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Title: Kondo Physics and Unconventional Supercondutivity in the U Intermetallic U2PtC2 Revealed by NMR

Author(s): Mounce, Andrew M
Thompson, Joe David

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Kondo Physics and Unconventional Superconductivity in the U Intermetallic U_2PtC_2 Revealed by NMR

Andrew M. Mounce
and J. D. Thompson

Los Alamos
NATIONAL LABORATORY

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Strongly Correlated Electron Group

Mentors - Joe Thompson, Filip Ronning

Synthesis - Eric Bauer, Ni Ni

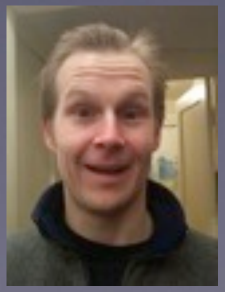
NMR - **Georgios Koutroulakis**, **Hiroshi Yasuoka**

Additional measurement - Nick Wakeham

NORTHWESTERN UNIVERSITY

Bill Halperin Group

Ultra low temperature - Johannes Pollanen



Outline

<u>NMR of Heavy Fermion Superconductors</u>

•Heavy fermion materials

•Superconductivity

•Nuclear Magnetic Resonance

<u>Experimental NMR Results</u>

•U_2PtC_2 - Intermediately heavy fermion

•Pu -115’s (Will there be time?!)

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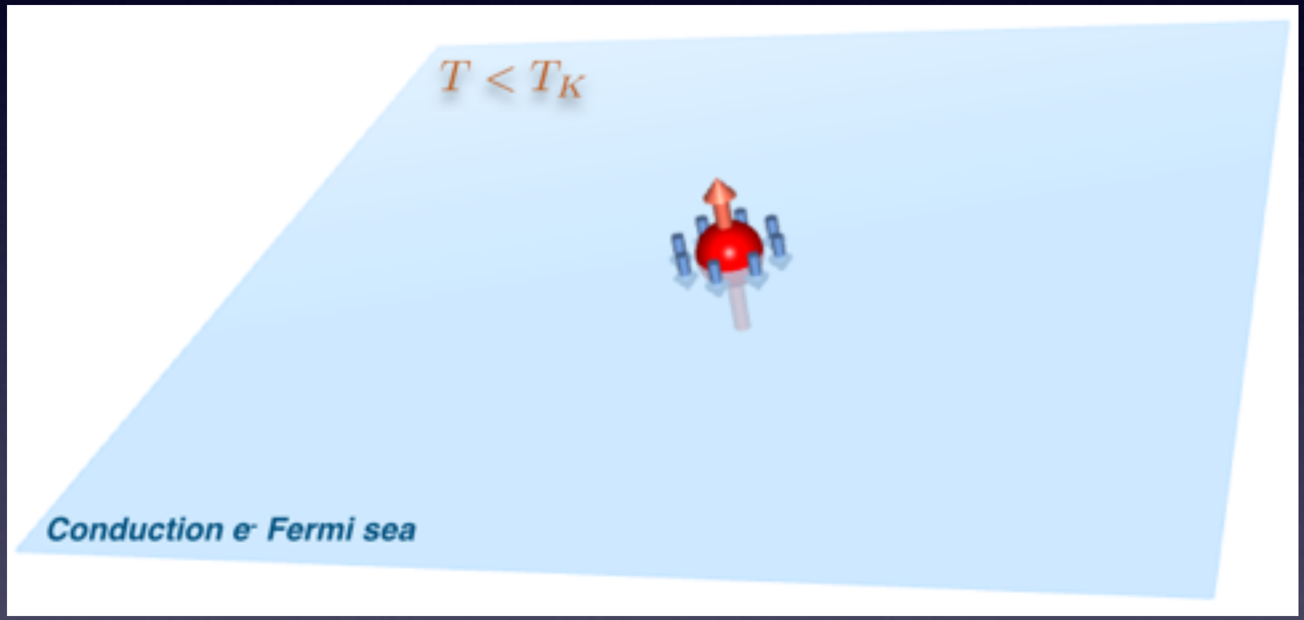
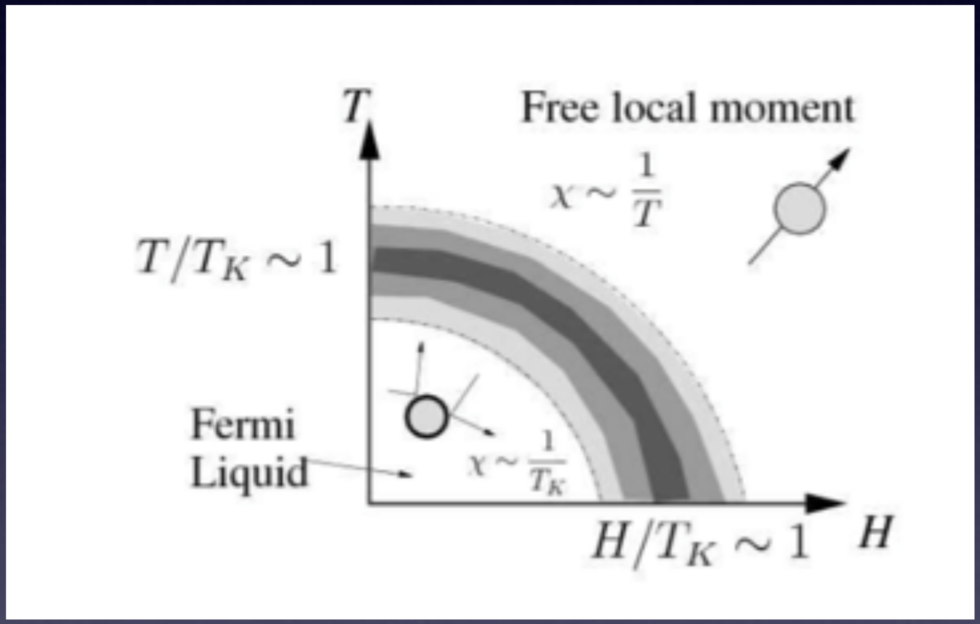
Kondo effect

- 1930s a resistance minimum was observed in metals with dilute magnetic impurities
- 1960s Anderson and Kondo formulated theories of local moments antiferromagnetically coupling with the conduction e^- below T_K



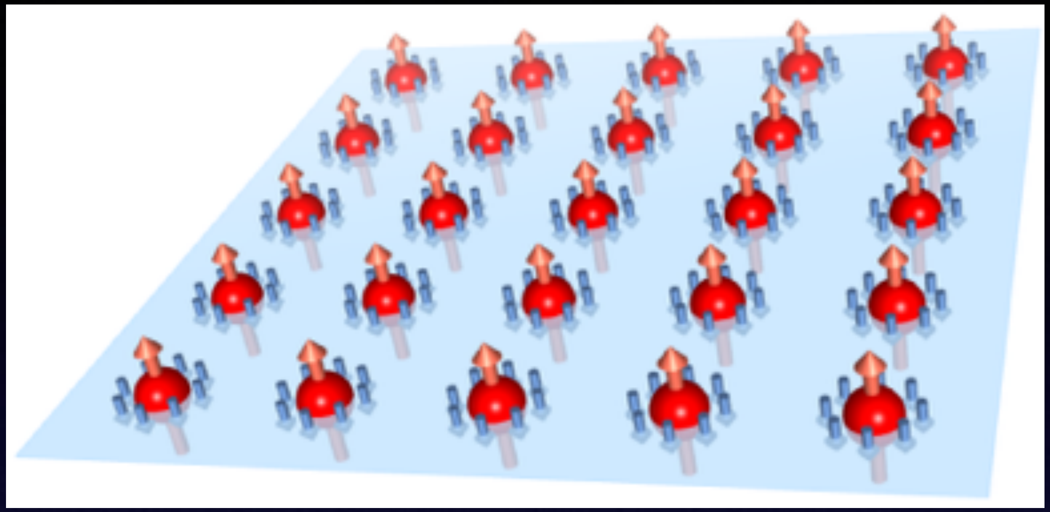
G. Koutroulakis, Plutonium Futures (2012)



P. Coleman, Handbook of magnetism and advanced magnetic materials (2007)

- A free magnetic ion, with a Curie susceptibility, becomes screened by conduction electrons and becomes a spin-less scattering center at low T and H

Kondo lattice



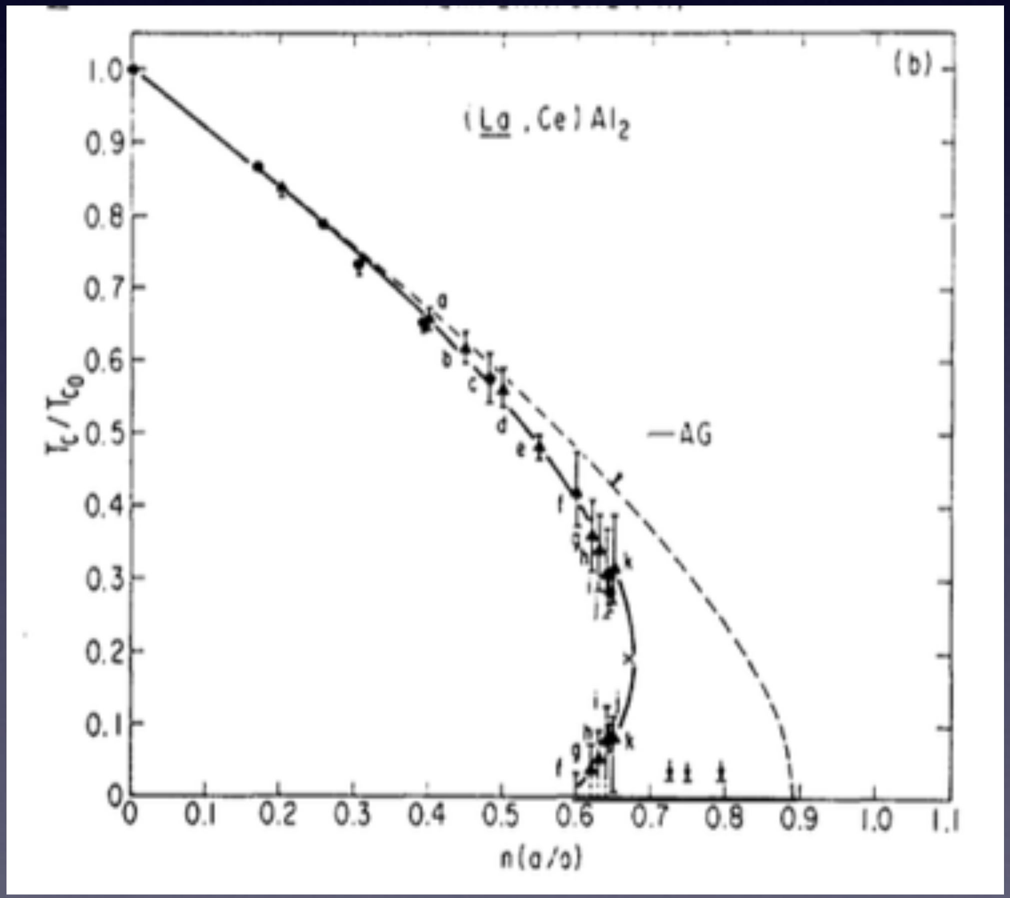
G. Koutroulakis, Plutonium Futures (2012)

- Lattice of 4*f* or 5*f* electrons
- Effective electron mass up to $1000m_e$
- Two distinct temperature ranges:
  1. High temperature - local moment, Curie suscept.
  2. Low temperature *T** - itinerant, Pauli suscept.

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	No	Lw

Local moments and superconductivity

- Traditionally, magnetism and superconductivity thought to be mutually exclusive
- Ce (Kondo) Impurities in $LaAl_2$ (conventional superconductor) rapidly suppress superconductivity   Maple et al. SSC (1972)



- Many materials issues with supposed superconducting Kondo metal $CeCu_2Si_2$ - some samples non-SC, even magnetic

HF SC coming around

- 1975 local moment metal UBe_{13} was shown to be SC but dismissed as filamentary Butcher et al. PRB (1985)
- 1976 $CeCu_2Si_2$ also SC. 1*f* per unit cell. Also disbelieved! Coined the term heavy fermion superconductor Steiglich et al. PRL (1986)

VOLUME 43, NUMBER 25 PHYSICAL REVIEW LETTERS 17 DECEMBER 1979

Superconductivity in the Presence of Strong Pauli Paramagnetism: $CeCu_2Si_2$

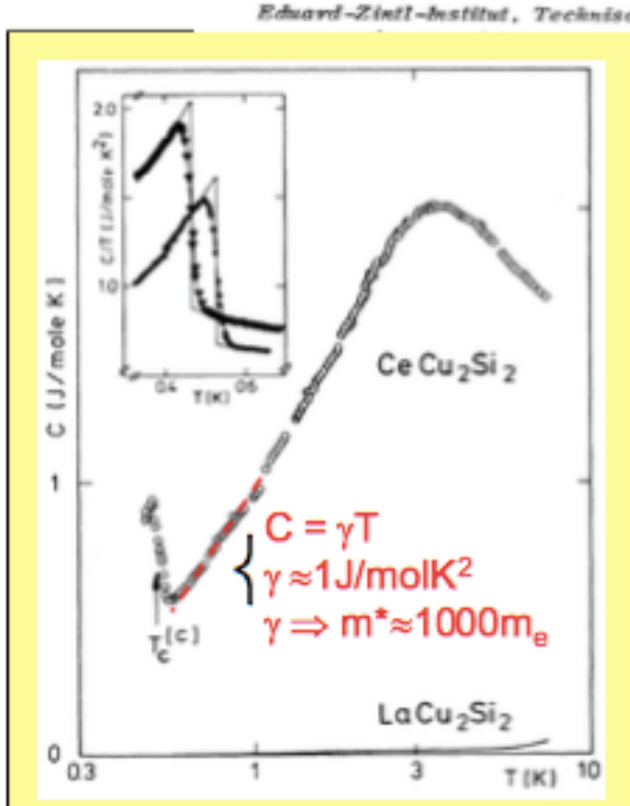
F. Steglich
Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany

and

J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, and W. Franz
II. Physikalisches Institut, Universität zu Köln, D-5000 Köln 41, West Germany

and

H. Schäfer
Eduard-Zintl-Institut, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany



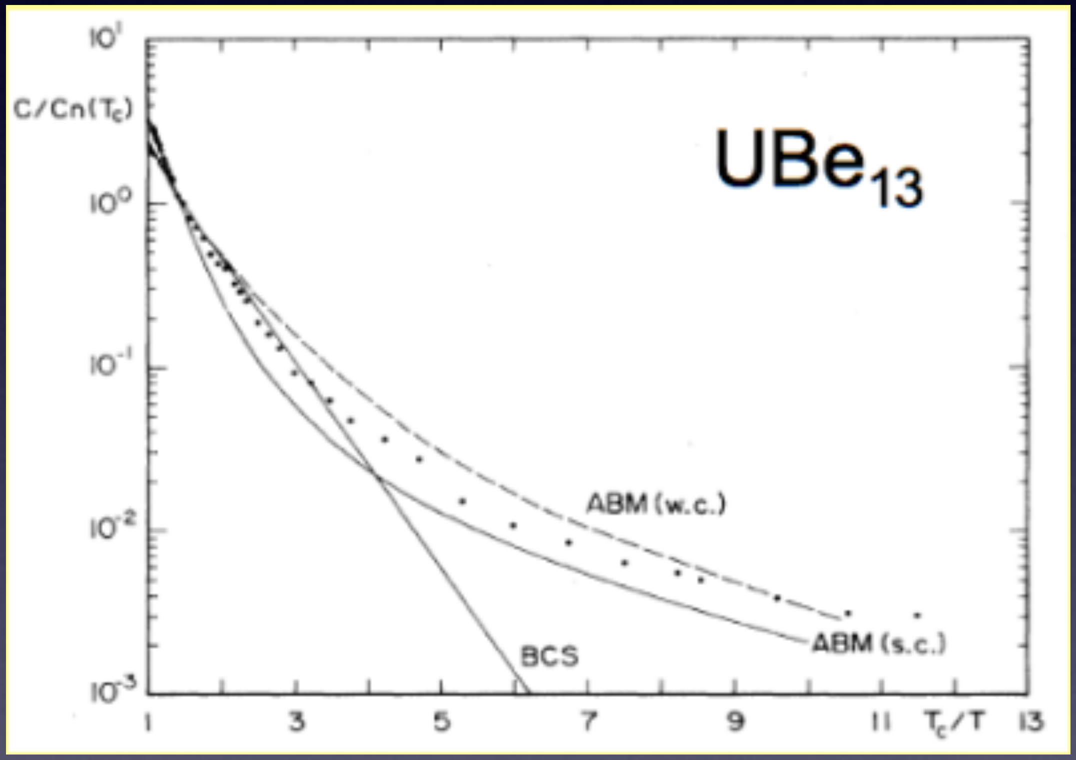
Well below $T^* = 10$ K, a large γT term predominates the specific heat. We interpret this term as being due to very heavy fermion quasiparticles with degeneracy temperature $T_F \simeq T^*$.

The size of the specific-heat jump at T_c, in proportion to γT_c, suggests that Cooper-pair states are formed by these heavy fermions.

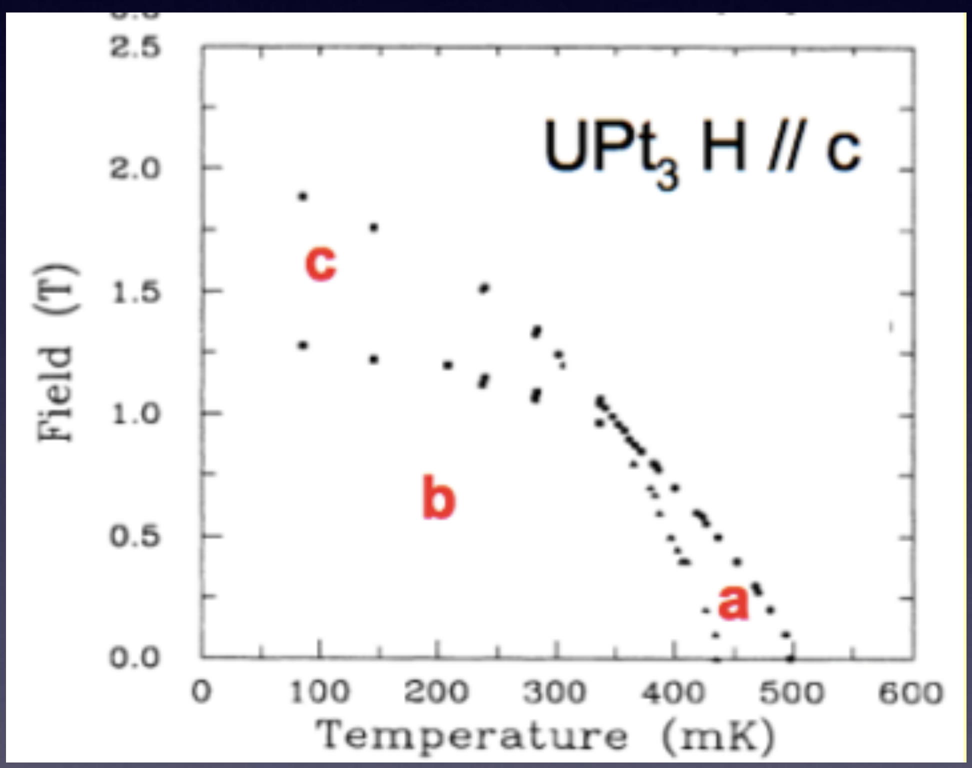
Since the Debye temperature, Θ, is of the order of 200 K,[5] we find $T_c < T_F < \Theta$ with $T_c/T_F \simeq T_F/\Theta \simeq 0.05$. This suggests that $CeCu_2Si$ (i) behaves as a "high-temperature superconductor" and (ii) cannot be described by conventional theory of superconductivity which assumes a typical phonon frequency $k_B\Theta/h \ll k_BT_F/h$, the characteristic frequency of the fermions.

Further evidence and unconventional SC

- 1983 UB_{13} revisited and C_p showed large discontinuity i.e. bulk superconductivity   Ott et al PRL (1983)
- 1988 dHva (measures cyclotron frequency of electrons) $CeCu_6$ and UPt_3 were found to have heavy electron mass   Taillefer et al PRL (1988)



Ott et al. PRL (1984)



Fischer et al. PRL (1989)

- Specific heat, thermal conductivity, and NMR show power laws
- H_{c2} in UPt3 shows multiple phases

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<u>NMR of Heavy Fermion Superconductors</u>

- Heavy fermion materials
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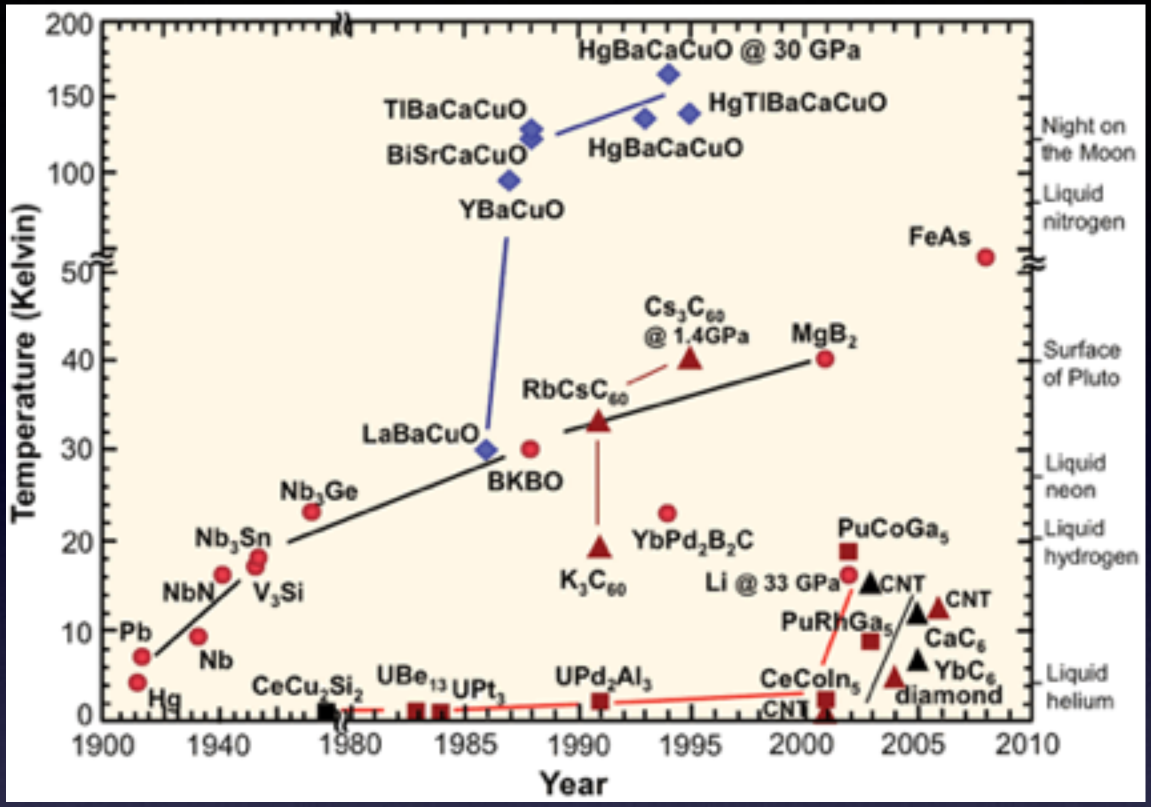
- Nuclear Magnetic Resonance

<u>Experimental NMR Results</u>

- U_2PtC_2
- Pu -115's

Superconductivity - zero resistivity/perf. diamag.

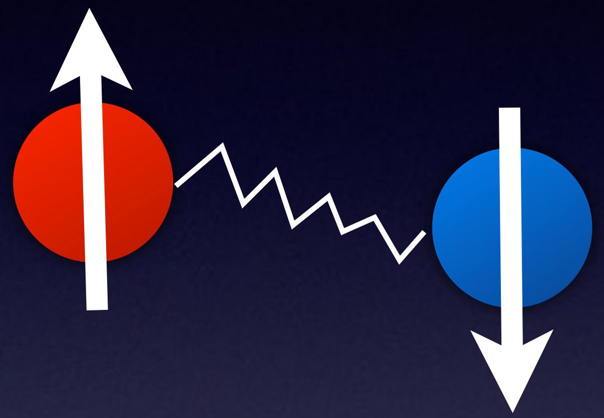


- Discovered in 1911- Onnes
- Explained in 1957 - conventional BCS theory
- New mysteries - 1976 heavy fermion and 1986 high T_c
- No microscopic theory to describe newer

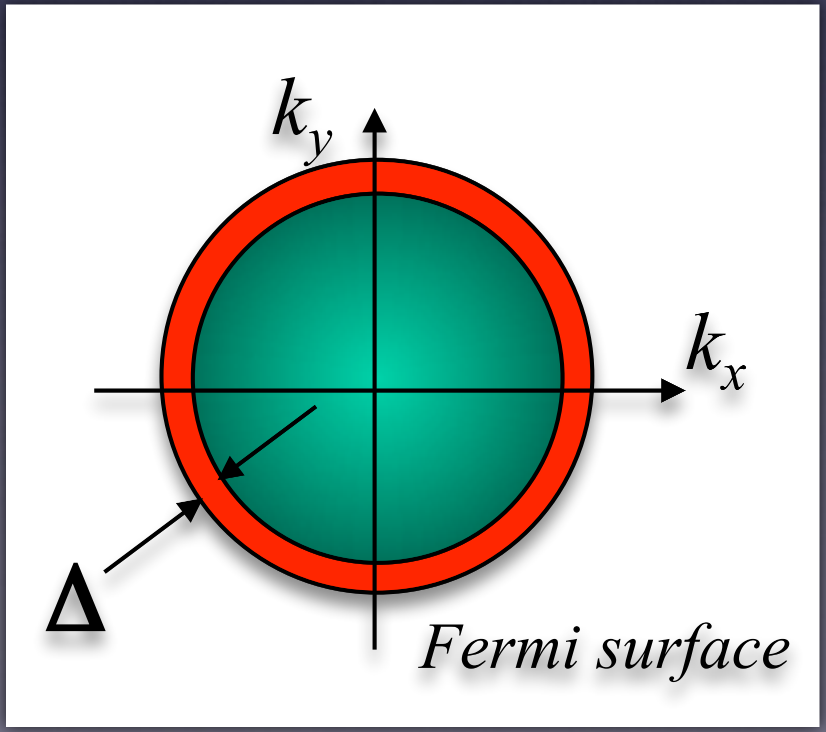
"unconventional" superconductors

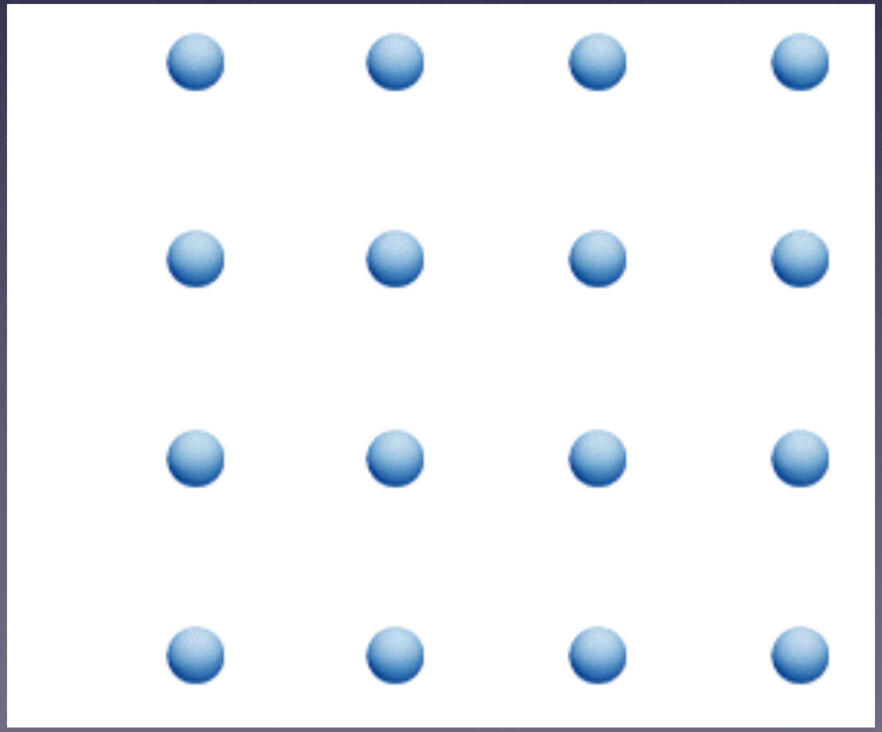
Conventional superconductivity

- Electrons (fermions) form a Bose Einstein condensate
- To achieve integer spin electrons must pair
- Described by BCS theory
  - $\Psi = L \times S$ must be even (boson)
  - $L = 0$ (s-wave energy gap)
  - $S = 0$ (singlet) $1/\sqrt{2}\,|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$



- Electrons are attractive due to coupling to phonons
- Elemental S.C.s MgB_2 etc.

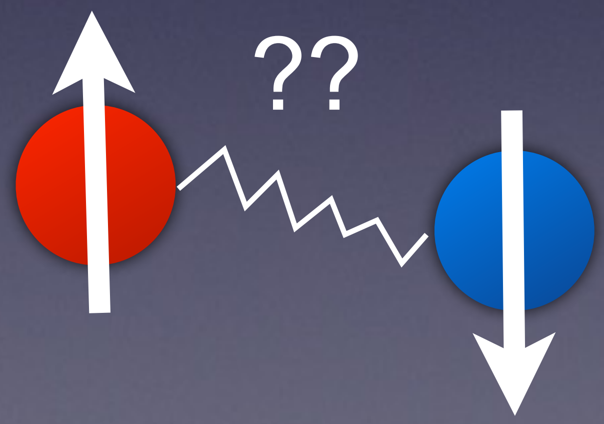


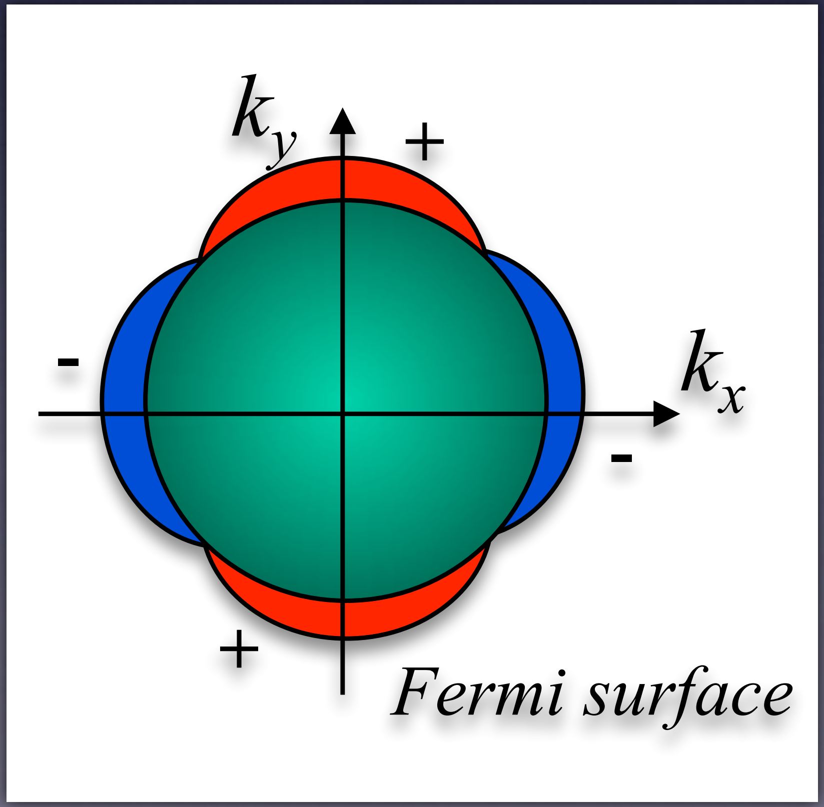


wikimedia.org

Unconventional superconductivity

- Heavy fermion (1978), cuprate (1986), iron pnictide (2006)
- Non-phonon mediated superconductivity
- High T_c (up to ~150 K)
- More complicated spin/orbital wavefunction



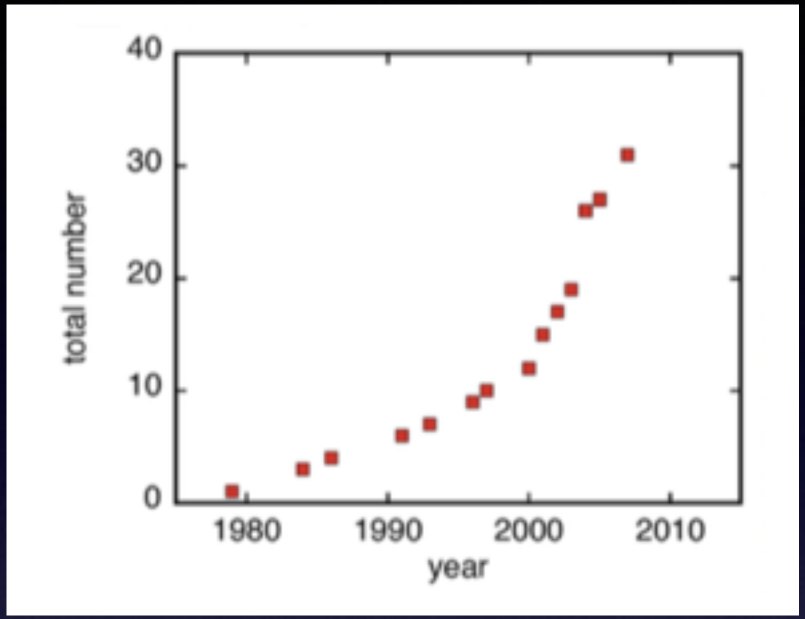


Classification of superconductivity

Total wave function $\Psi = L \times S$ must be a boson (even)

Orbital (L)	Spin (S)	Classification
s ($L = 0$)	$1/\sqrt{2}\ \|\uparrow\downarrow\rangle - \|\downarrow\uparrow\rangle$	Singlet
Elemental S.C., Iron Pnictides		
d ($L = 2$)	$1/\sqrt{2}\ \|\uparrow\downarrow\rangle - \|\downarrow\uparrow\rangle$	Singlet
Cuprates, Ce & Pu -115		
p ($L = 1$)	$\|\uparrow\uparrow\rangle$, $\|\downarrow\downarrow\rangle$, $1/\sqrt{2}\ \|\uparrow\downarrow\rangle + \|\downarrow\uparrow\rangle$	Triplet
Sr_2RuO_3, ^3He, UCoGe		
f ($L = 3$)	$\|\uparrow\uparrow\rangle$, $\|\downarrow\downarrow\rangle$, $1/\sqrt{2}\ \|\uparrow\downarrow\rangle + \|\downarrow\uparrow\rangle$	Triplet
UPt_3		

Heavy Fermion Superconductors



Pfleiderer, RMP (2009)

- Number and quality rapidly increasing

- U and Ce at the beginning
- 2002 - Pu
- Np, Pr

Low T_c

- Ce T_{cmax} ~ 2.3 K in $CeCoIn_5$
- Pu T_{cmax} ~ 18.5 K in $PuCoGa_5$ (quite incredible)

Variety of SC-preempting and coexisting phases

- Antiferromagnetism - UNi_2Al_3, UPd_2Al_3, UPt_3, URu_2Si_2
- Ferromagnetism - UGe_2, UCoGe, URhGe, UIr

SC can even precede magnetism

- SC -> Antiferromagnetism - $CeCoIn_5$, $CeRhIn_5$ (pressure)

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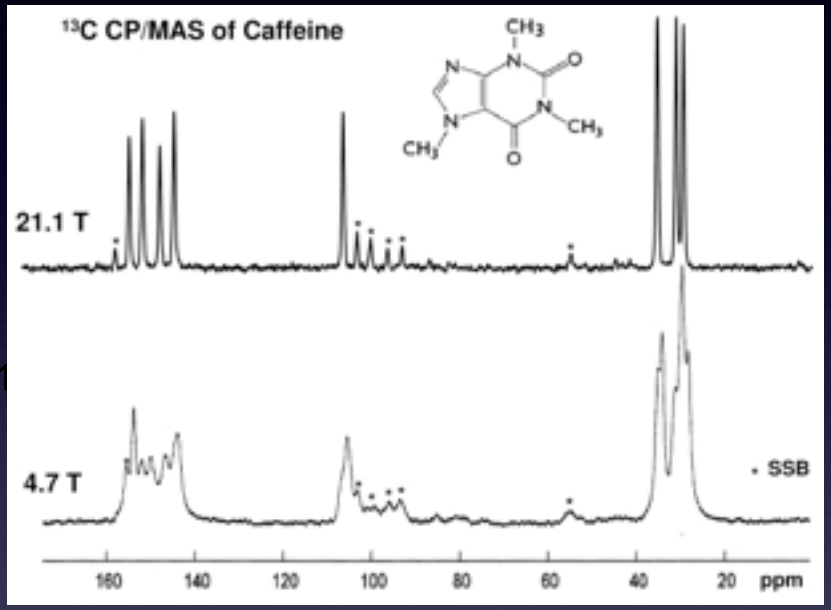
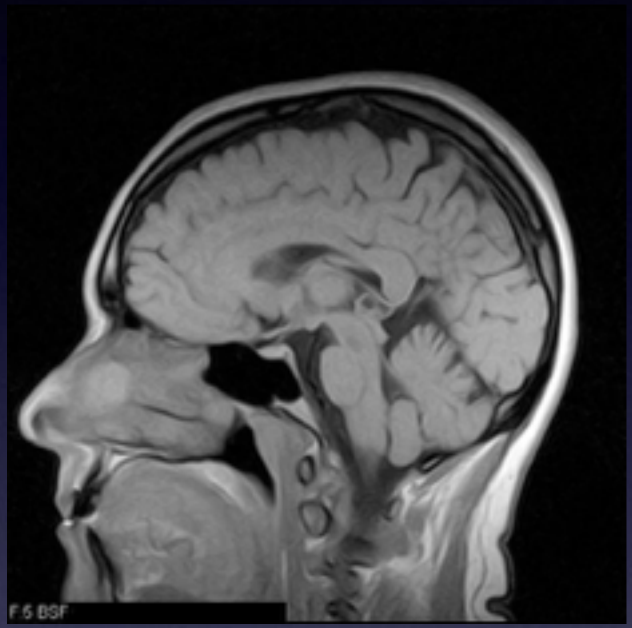
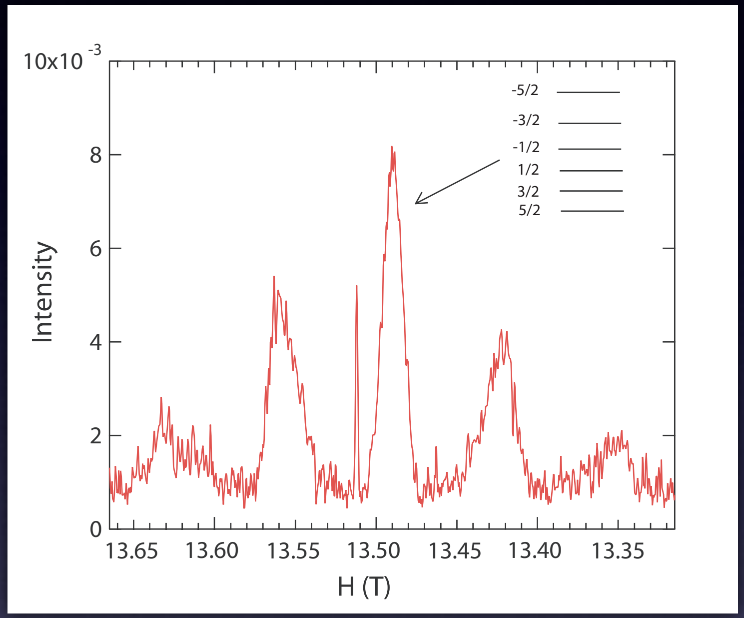
NMR uses

- Originally discovered by physicists 1946
- 6 Nobel prizes



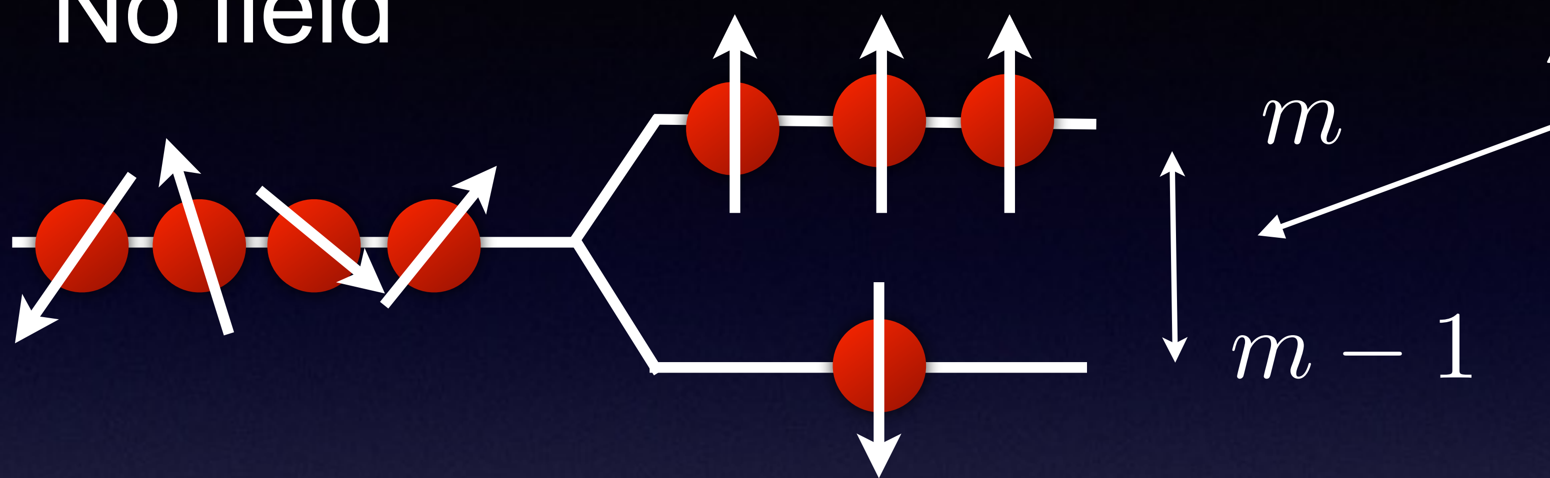




- Internal magnetic fields - spectrum/shift
- Magnetic fluctuations - T_1
  - -Hyperfine interaction
  - -Magnetism
  - -Superconductivity

Nuclear resonance conditions

No field — Field



$$\Delta E = \hbar\omega = \hbar\gamma H_0$$

Spin state degeneracy lifted

Magnetic field

$$I \neq 0$$

$$\mathcal{H}_Z = \hbar\gamma\vec{I}\cdot\vec{H}_0$$

$2I+1$ Equally spaced levels

Electric field gradient

$$I > 1/2$$

$$\mathcal{H}_Q = \frac{\hbar\nu_Q}{6}\left[3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2}\left(\hat{I}_+^2 + \hat{I}_-^2\right)\right]$$

Lifts degeneracy of spin transitions

Tool box: shift/spectrum

$$\mathcal{H}_Z = \hbar\gamma \vec{I} \cdot \vec{H}_0$$

$$\mathcal{H}_Z = \hbar\gamma \left(\hat{\mathbf{1}} + \hat{\mathbf{K}}\right) \vec{I} \cdot \vec{\mathbf{H}}_0$$

Magnetic "shift" due to internal magnetic fields

Spin shift: $$K_s(T) = A_{hf}\chi_s(T)$$

Magnetic field at nucleus due to electrons

Electronic spin susceptibility

$K_s \propto 1/T$ — Local Moment

$K_s \propto \text{constant}$ — Fermi liquid

$K_s \rightarrow 0 \text{ or } \propto \text{constant}$ — Superconductivity (*S* Spin component)

Tool box: spin lattice relaxation T_1

Perturb the equilibrium spin population and find the time scale in which it relaxes (T_1) by giving energy up to the “lattice” including electrons

$$\frac{1}{T_1 T} \propto \sum \lim_{\omega_0 \to 0} A_{hf}(\vec{q})^2 \frac{\chi''(\vec{q}, \omega_0)}{\omega_0}$$

low frequency limit

q dependent hyperfine field

dissipative component of dynamic susceptibility

$$\frac{1}{T_1} \propto \mathrm{constant}$$

Local Moment

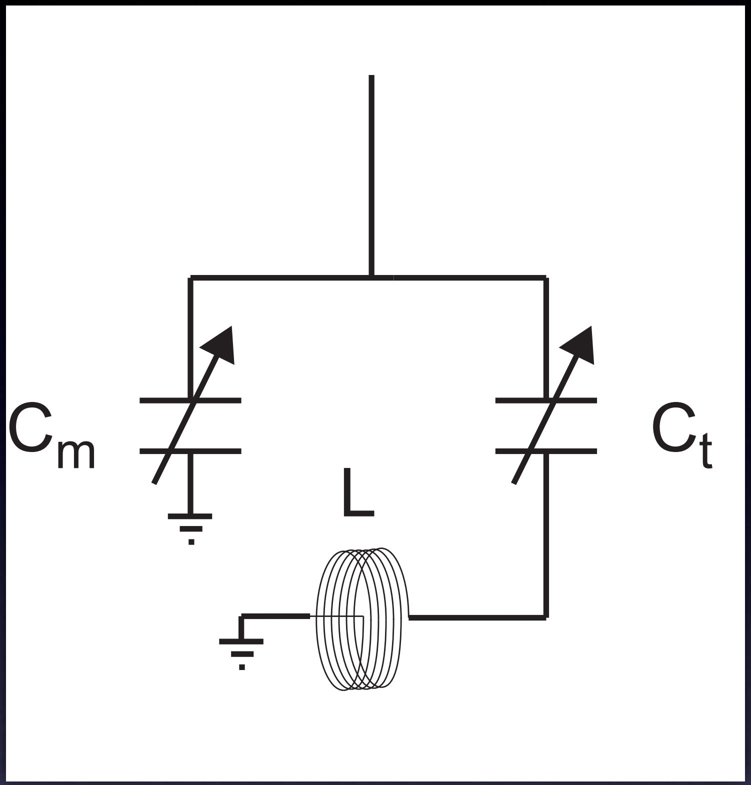
$$\frac{1}{T_1} \propto T$$

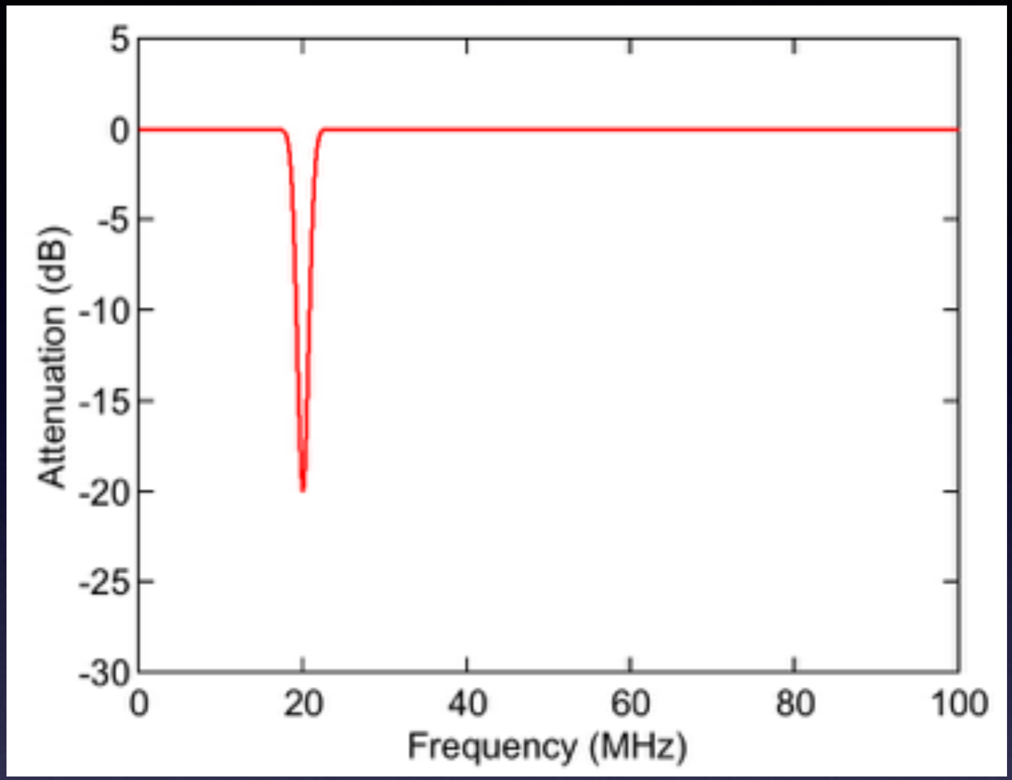
Fermi liquid

$$\frac{1}{T_1} \propto T^{\alpha} \text{ or } e^{-T/\Delta}$$

Superconductivity (*L* angular momentum component)

Tool box: AC - susceptibility





- Sample (inside coil) begins to expel magnetic field upon transition to the superconducting state
- Characteristic impedance of the circuit changes altering
  - Resonance frequency
  - Quality factor
  - Attenuation

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- U_2PtC_2 - Intermediately heavy fermion
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U_2PtC_2 intermediate U material

- For *f* electron systems physics largely determined by inter *f* atom spacing d_{ff}

U_2PtC_2

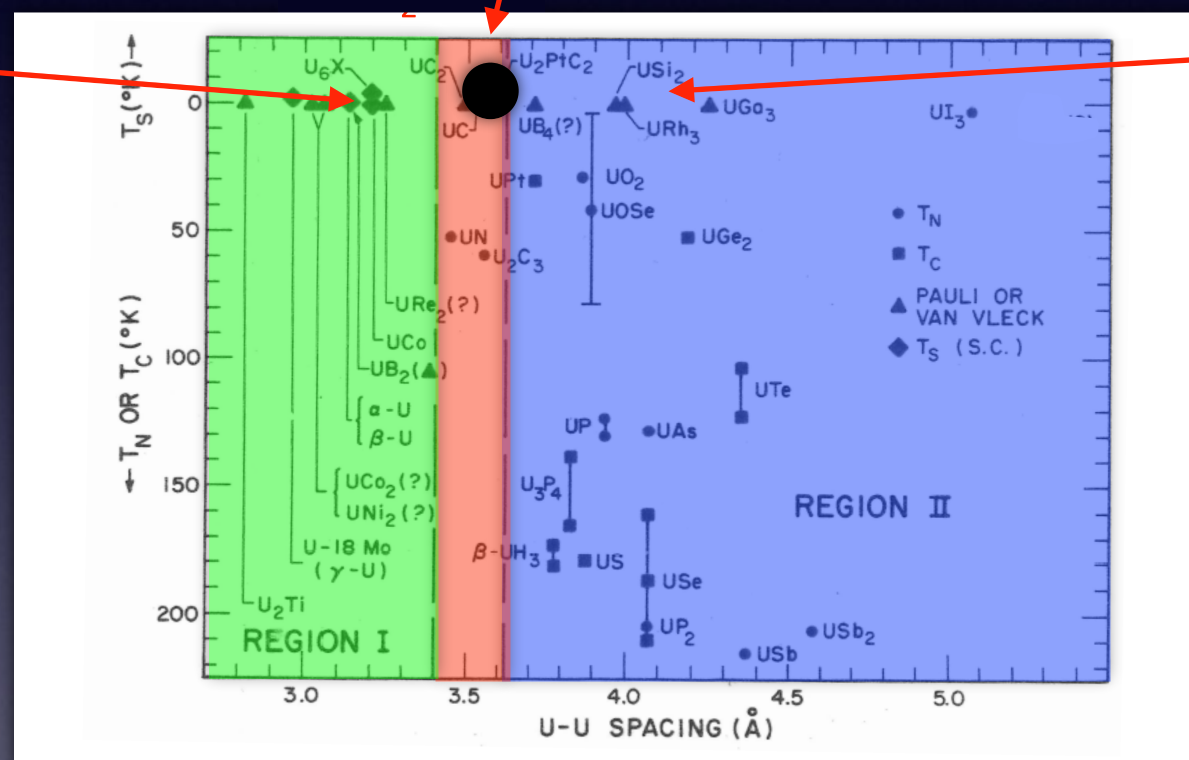
γ = 75 $mJ/molK^2$

U_6Fe

γ = 25 $mJ/molK^2$

UPt3

γ = 450 $mJ/molK^2$



<u>Small d_{ff}</u>

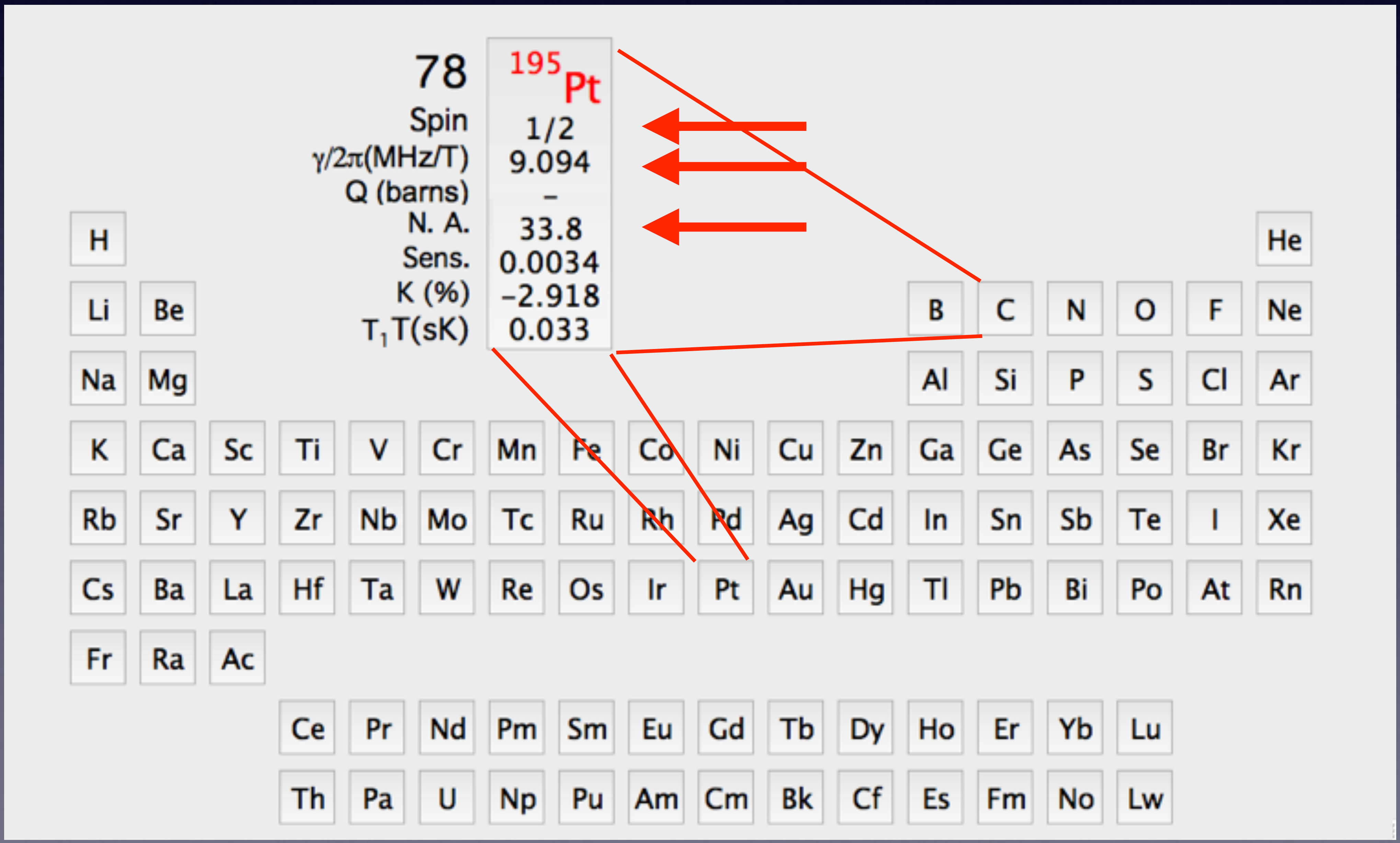
- *f* wave function overlap
  - Itinerant electrons
  - Conventional S.C.

<u>Large d_{ff}</u>

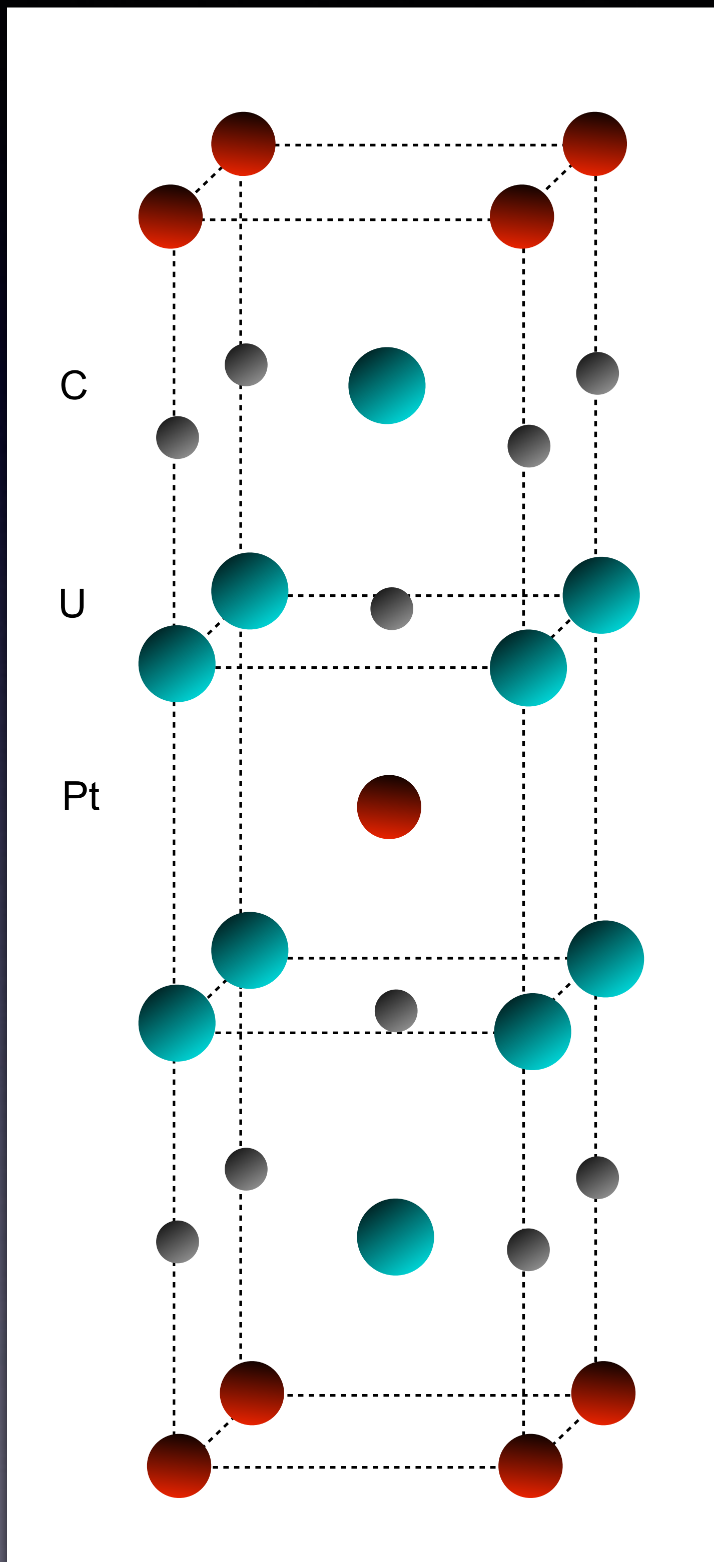
- *f* wave function separate
  - Localized electrons
  - Unconventional S.C.

NMR Periodic Table

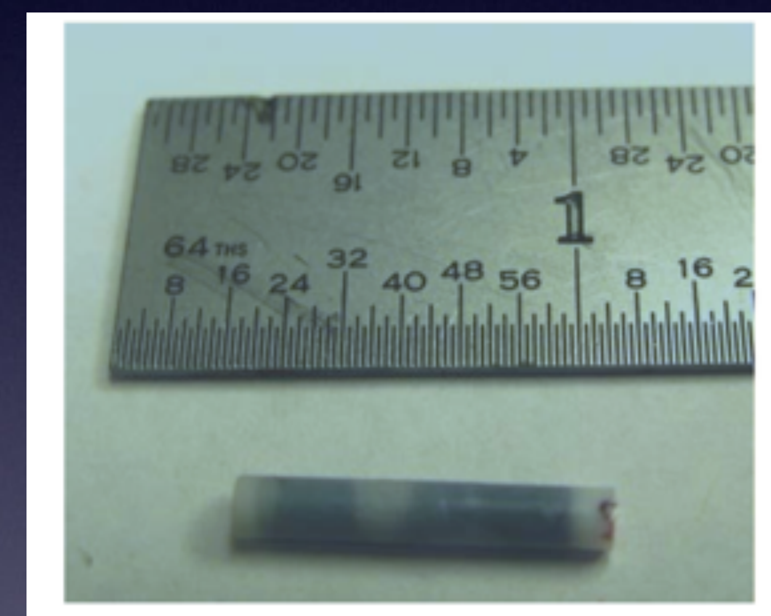
- U_2PtC_2: two (reasonable) isotopes
- Only one ^{195}Pt with high natural abundance
- Spin 1/2, no NQR, only NMR



U_2PtC_2 physical properties



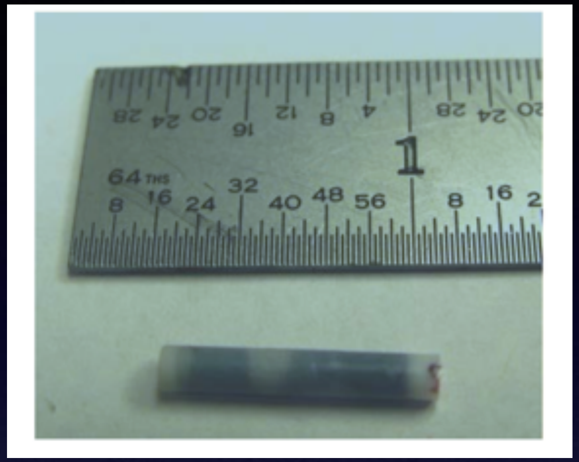
- No magnetic order
- T_c = 1.47 K
- *RRR* = 30
- Powdered and mixed with stycast 1266 1:1
- Oriented in 9 T for 24 h

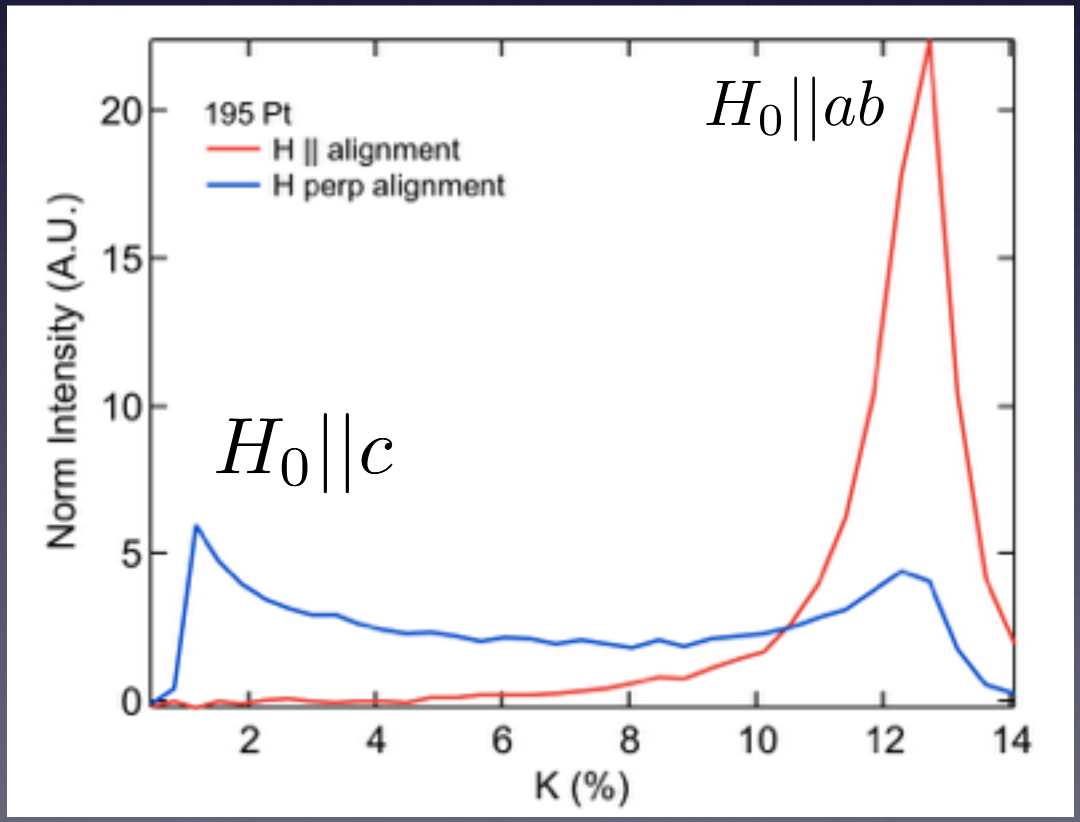


^{195}Pt spectrum

$H_0||\text{alignment}$

$H_0 \perp \text{alignment}$

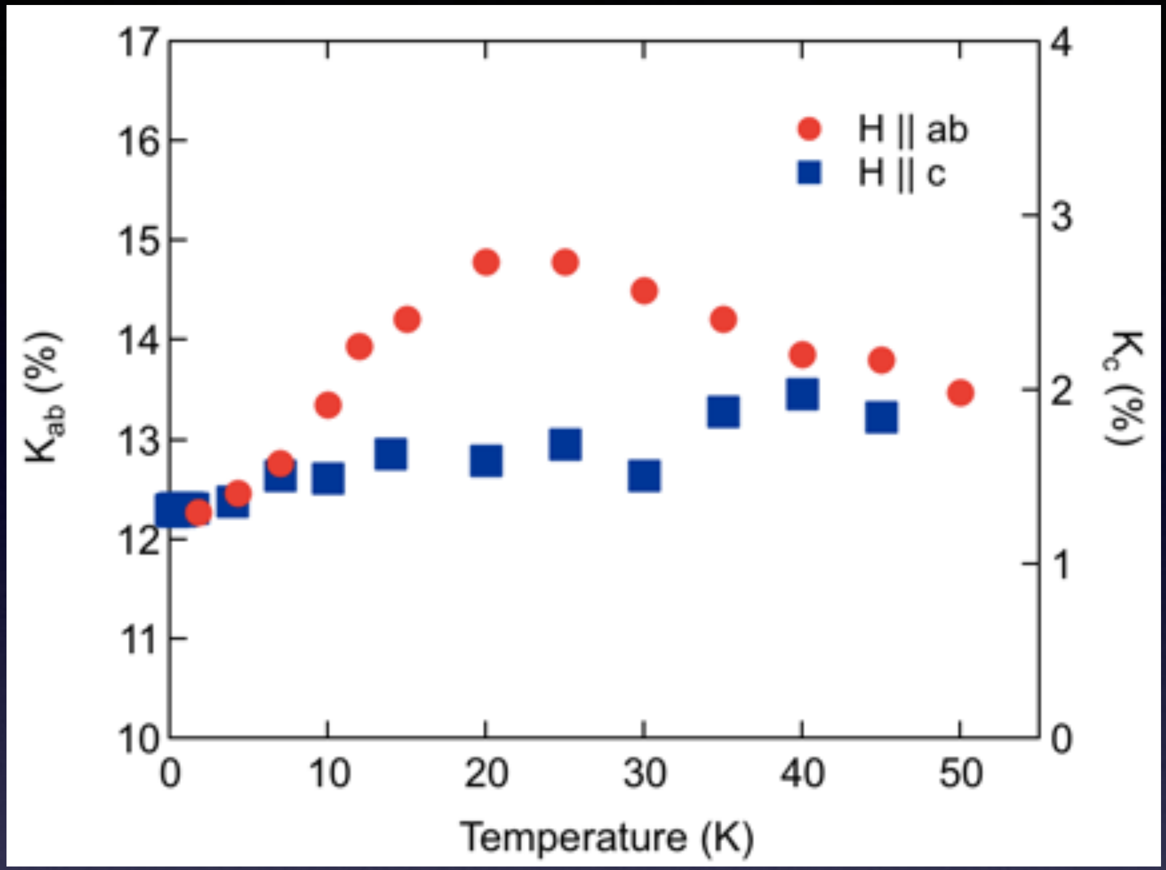


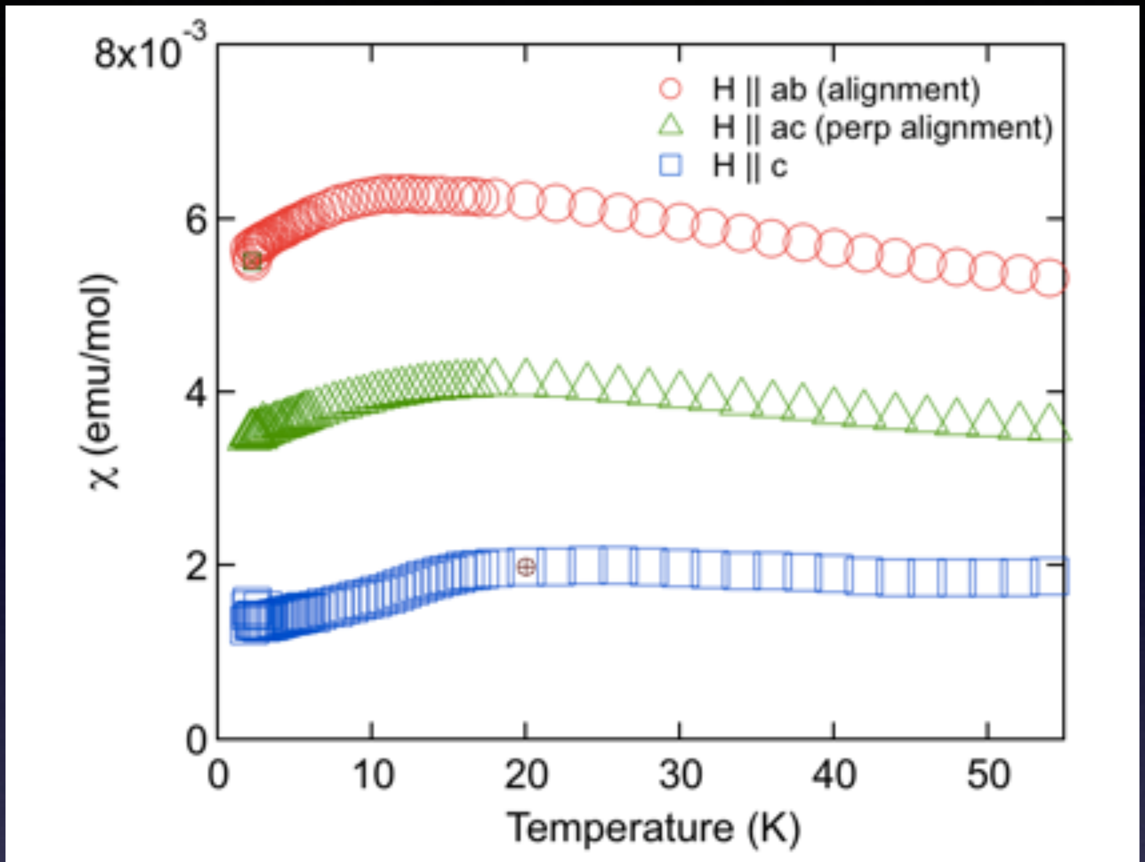


$$\mathcal{H}_Z = \hbar\gamma\left(\hat{\mathbf{1}} + \hat{\mathbf{K}}\right)\vec{I}\cdot\vec{\mathbf{H}}_0$$

- For an aligned powder we expect sharp peaks for H||c and H||ab
- For a full powder we expect a maximum for H||ab and minimum at H||c
- Conclusion: alignment along ab - plane i.e. magnetic easy axis

Temperature dependence of K normal state

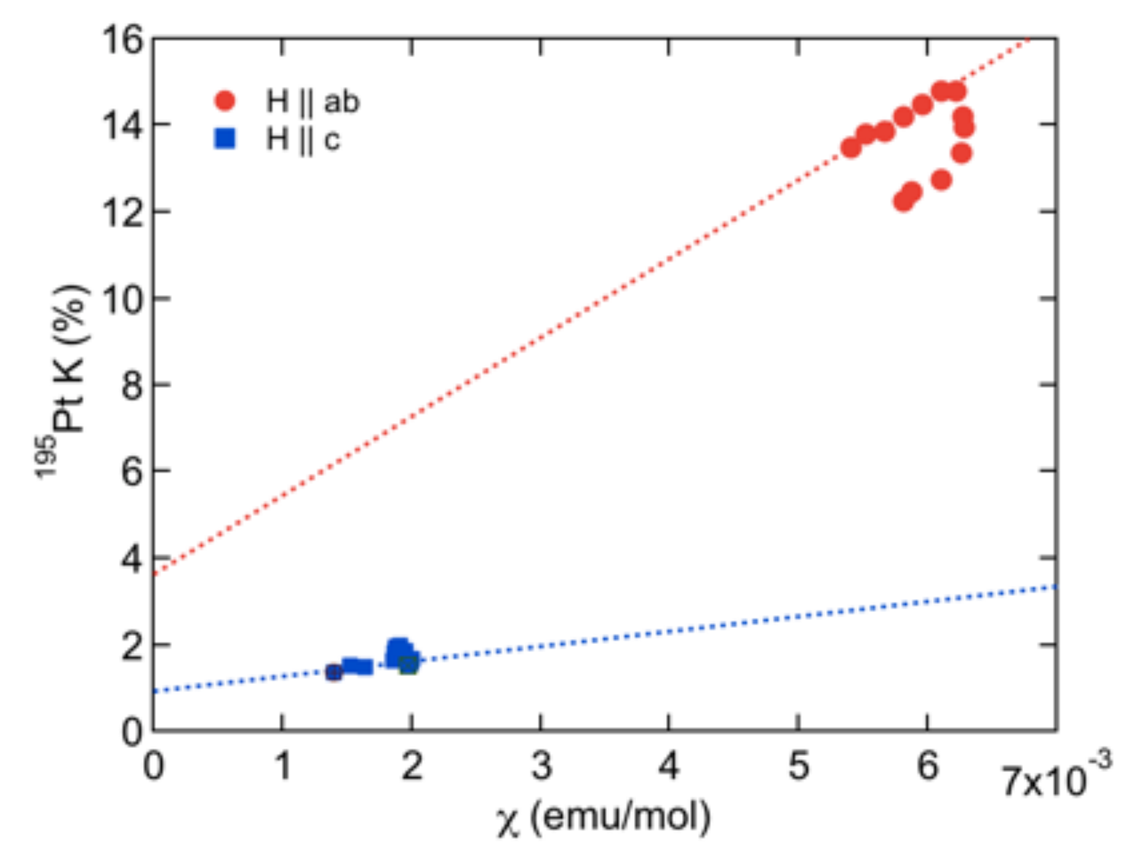




$$K(T) = K_s(T) + K_o$$

$$K_s(T) = A_{hf}\chi_s(T)$$

- $A_{hf,c} << A_{hf,ab}$ very anisotropic electronic interactions
- $K_{s,ab}$ (T_c) ~ 8% (quite large)



NMR determination of superconductivity: *S*

S determined by spectral shift

Singlet ($L = s$ & d)

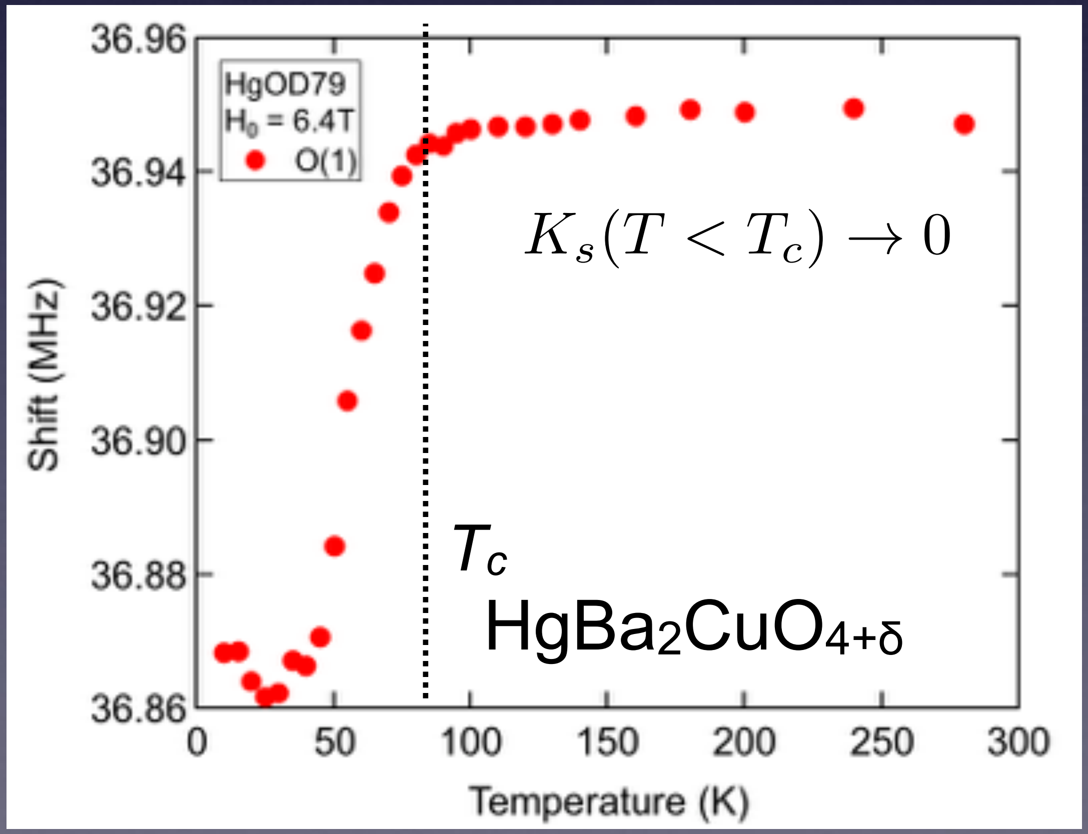
$S = 1/\sqrt{2}\ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$

T-dep. shift below T_c

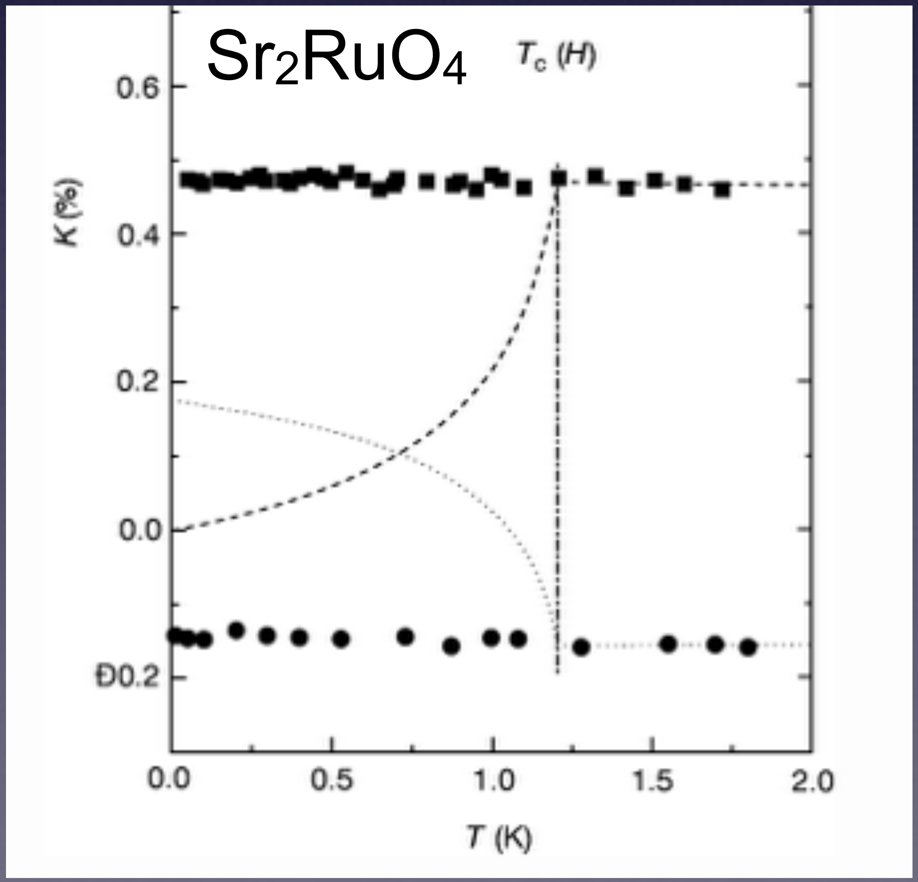
Triplet ($L = p$ & f)

$S = |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, 1/\sqrt{2}\ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$

T-indep. shift below T_c

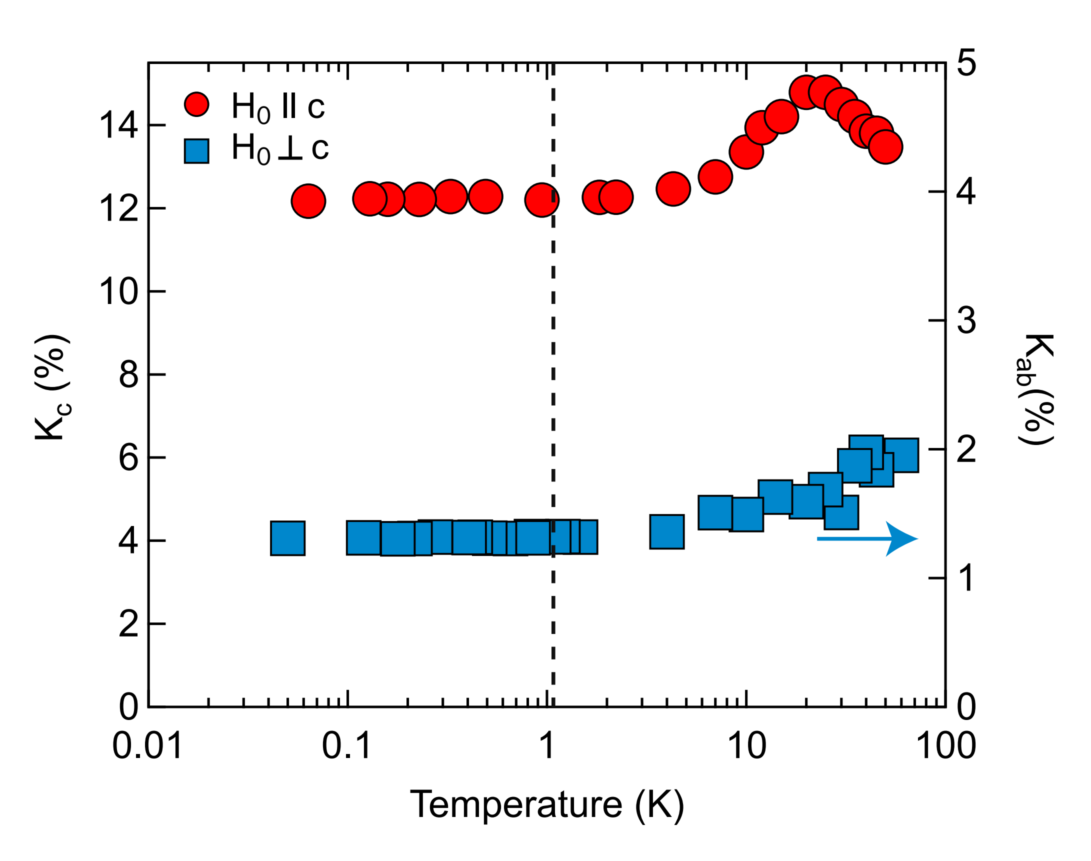


A. M. Mounce, thesis (2013)



K. Ishida Nature **396**, 658 (1998)

NMR probe of spin pairing in U_2PtC_2

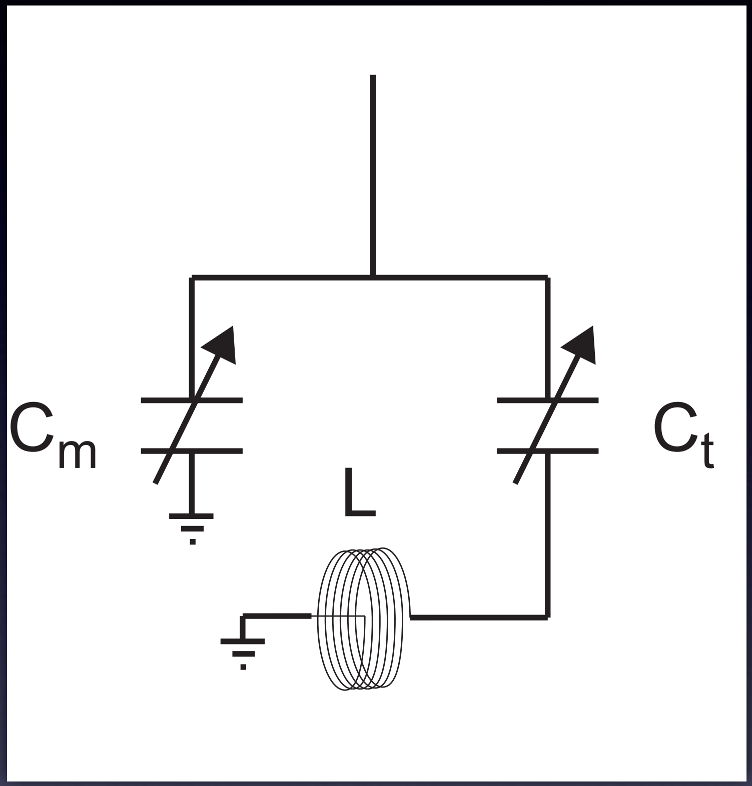


- Shift is independent of temperature down to 50 mK
- *T*-independent in both field directions

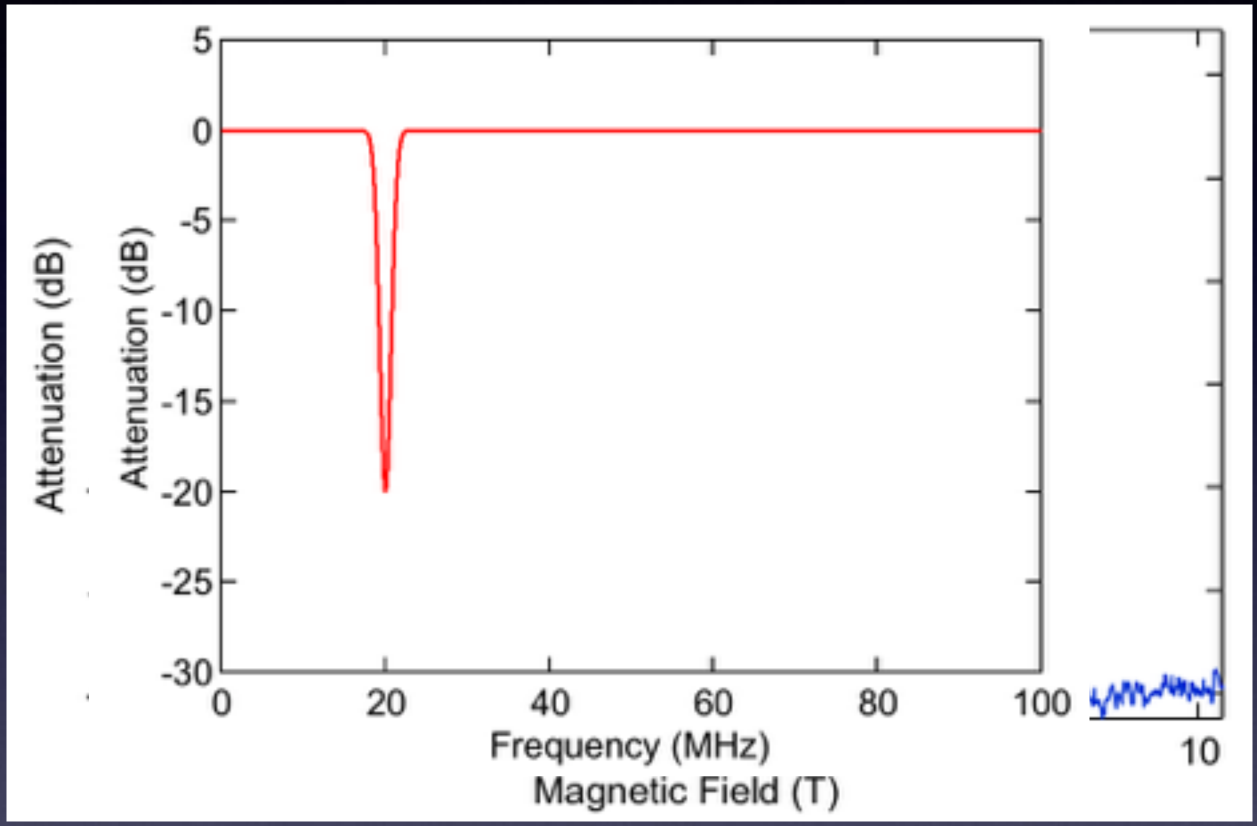
•Equal spin pairings state |↑↑⟩ free to rotate with field

AC-susceptibility

NMR tank circuit



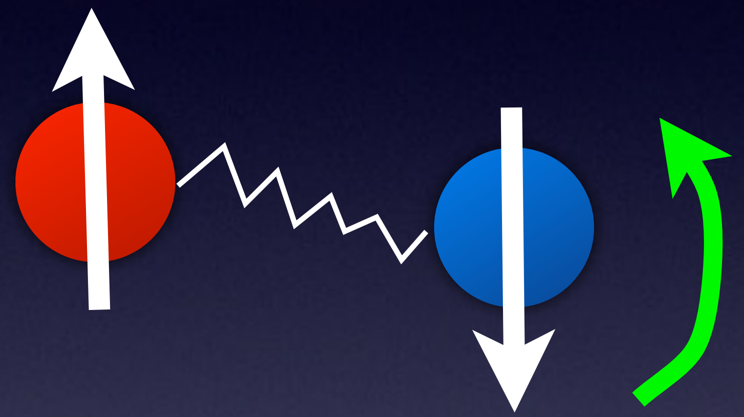
Network analyzer



- Sample (inside coil) begins to expel magnetic field upon transition to the superconducting state
- Characteristic impedance of the circuit changes altering
  - -Resonance frequency
  - -Quality factor
  - -Attenuation

Upper critical field

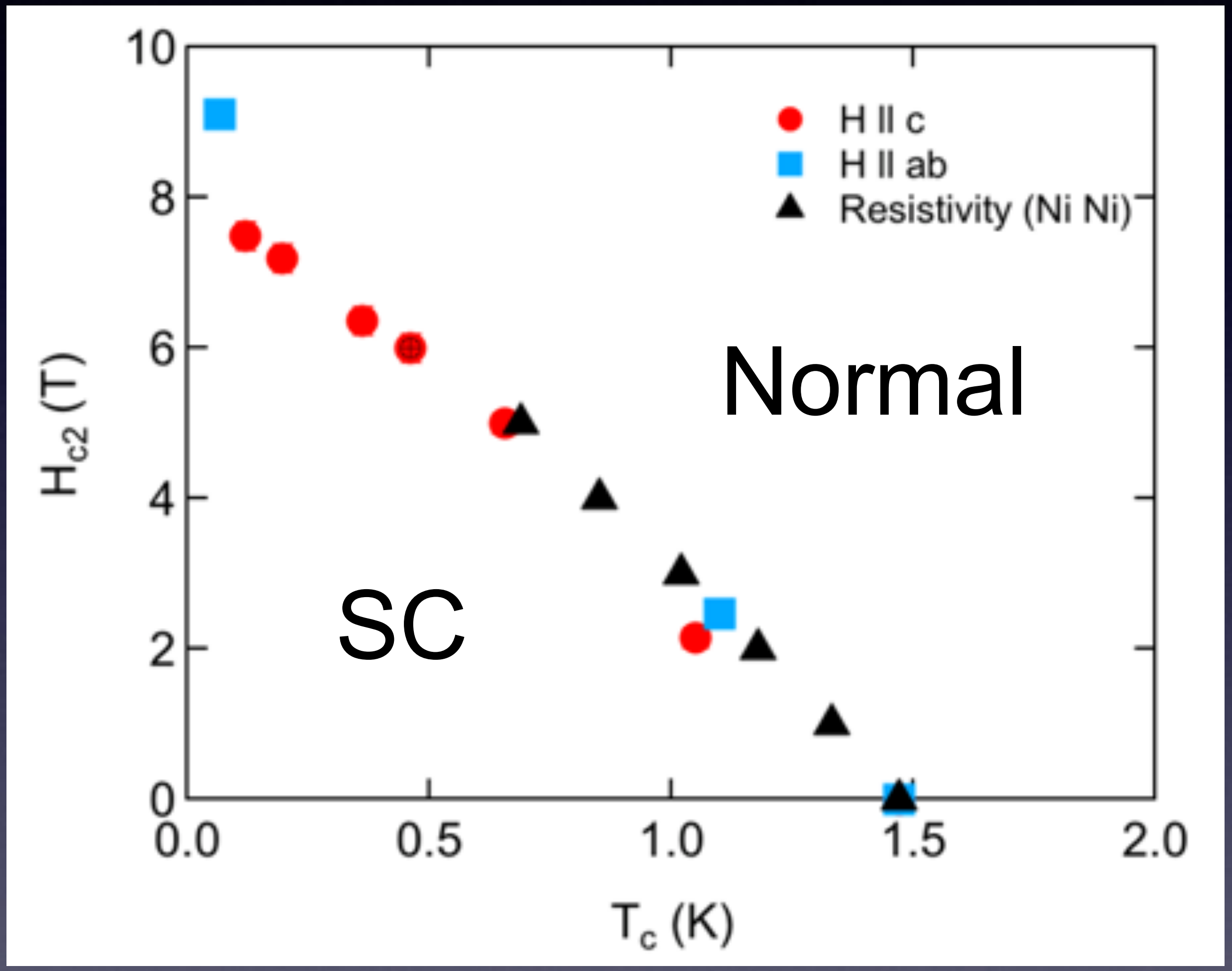
•Pauli limiting field : the field that rips singlet electrons apart



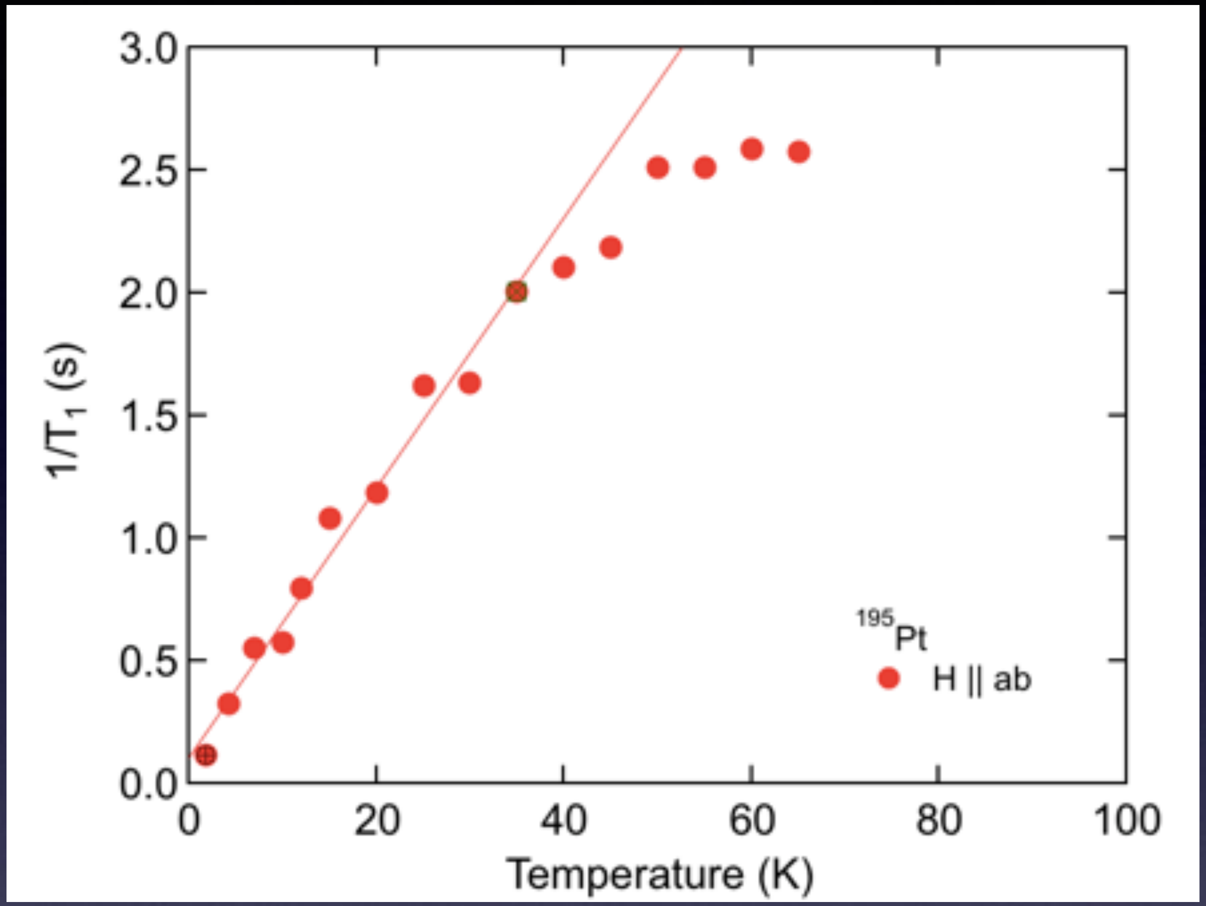
$$H_{c2,Pauli} \approx 1.8T_c = 2.6T$$

•Measured H_{c2} greatly exceeds Pauli limit

•Novel pairing symmetry necessary



Spin lattice relaxation: normal state



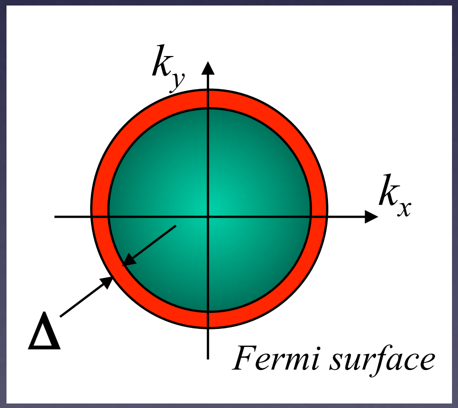
- $1/T_1 \propto T$ for T < 40 K, heavy Fermi liquid
- $1/T_1 \rightarrow \mathrm{constant?}$ for T > 100 K
- Signal to noise not sufficient for H||c

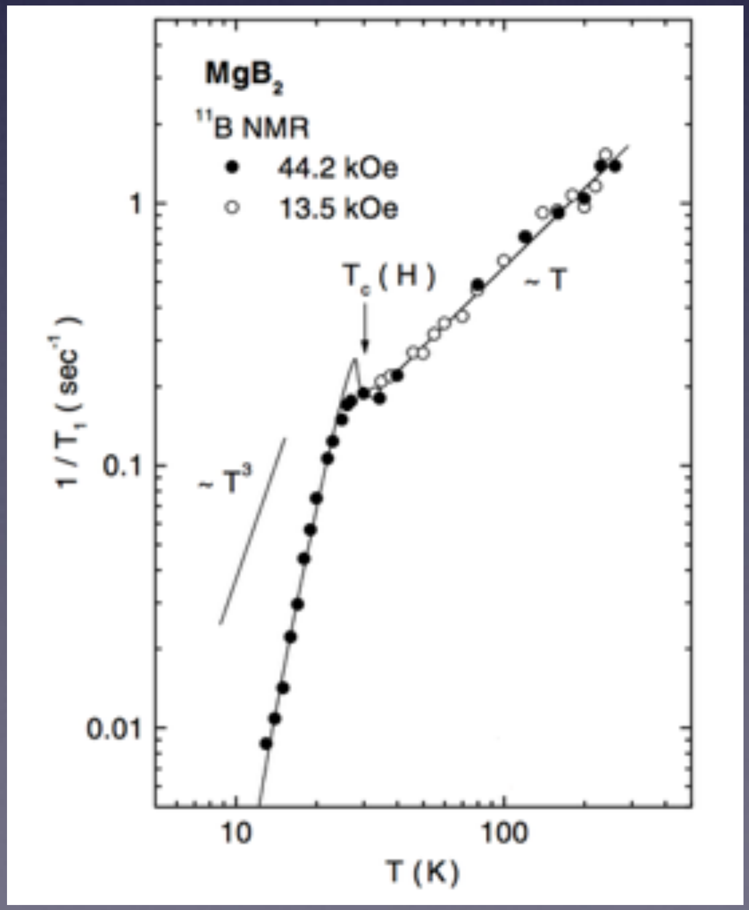
NMR determination of superconductivity: *L*

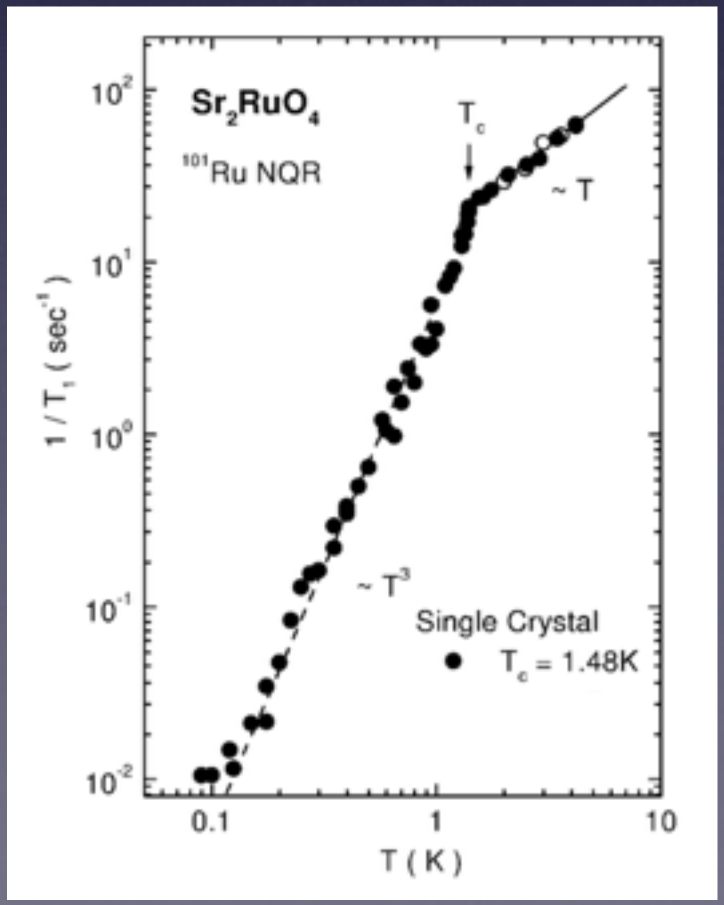
L determined by spin lattice relaxation

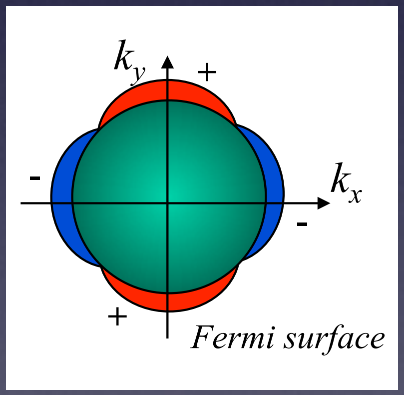
$$1/T_1 \propto \begin{cases} e^{-\Delta/k_B T} & \text{fully gapped,} \\ T & \text{gapless ,} \\ T^3 & \text{line zeros ,} \\ T^5 & \text{point zeros .} \end{cases}$$

- fully gapped → *s*-wave conv.
- gapless → metal
- line zeros, point zeros → *p,d,f*-wave unconv.







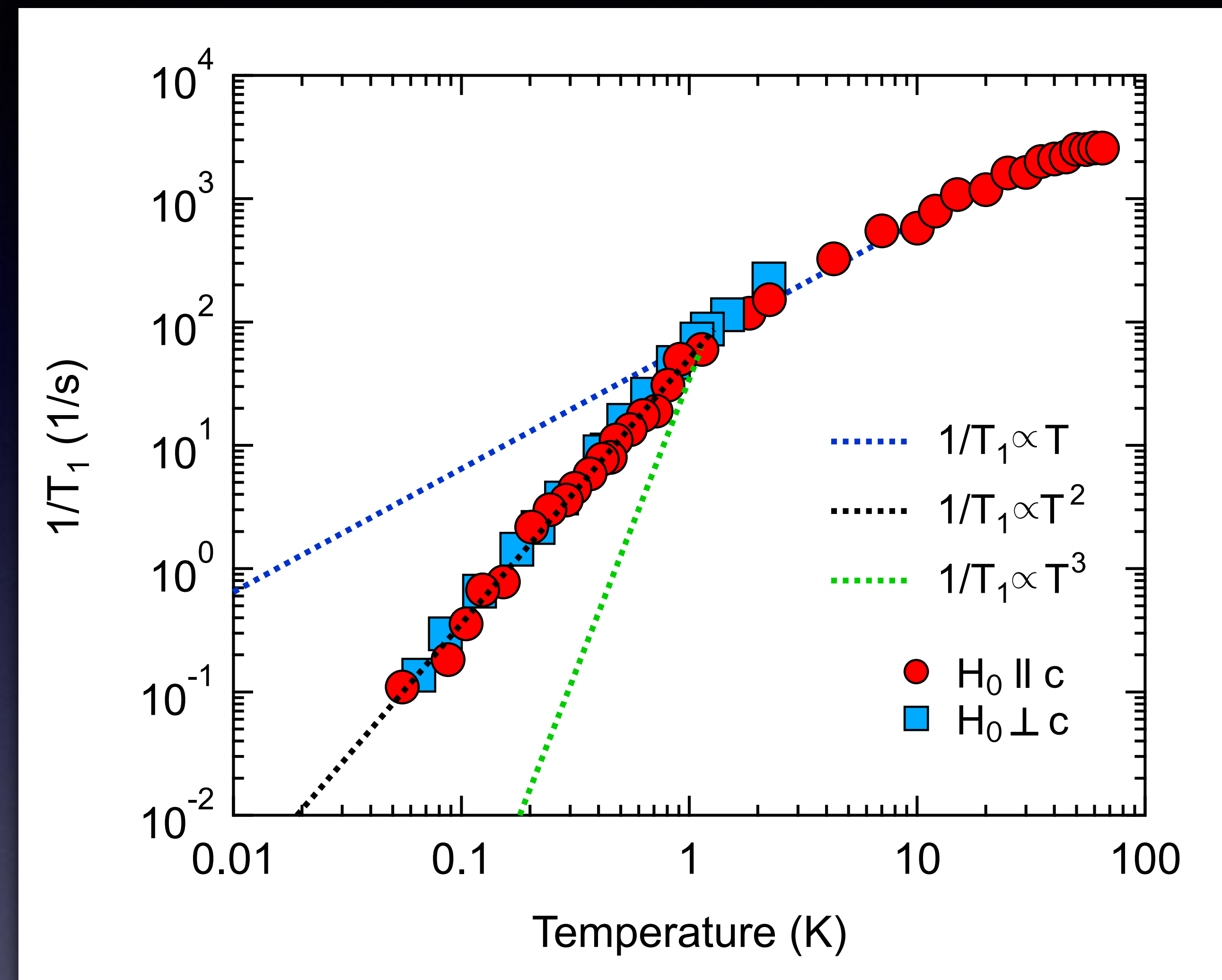


H. Kotegawa *et al*, Phys. Rev. Lett. **87**, 127001 (2001).

K. Ishida *et al*, Phys. Rev. Lett. **84**, 5387 (2000).

NMR probe of orbital wave function

$$1/T_1 \propto \begin{cases} e^{-\Delta/k_B T} & \text{fully gapped,} \\ T & \text{gapless ,} \\ T^3 & \text{line zeros ,} \\ T^5 & \text{point zeros .} \end{cases}$$

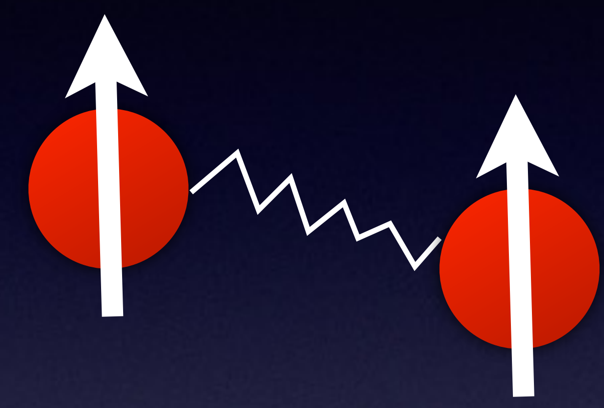


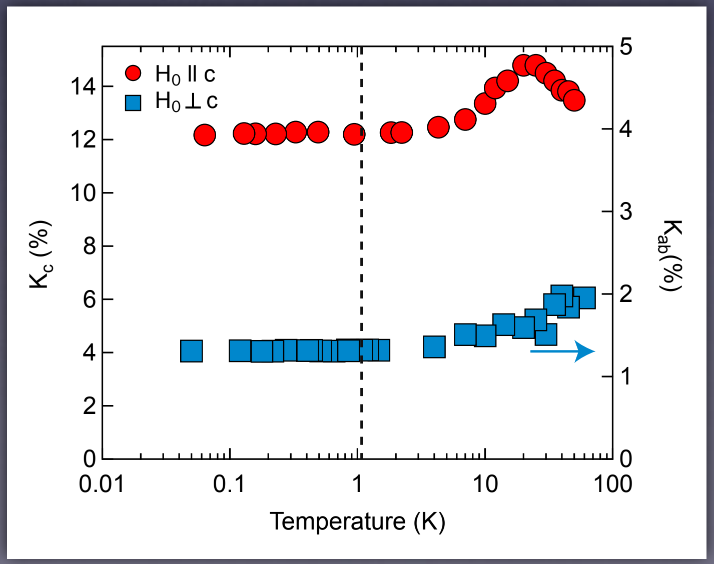
- $1/T_1 \propto T^2$
  - -Unusual power law
  - -No Coherence peak
- Predicted for a spin triplet superconducting state

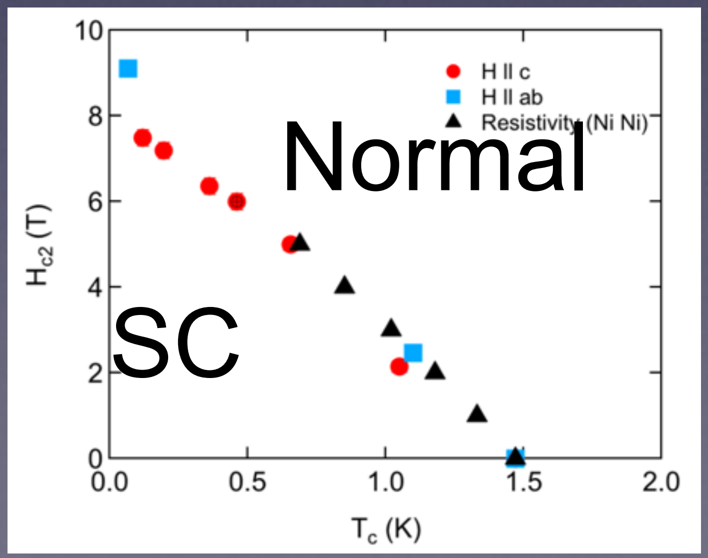
T. Ohmi and K. Machida, Phys. Rev. Lett. **71**, 625 (1993)

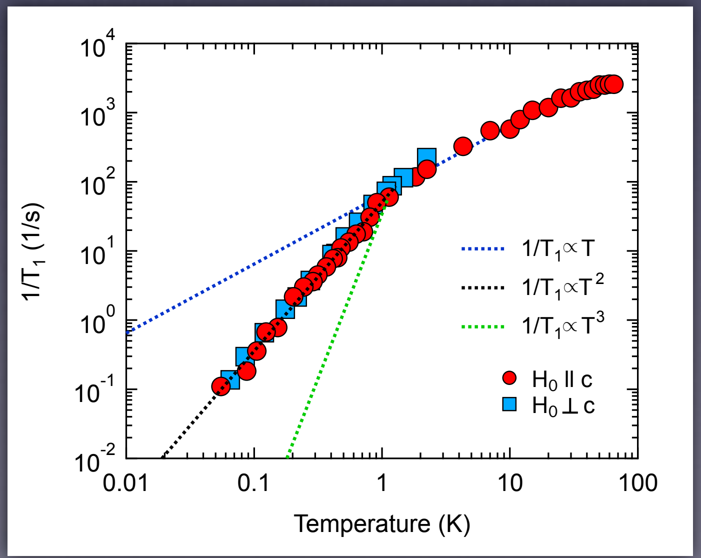
U_2PtC_2 summary

- Evidence for an equal spin pairing triplet state
  - *T-indep.* Shift
  - AC-susceptibility
  - T^2 relaxation
- Future: ^{13}C NMR to verify results
- Hopefully, work will inspire theoretical work







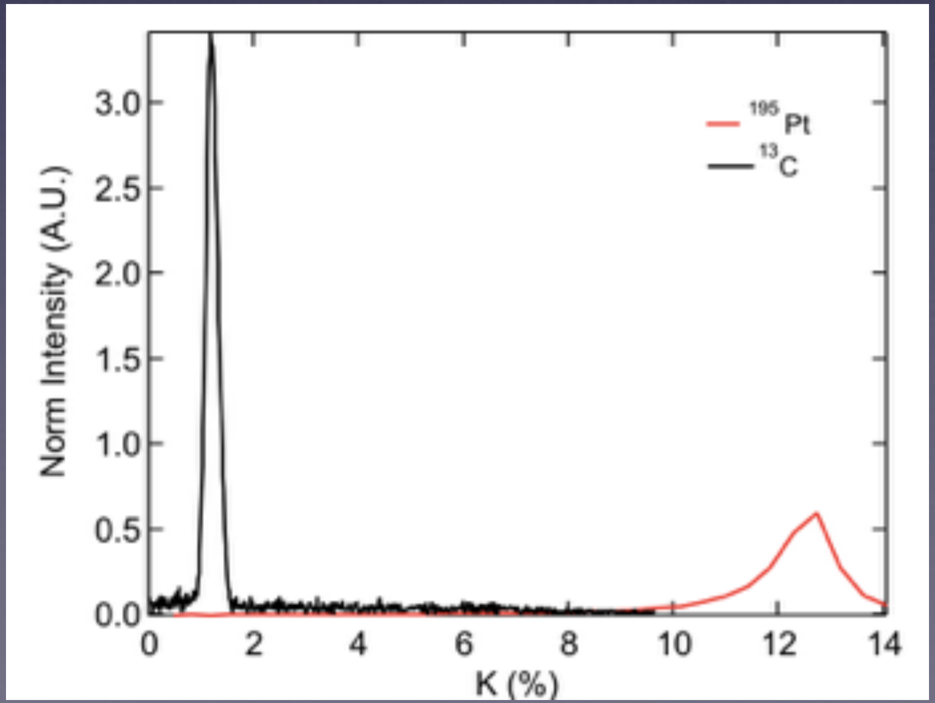


The story is not over…

- Isotopically enrich ^{13}C from ~1% to 99.9%!

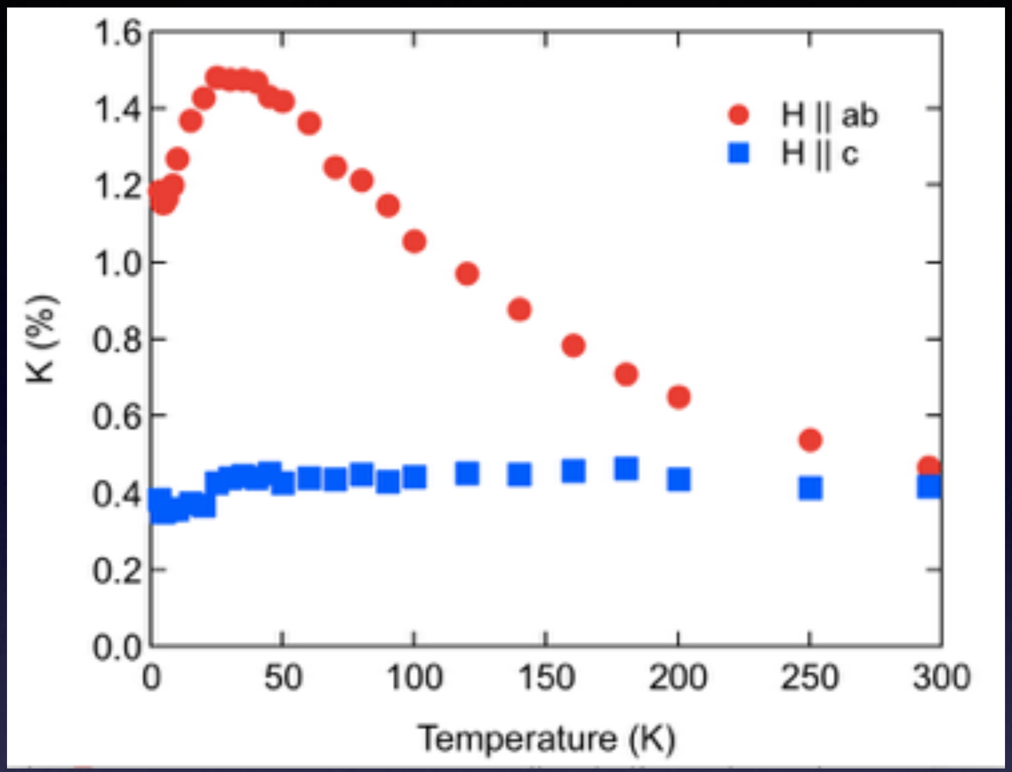
^{13}C	^{195}Pt
Larger signal	Smaller signal
2*p* electrons	5*d* electrons
Small A_{hf}	Larger A_{hf}
Smaller K	Larger K
Longer T_1	Shorter T_1

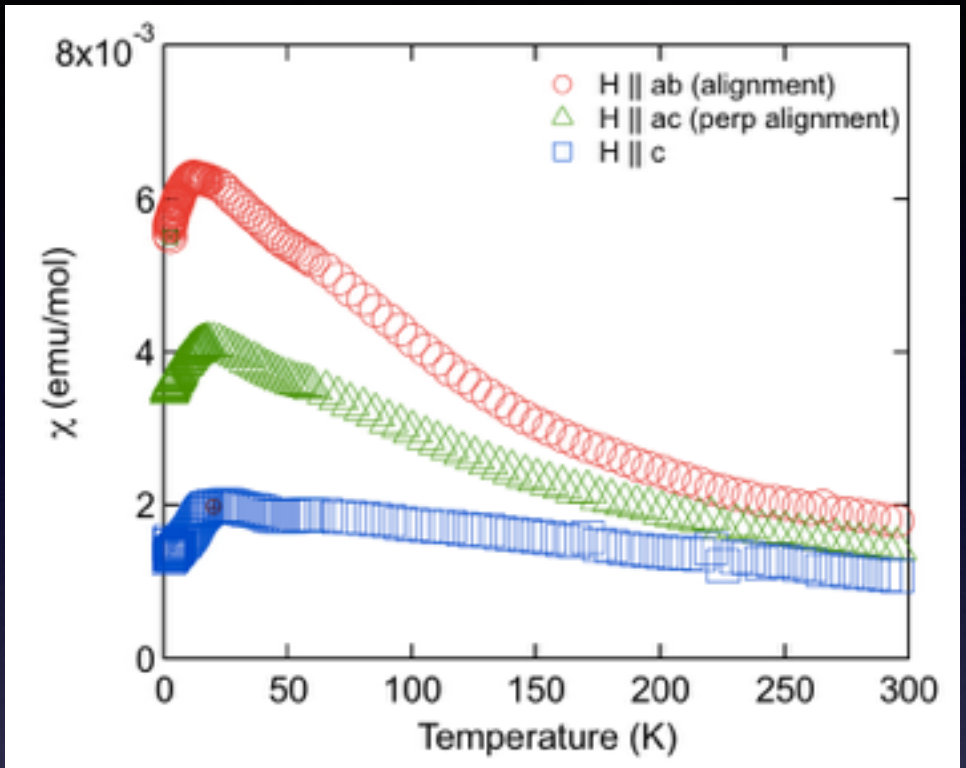
$^{13}T_1 \approx .25\text{s}$



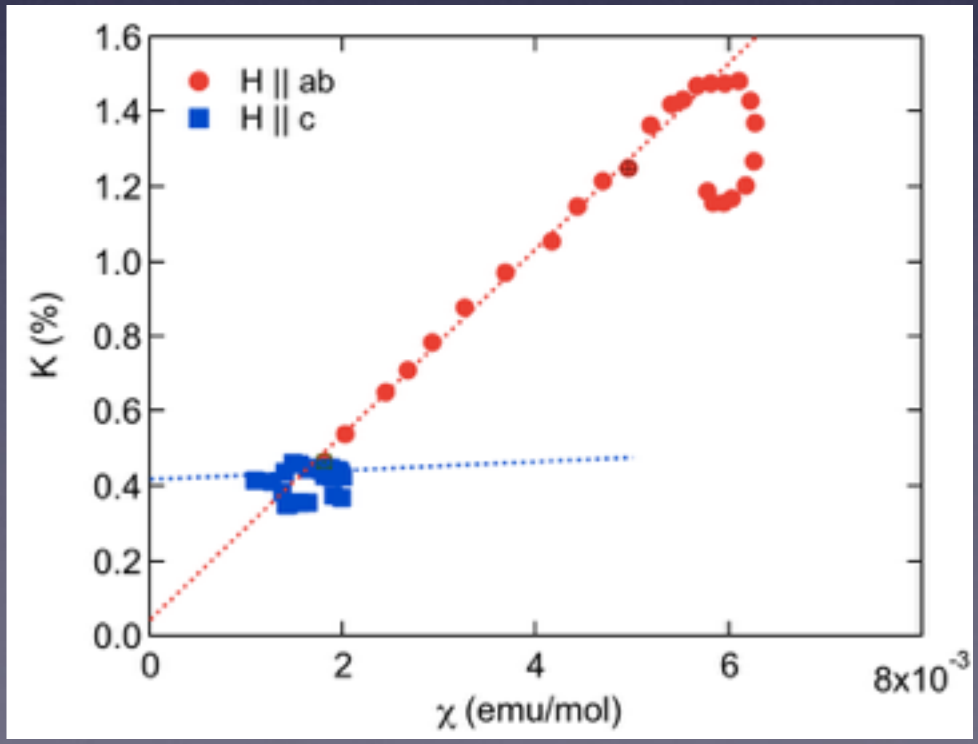
$^{195}T_1 \approx .01\text{s}$

The normal state K

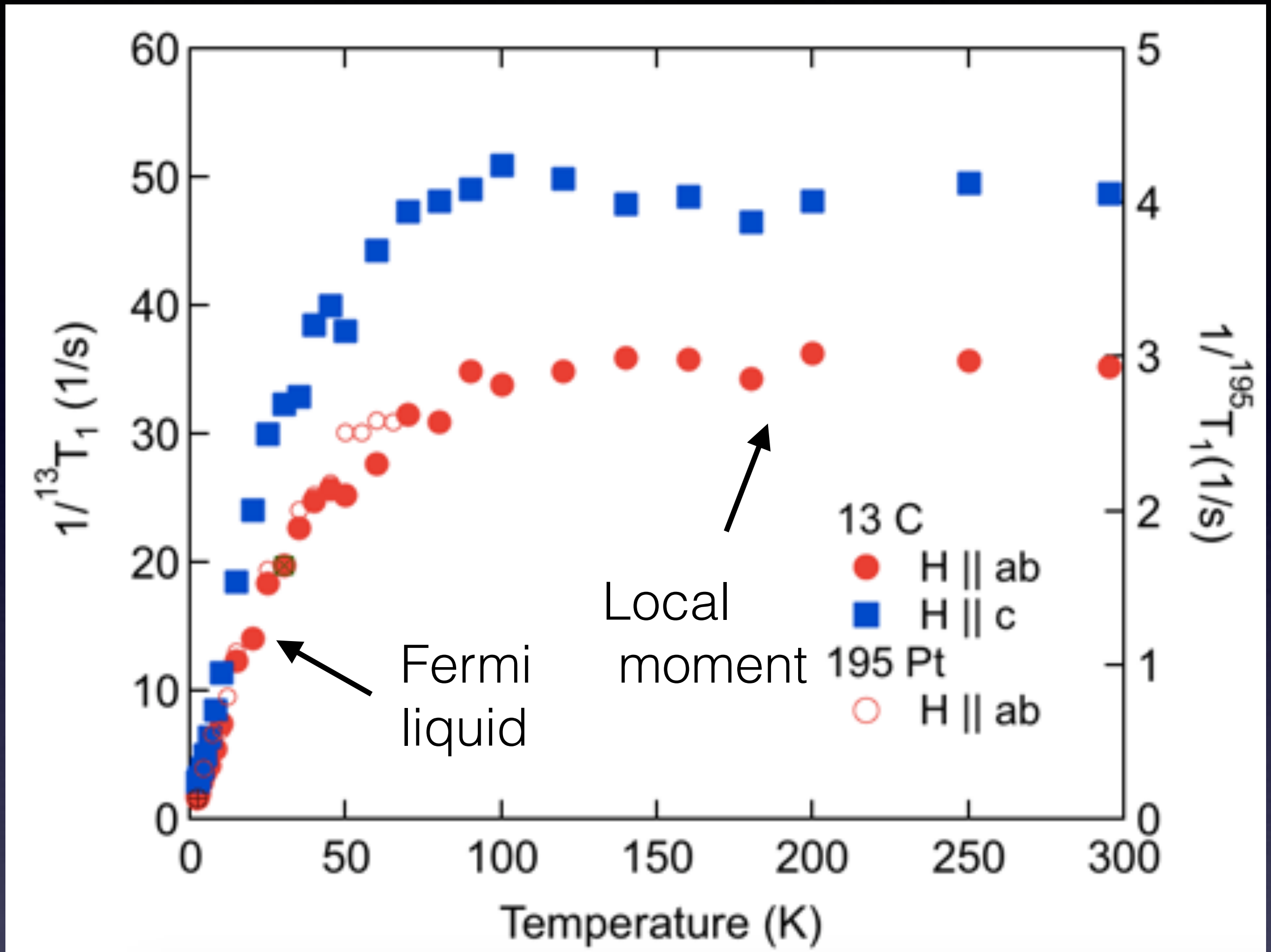




- ^{13}C allows for full temperature dependence of measurement
- ^{13}C K_{ab} is quite large due to large magnetic field of U-5*f* e^-
- $A_{hf,c} \sim 0$!



The normal state T_1

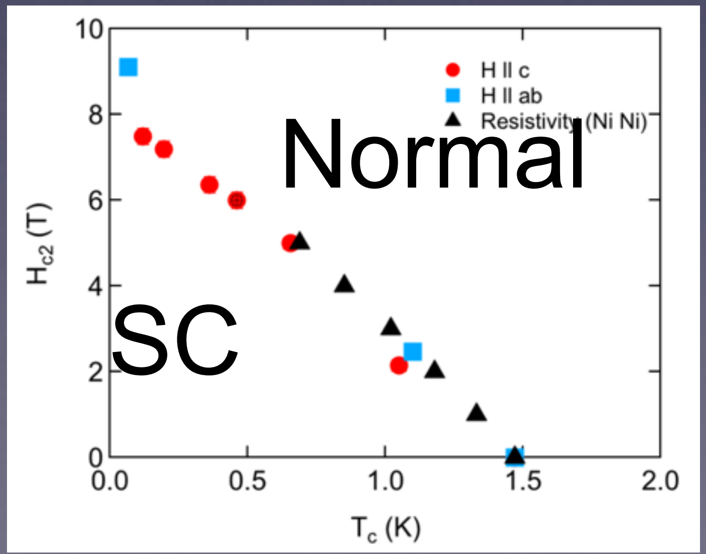


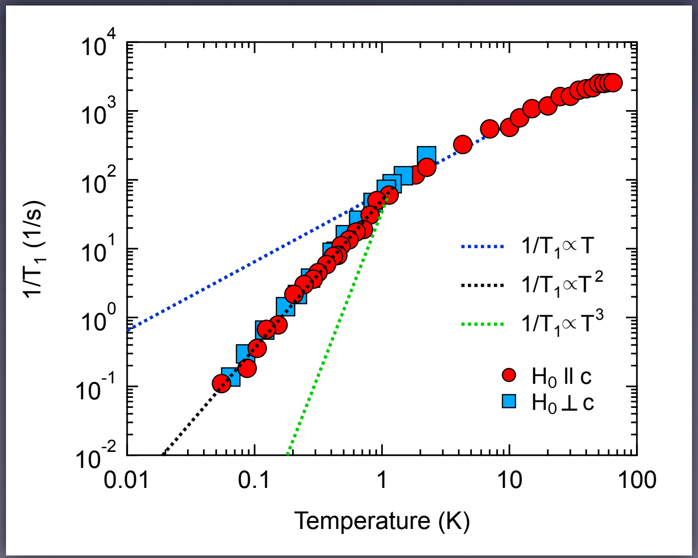
- $1/T_1$ further confirms Kondo coherence picture in the normal state
- $1/T_1 \propto \text{constant}$ for T >100 K (local magnetic *f* moment)
- $1/T_1 \propto T$ heavy Fermi liquid

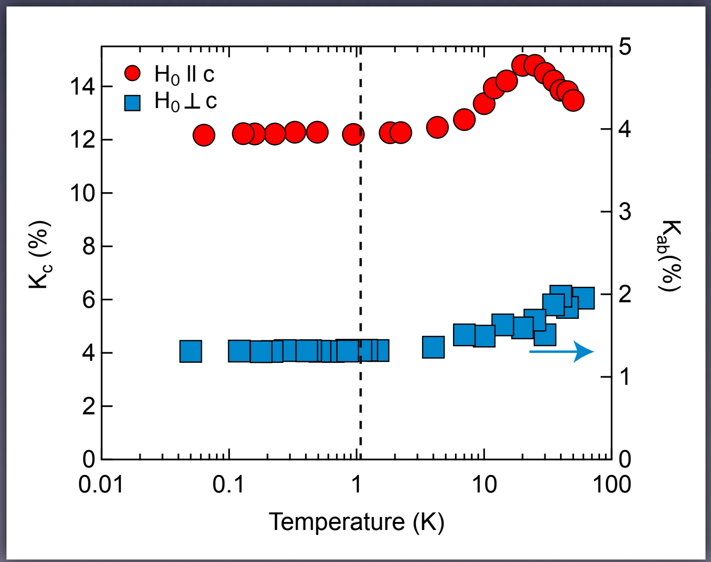
U_2PtC_2 summary

- Evidence for an equal spin pairing triplet state from ^{195}Pt
  - AC-susceptibility
  - *T*-indep. shift
  - T^2 relaxation

- ^{13}C NMR demonstrates Kondo Physics
- Inspire theoretical work on superconductivity?







Outline

NMR of Heavy Fermion Superconductors

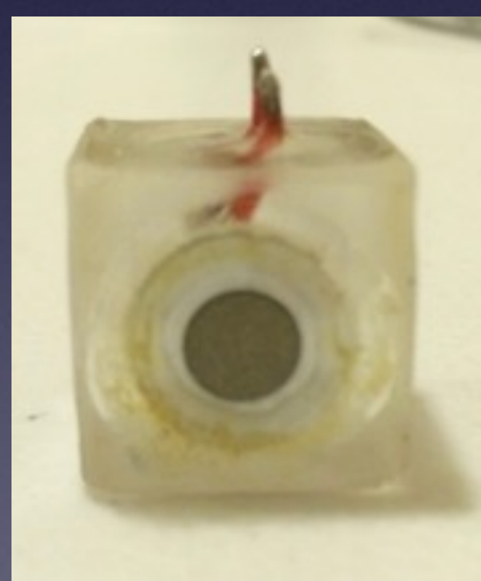
- Heavy fermion materials
- Superconductivity
- Nuclear Magnetic Resonance

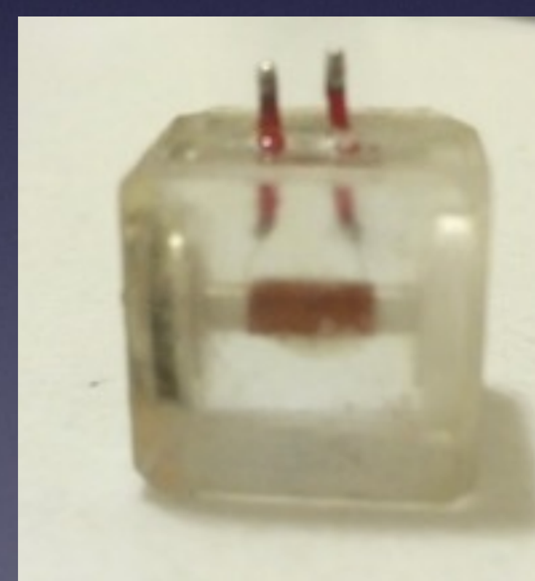
Experimental NMR Results

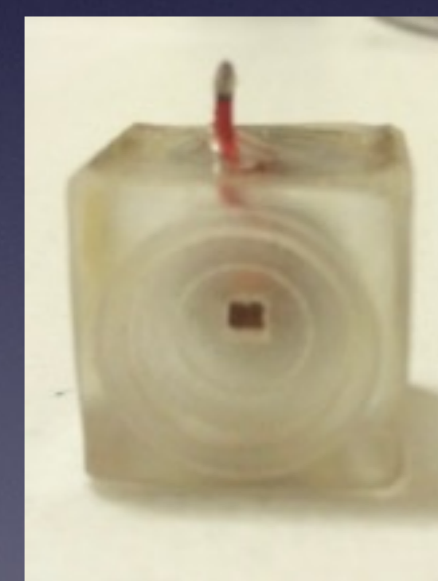
- U_2PtC_2
- Pu -115’s

Safety!

There are two aspects to the harmful effects of plutonium: the radioactivity and the heavy metal poison effects. Isotopes and compounds of plutonium are radioactive and accumulate in bone marrow. Contamination by plutonium oxide has resulted from nuclear disasters and radioa



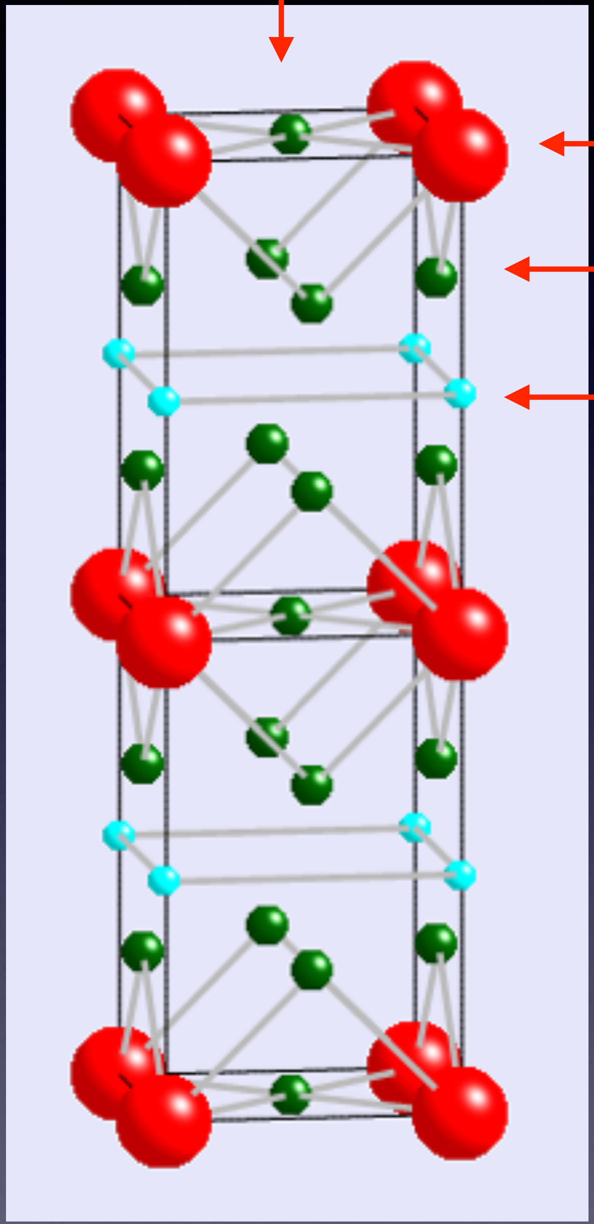




A commonly cited quote by Ralph Nader states that a pound of plutonium dust spread into the atmosphere would be enough to kill 8 billion people.[123] However, calculations show that one pound of plutonium could kill no more than 2 million people by inhalation. This makes the toxicity of plutonium roughly equivalent with that of nerve gas.[124] Nader's views were

Plutonium has a metallic taste.[127]

Pu115's

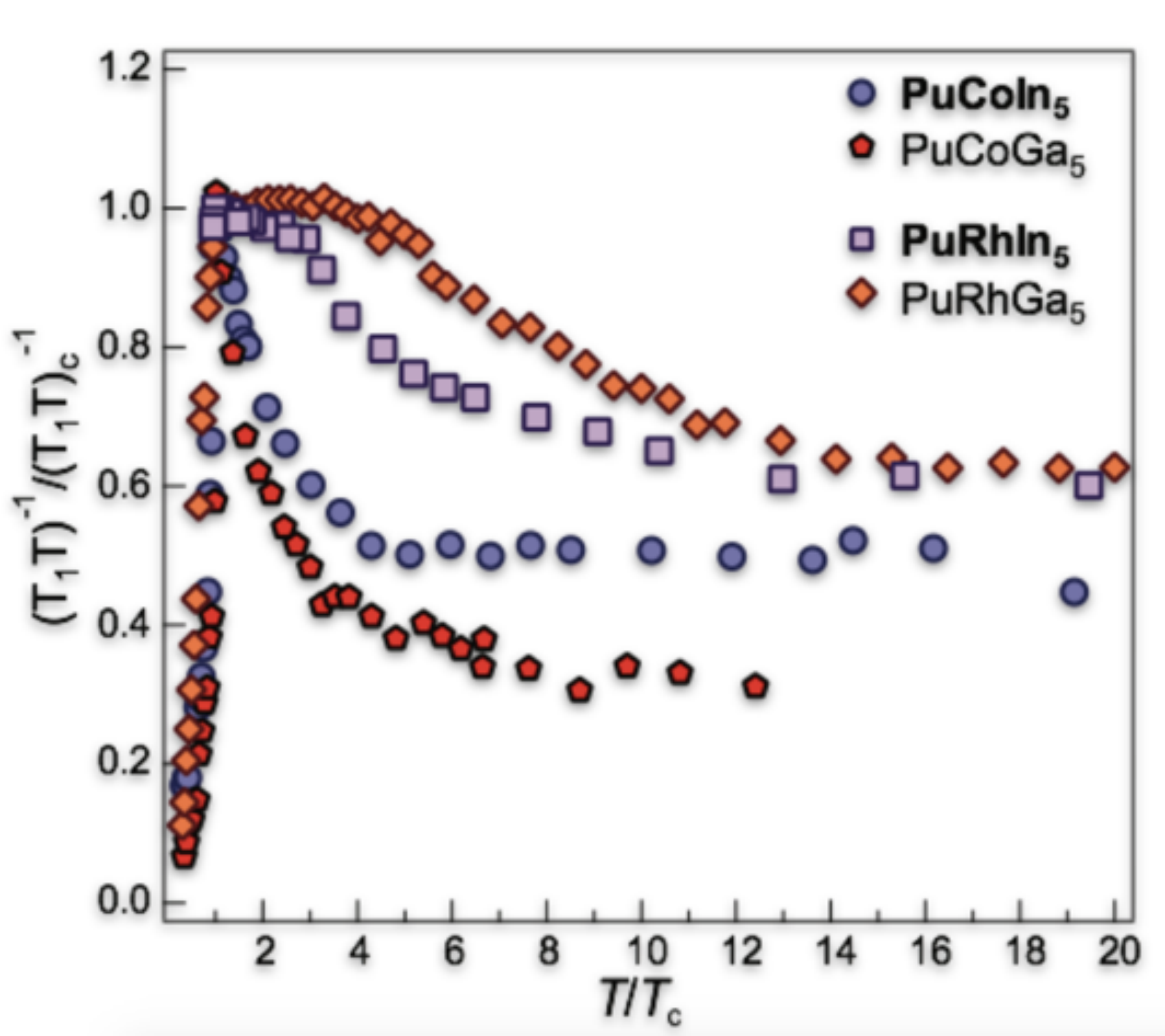


	T_c
$PuRhIn_5$	1.6 K
$PuCoIn_5$	2.5 K
$PuRhGa_5$	8.7 K
$PuCoGa_5$	18.5 K

	^{69}Ga	^{71}Ga	^{115}In
Spin	3/2	3/2	9/2
$\gamma/2\pi$(MHz/T)	10.219	12.985	9.3295
Q (barns)	0.178	0.112	0.83
N. A.	60	40	95.7
Sens.	0.04158	0.05596	0.33158
K (%)	0.155	0.155	0.82
T_1T(sK)	0.46	–	0.079

High spin nuclei with I > 1/2
NQR possible!

Pu115's T_1



- Strong AF fluctuations in the normal state
- For PuRhA5 fluctuations soften near T_c
- Line notes from T^3 relaxation
- Unconventional superconductivity