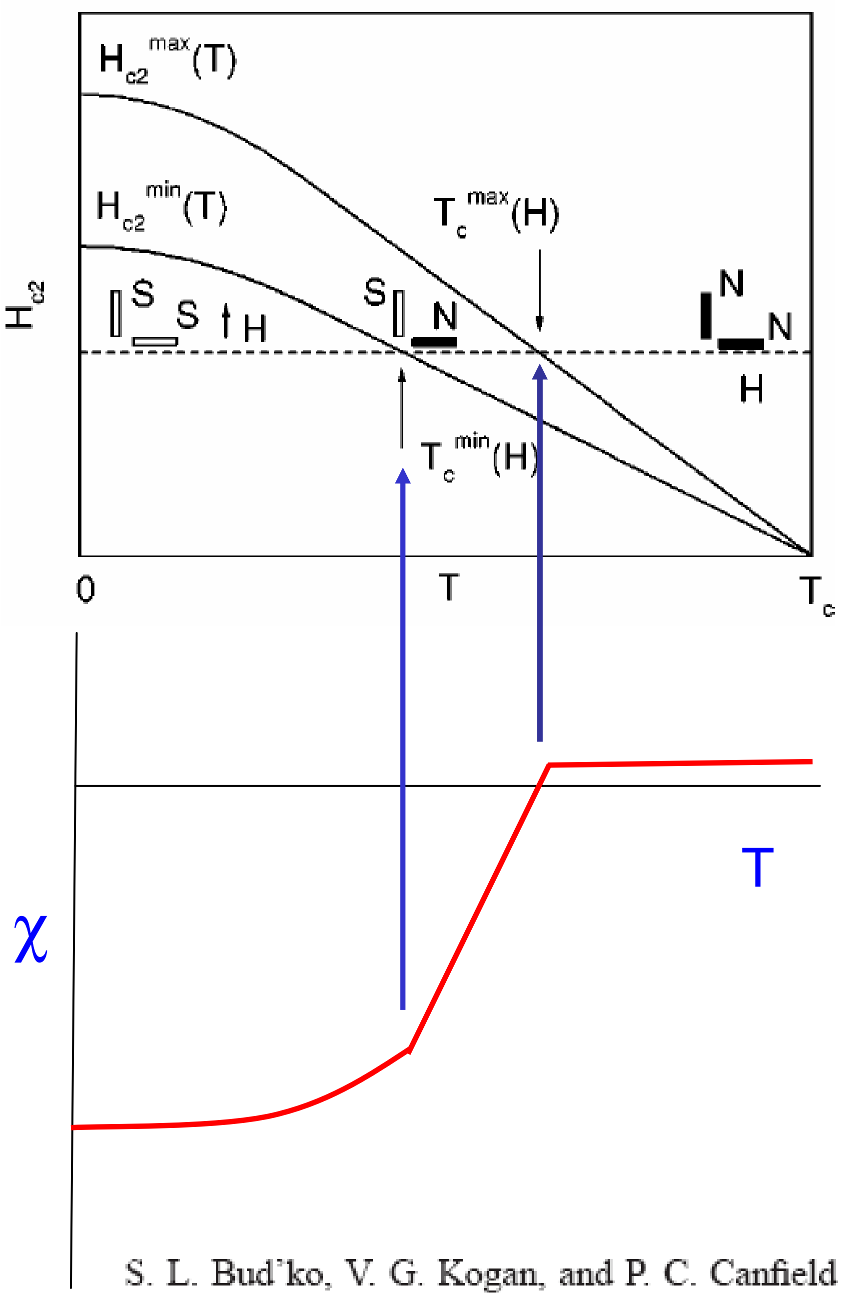


S.L. Bud'ko et al., Phys. Rev. B 63 (2001) 220503

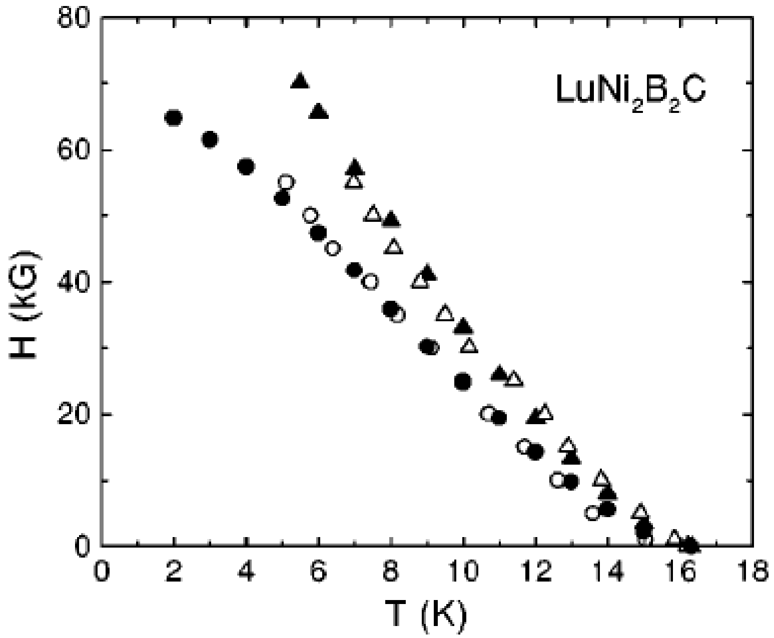
Two questions arise:

Are we missing hidden anisotropies?

Can we improve H_{c2} to be better than the ~30 T of Nb_3Sn?

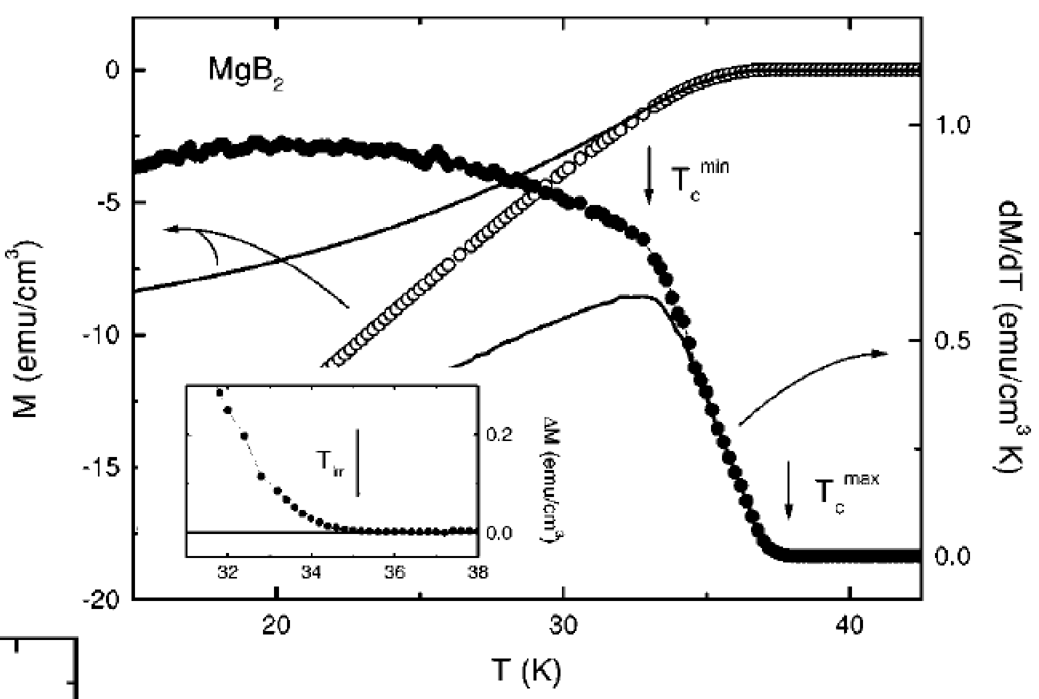


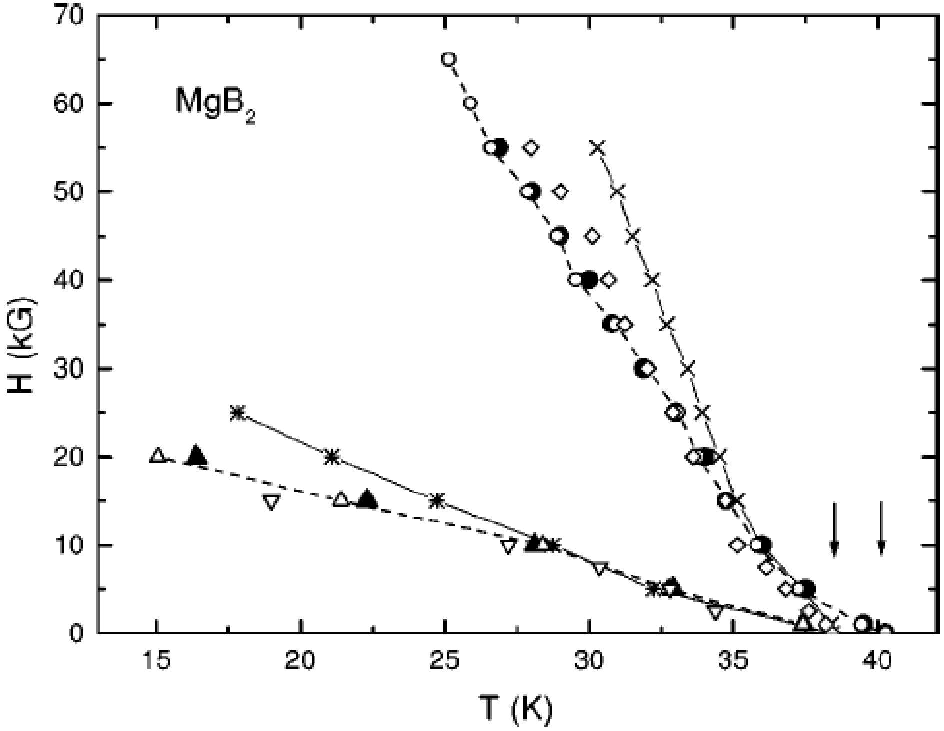
Given our experience with single crystals and anisotropy we were motivated to develop a new method for inferring H_{c2} anisotropy from polycrystalline data. We tested it on YNi_2B_2C and $LuNi_2B_2C$ since we could measure directly on these samples as well.



S. L. Bud'ko, V. G. Kogan, and P. C. Canfield PHYSICAL REVIEW B, VOLUME 64, 180506(R) 12 October 2001

We used this method to deduce that MgB_2 had an exceptionally large anisotropy in H_{c2}.

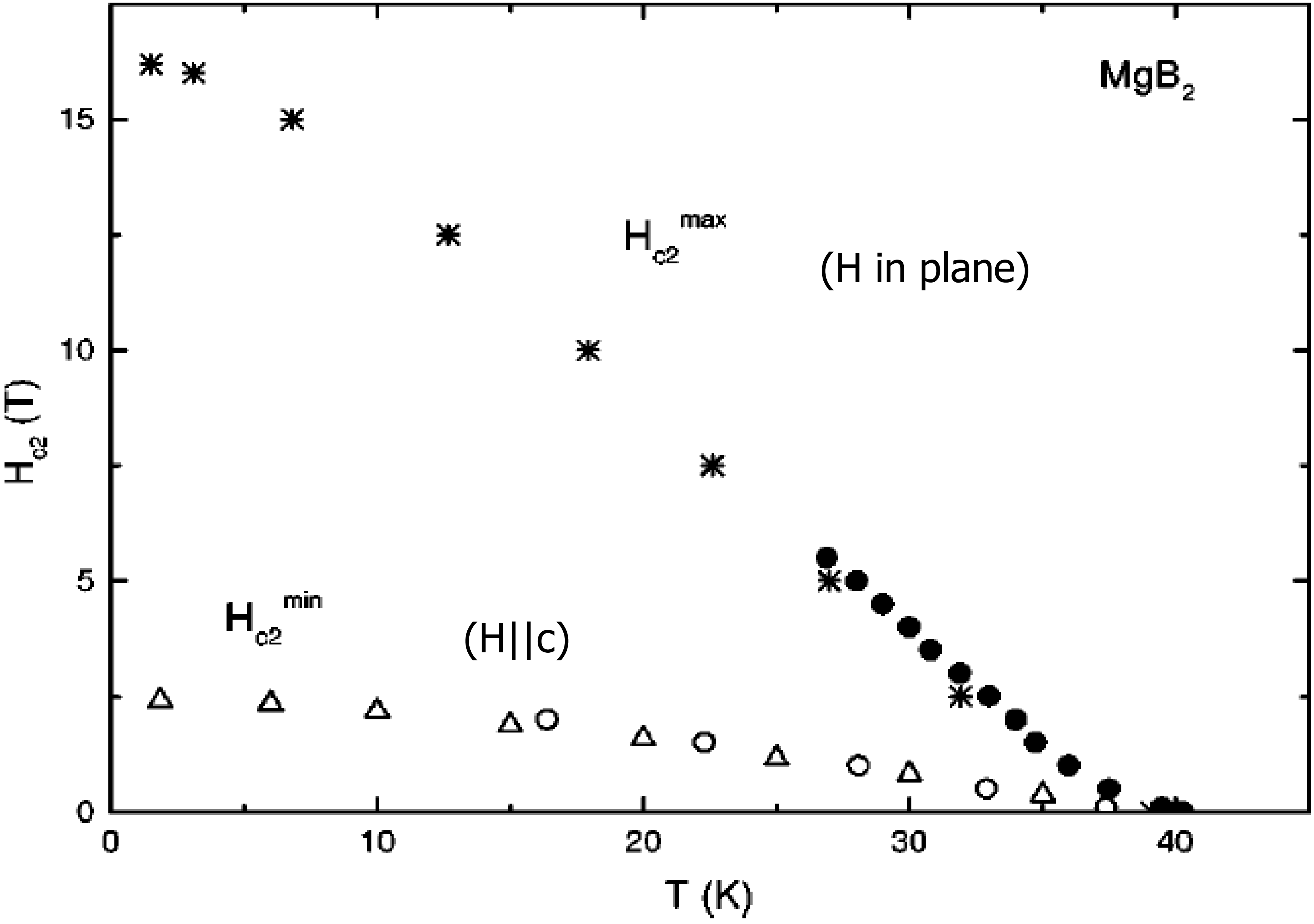




Anisotropic $H_{c2}(T)$ data inferred from polycrystalline measurements!

S. L. Bud'ko, V. G. Kogan, and P. C. Canfield PHYSICAL REVIEW B, VOLUME 64, 180506(R) 12 October 2001

The full H_{c2} anisotropy as well as direction could be determined by adding in resistivity data.



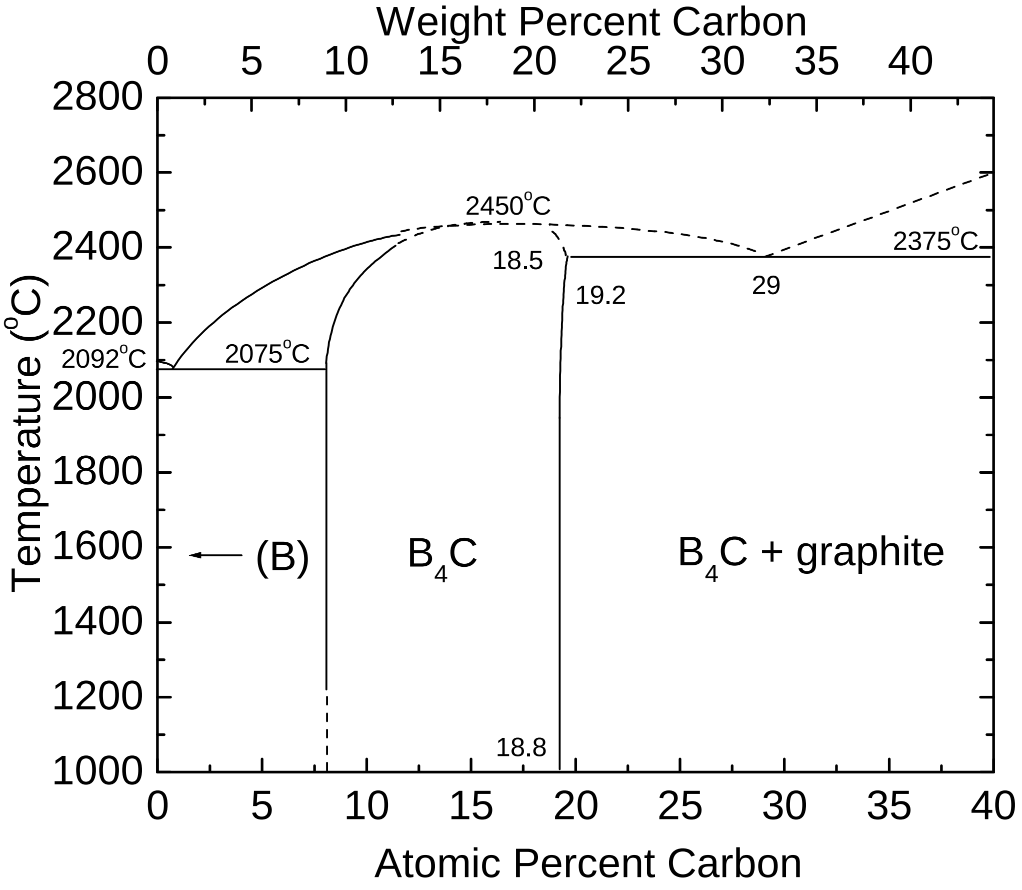
Sergey L. Bud'ko and Paul C. Canfield PHYSICAL REVIEW B 65 212501 May 2002

The other H_{c2} related question was, can we improve it? This can sometimes be done by adding non-magnetic impurities….Which one and how?

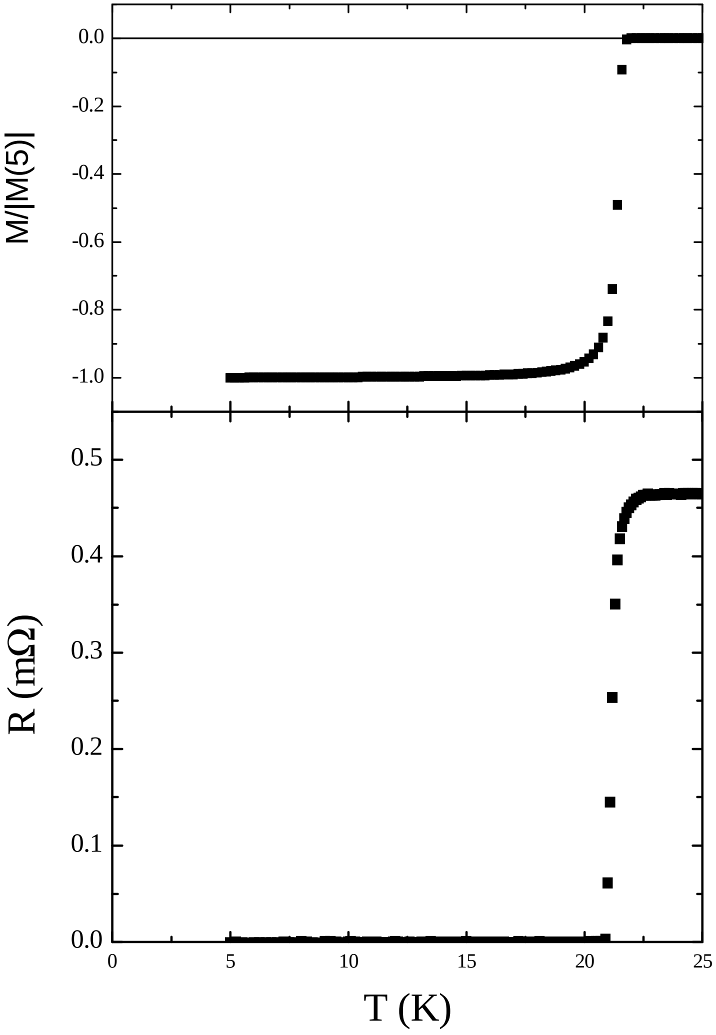
Recall we make MgB_2 by diffusing the Mg vapor into B. Any viable dopant will need to be compatible with this synthesis technique.

- B_4C only stable Binary
- Width of formation allows for ~ 8-19% C doping

B/C Phase Diagram



Ribeiro et al.: $5Mg + 2B_4C \rightarrow Mg(B_{1-x}C_x)_2$



Ribeiro et al. Physica C 384 (2003) 227.

- Sharp superconducting phase transition with $T_c \sim 22K$.
- X-ray spectra indicate presence of MgB_2C_2
- x in $Mg(B_{1-x}C_x)_2$ determined to be 0.10±0.02 by Rietveld Analysis of neutron diffraction pattern on $Mg(^{11}B_{1-x}C_x)_2$.

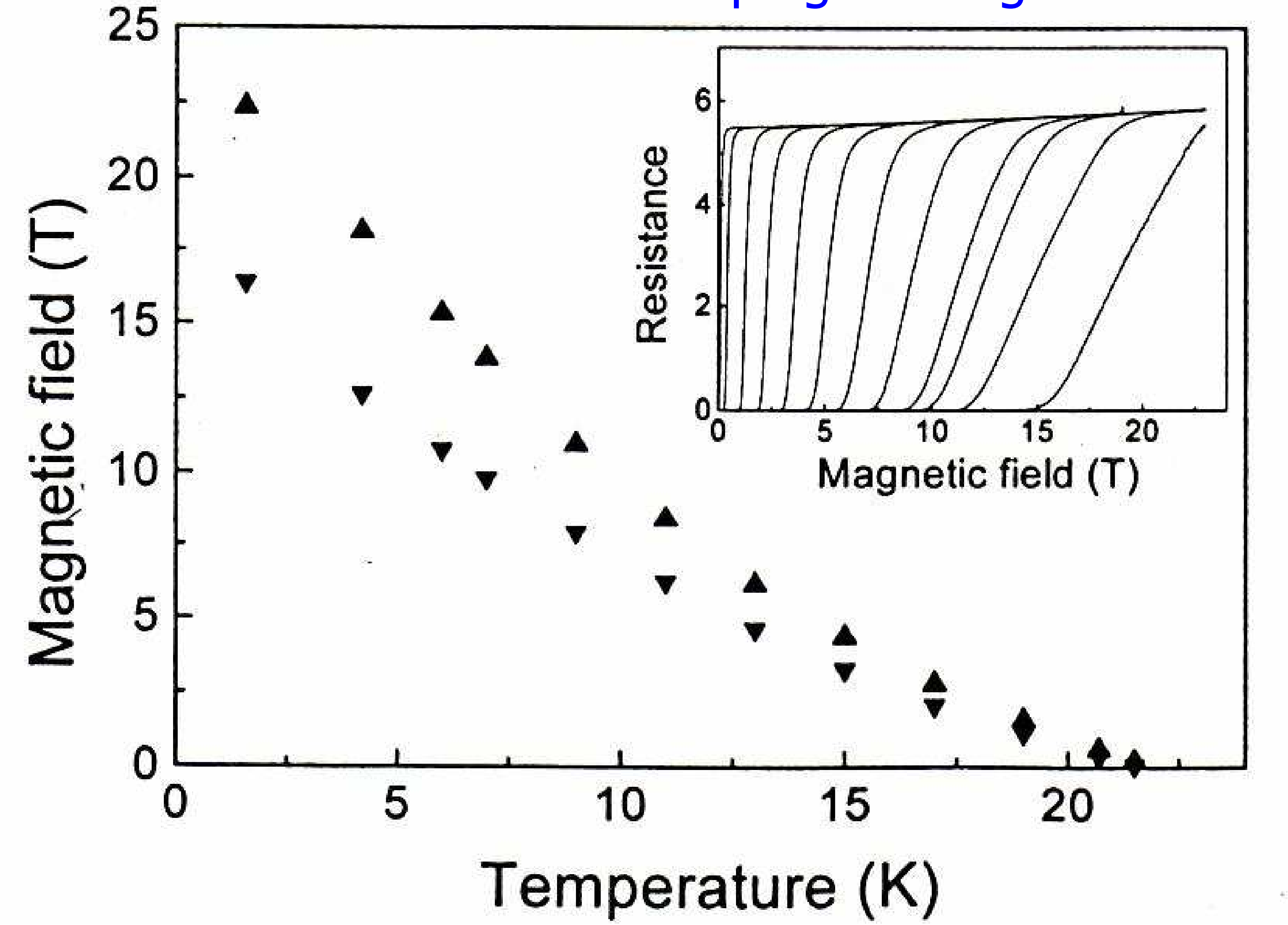
Phase	**Weight fraction**
$Mg(B_{1-x}C_x)_2$	73.4(1)
MgB_2C_2	20.4(1)
Mg	4.6(2)
MgO	1.6(1)

Avdeev et al. Physica C 387 (2003) 301

$Mg(B_{.9}C_{.1})_2$

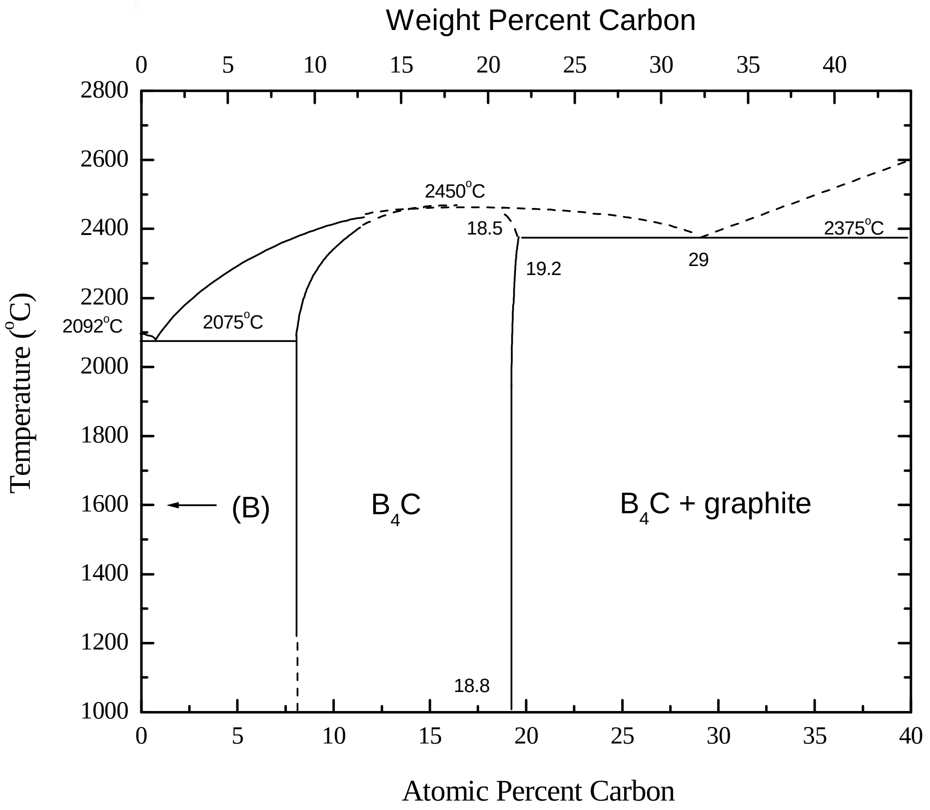
Even with T_c reduced to ~20 K H_{c2} is clearly enhanced!!

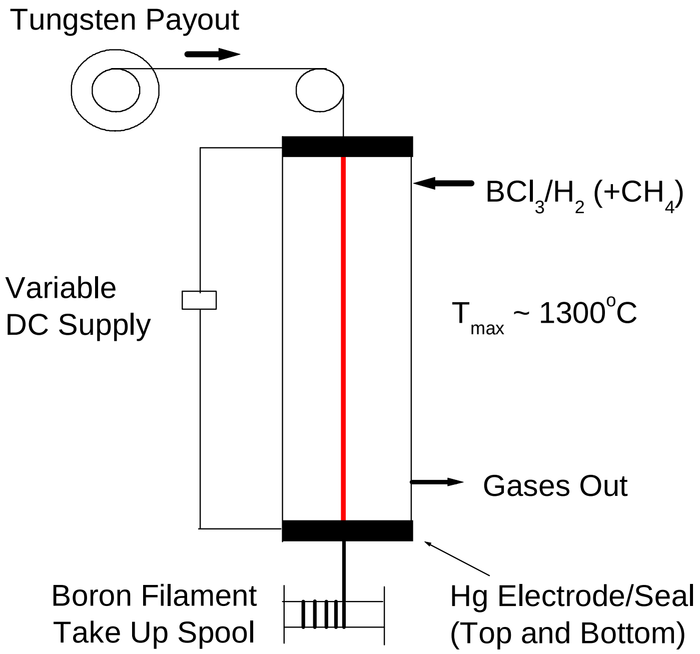
What would lower C-doping levels give?



Samuely et al., Phys. Rev. B 68 (2003) 020505

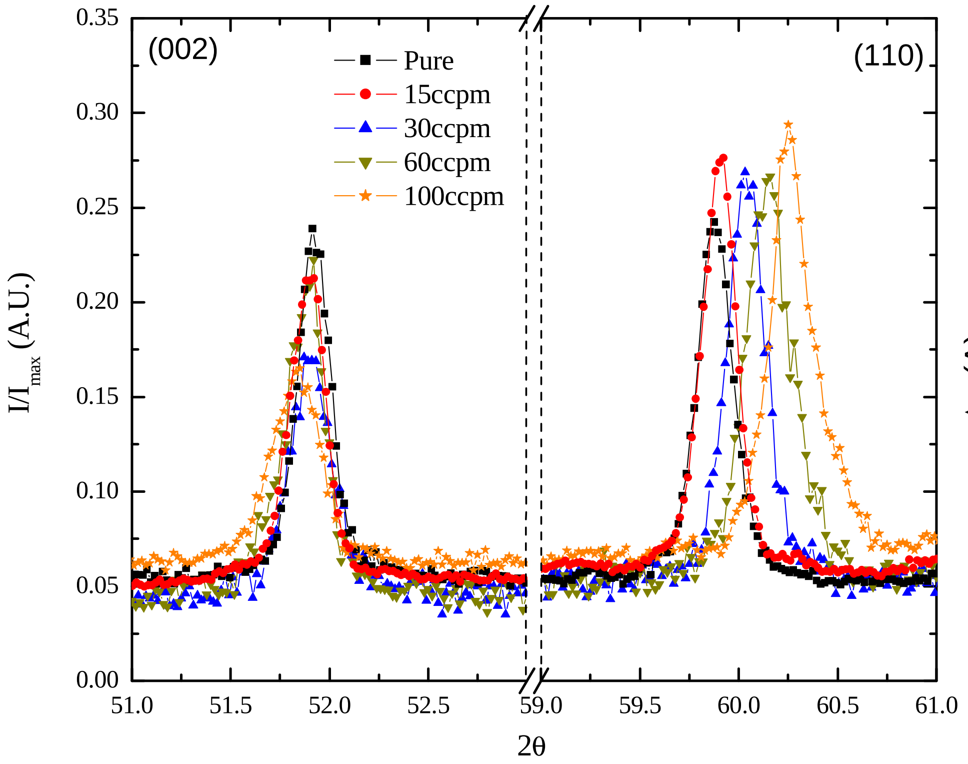
Systematic Carbon Doping

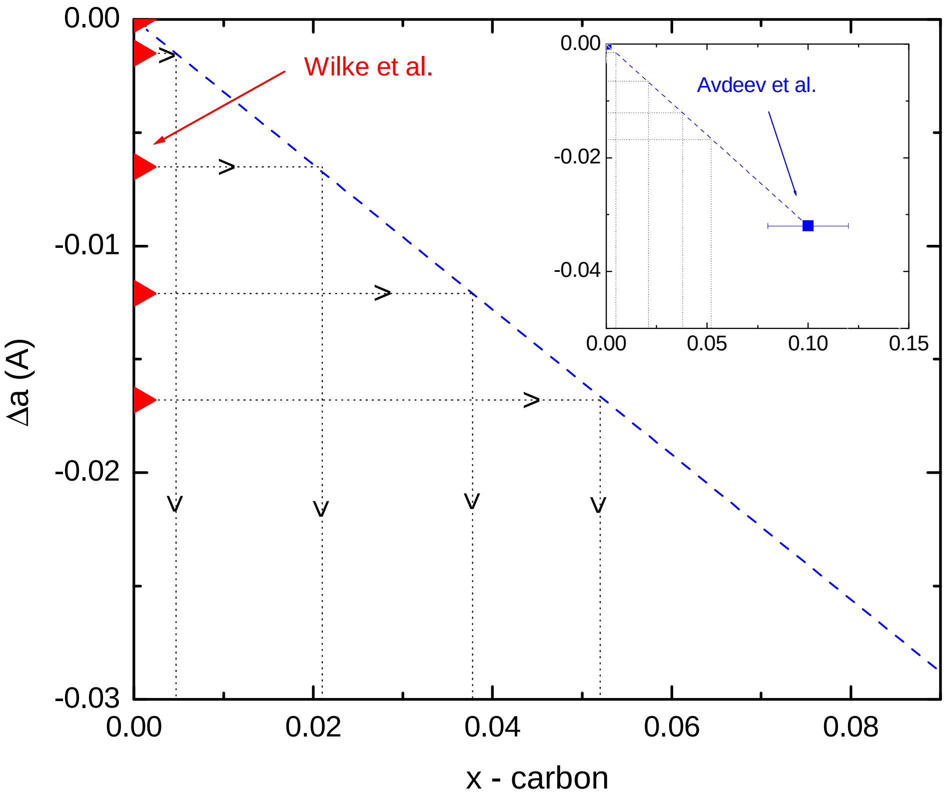




- If $Mg(B_{.9}C_{.1})_2$ has T_c ~ 22K and $H_{c2}(T=0)$ near 25T, $Mg(B_{1-x}C_x)_2$ may have maximum H_{c2} for $x<0.10$.
- Width of formation in B_4C limits C doping to above 8%.
- Carbon incorporation: add CH_4 to gas stream. Methane flow rates 15, 30, 60, and 100 ccpm (3000 ccpm BCl_3)

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



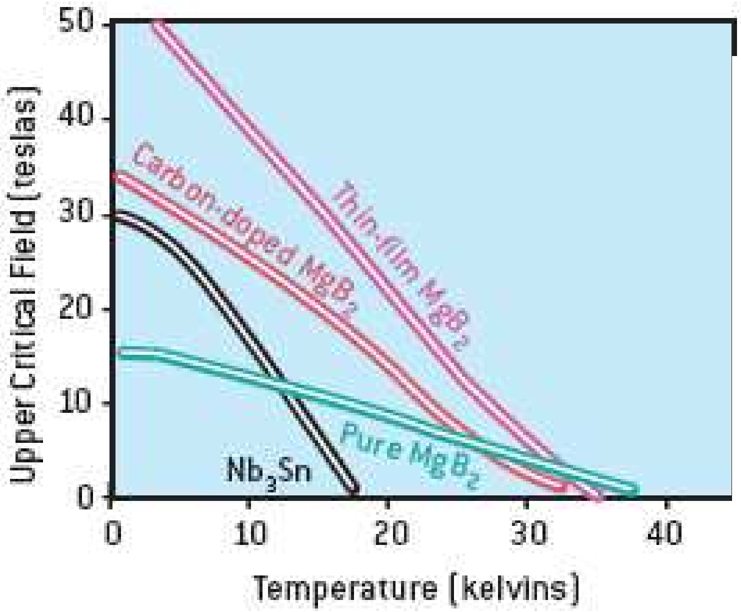


- Shift of (110) peak yields calculated carbon concentrations of x= 0.004, 0.021, 0.038, and 0.052.

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

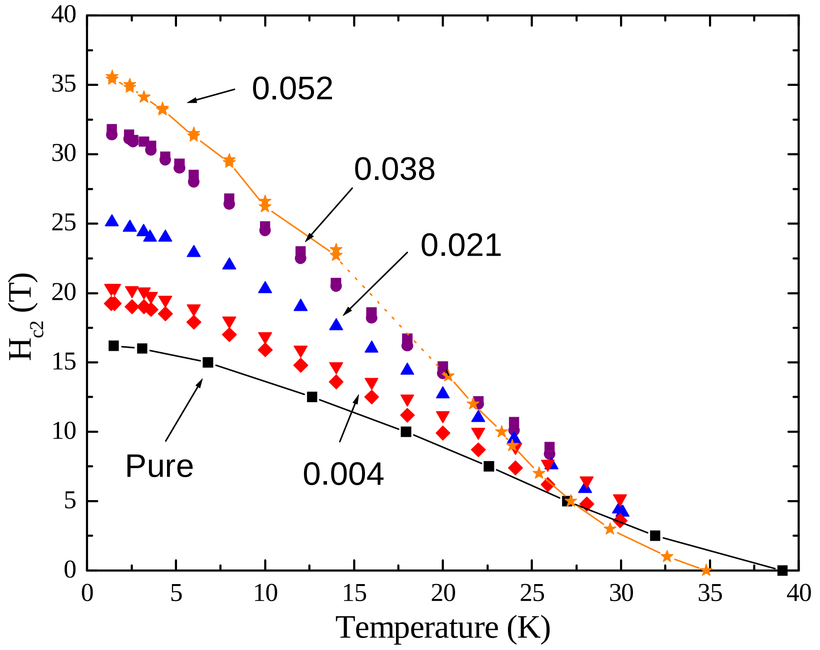
$Mg(B_{1-x}C_x)_2$ studies

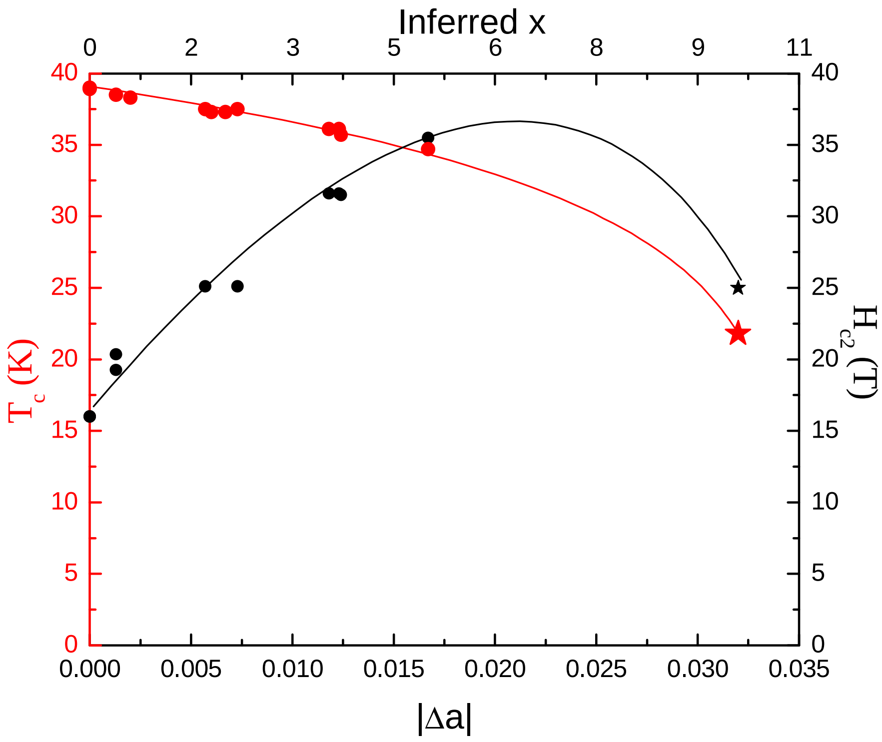
Tuning of T_C and H_{C2} with light carbon doping makes MgB_2 superior to Nb_3Sn (in H-T space).



PAUL C. CANFIELD AND SERGEY L. BUD'KO

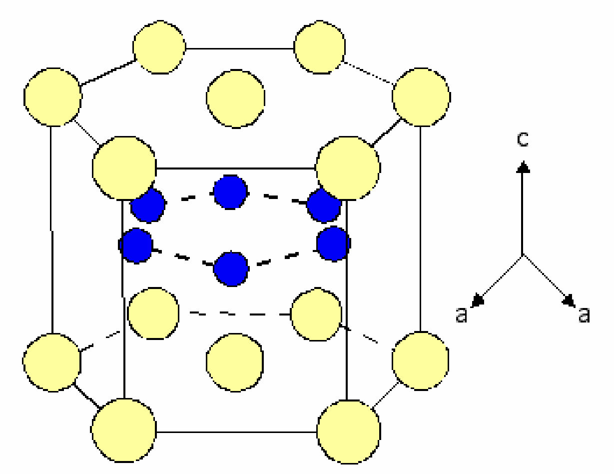
SCIENTIFIC AMERICAN APRIL 2005 81



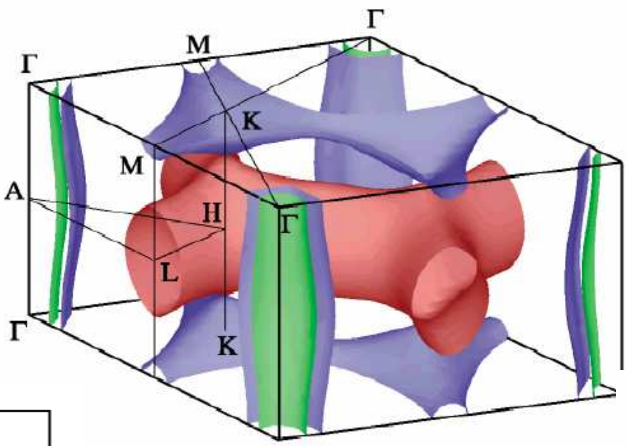


Phys. Rev. Lett. 92, 217003 (2004)

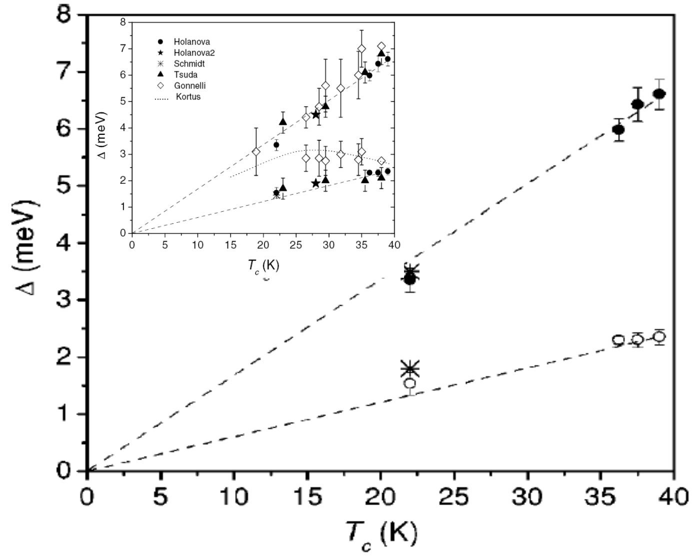
There is much, much more to MgB_2 than just $H_{c2}(T)$ and its tuning. There is the exceptionally clear two gap nature of the superconductivity as well as issues about J_c and making a practical, applied material.



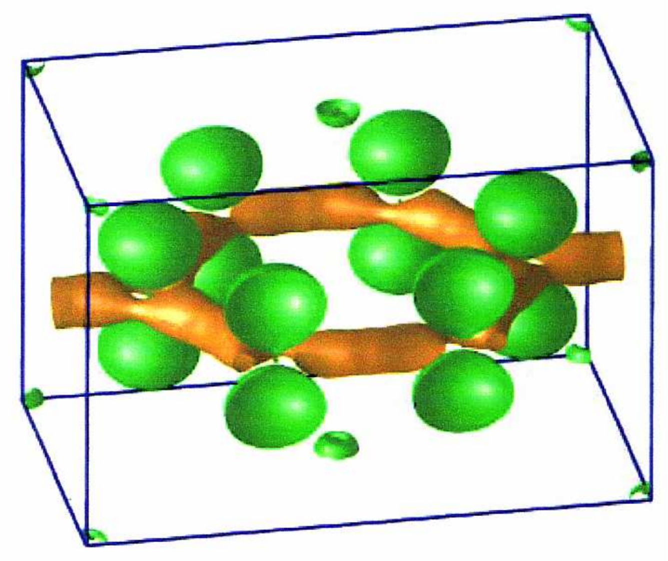
Origins of σ and π Bands



Korus et. al. Phys. Rev. Lett. 86 (2001) 4656

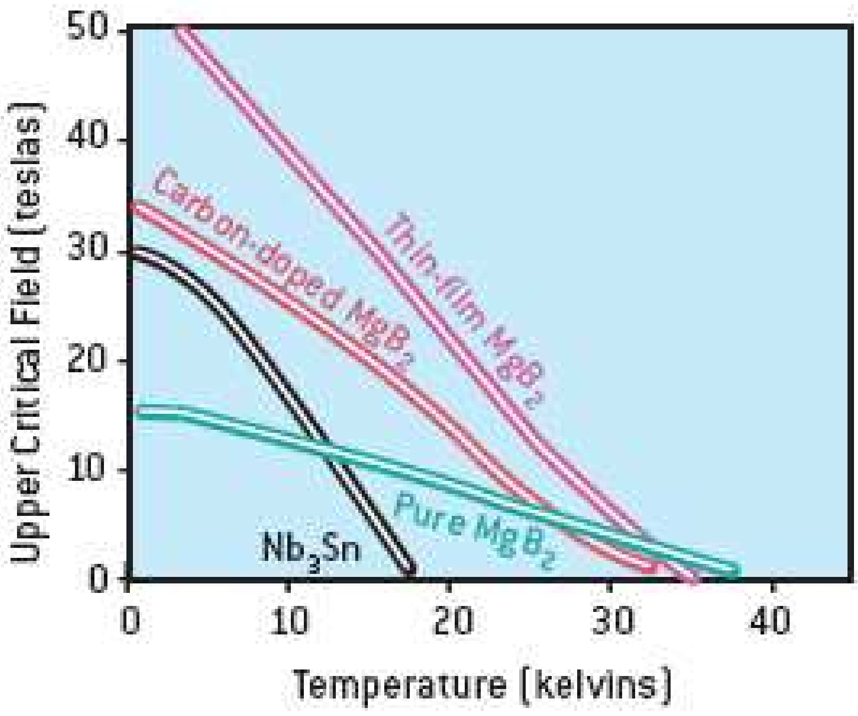


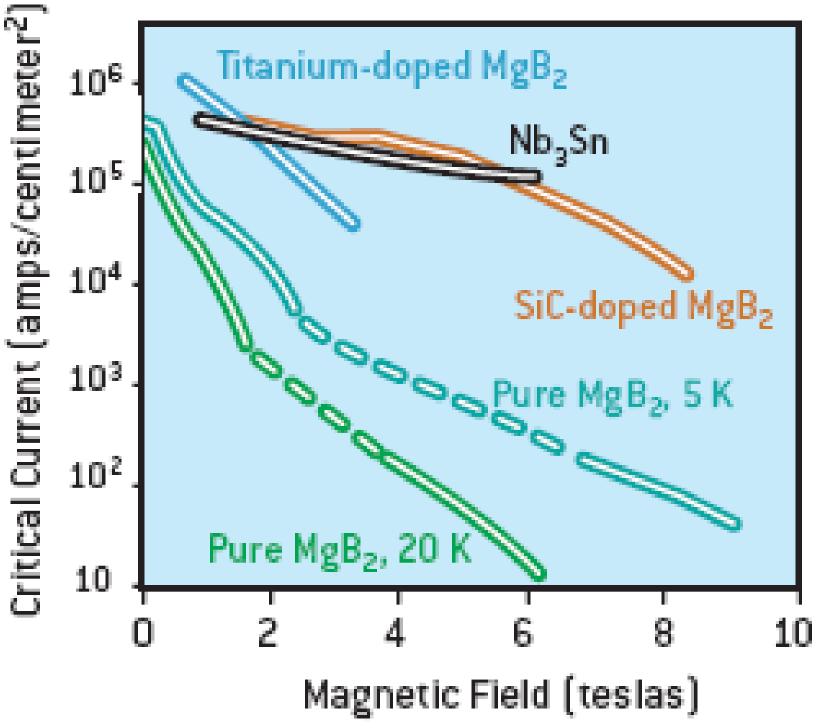
PRL **95**, 099701 (2005) P. Samuely,[1] P. Szabó,[1] P.C. Canfield,[2] and S.L. Bud'ko[2]



From O. Jepsen as appeared in Canfield et. al. Physics Today, March 2003, p.34

In addition, the current focus of applied research on MgB_2 is how to improve and preserve a good critical current, J_c, especially for high H_{c2} samples. This too goes beyond an introductory lecture and into advanced topics in superconductivity.





PAUL C. CANFIELD AND SERGEY L. BUD'KO SCIENTIFIC AMERICAN APRIL 2005 81

LOW-TEMPERATURE SUPERCONDUCTIVITY IS WARMING UP

Magnesium diboride defies the once conventional wisdom about what makes a good superconductor. It becomes superconducting near the relatively warm temperature of 40 kelvins—which promises a variety of applications

By **PAUL C. CANFIELD AND SERGEY L. BUD'KO**

NOTE:

This article is available on our web page in nine different languages.

To end this lecture, here is a final thought related to the search for new materials and ground states:

It is important to note that superconductivity in ***both*** RNi_2B_2C as well as MgB_2 was discovered by accident (as part of a search for other compounds), illustrating perhaps one of the most important aspects of new materials research: the importance of keeping our eyes open for new phases / ground states.

This is not a new idea:

To end this lecture, here is a final thought related to the search for new materials and ground states:

It is important to note that superconductivity in ***<u>both</u>*** RNi_2B_2C as well as MgB_2 was discovered by accident (as part of a search for other compounds), illustrating perhaps one of the most important aspects of new materials research: the importance of keeping our eyes open for new phases / ground states.

This is not a new idea:

Search and you shall find -- what is unsought goes undetected. Sophocles

That's All Folks