

Title: NMR Investigation of Iron-Based High Tc Superconductors

Date: Apr 22, 2010 11:00 AM

URL: <http://pirsa.org/10040080>

Abstract: I will discuss NMR study of two types of iron based superconductors, electron doped  $\text{Ba}(\text{Fe},\text{Co})_2\text{As}_2$  and stoichiometric  $\text{FeSe}$ . The primary focus will be on normal state spin fluctuations and its possible relation with the superconducting mechanism, and the pairing symmetry as probed by NMR.

# NMR investigation of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ and FeSe

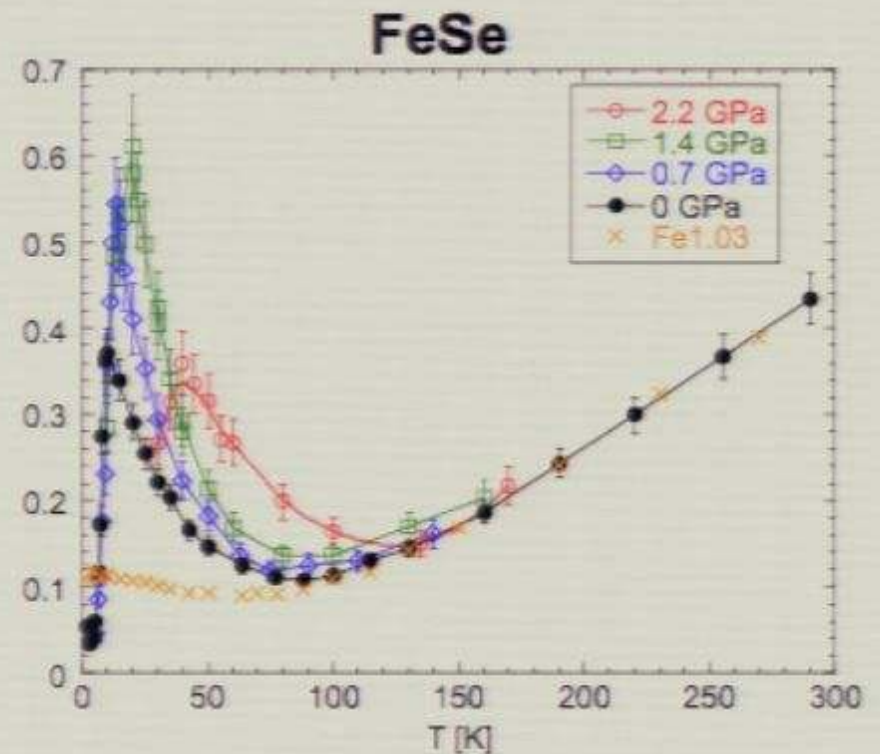
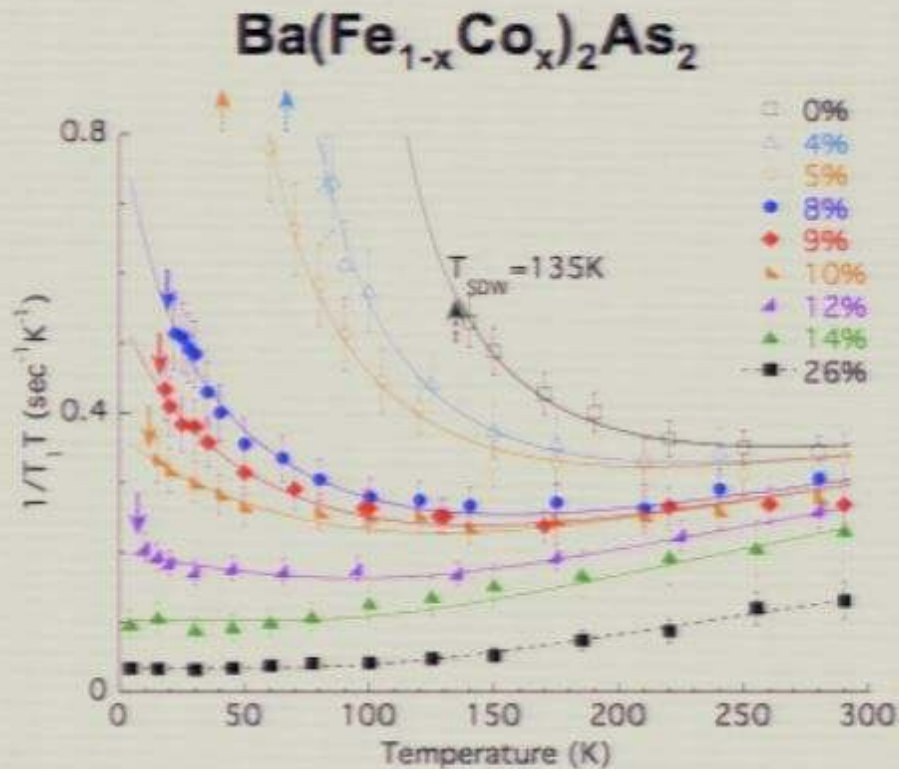
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A.S. Sefat, R. Jin, M. McGuire, B.C. Sales, D. Mandrus **Oak Ridge Nat. Lab.**

J. Chen, B. Shen, H.H. Wen **Chinese Academy of Sciences**

J.M. McQueen, R.J. Cava **Princeton University**

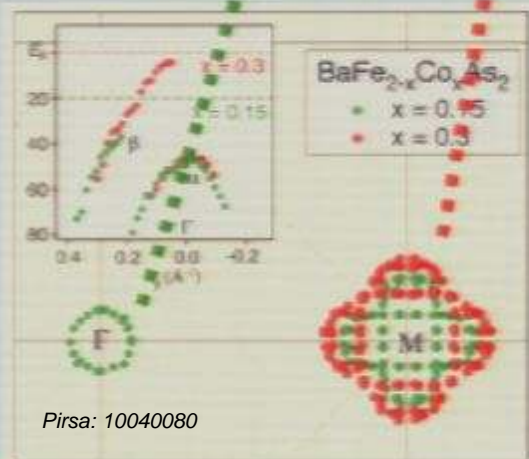
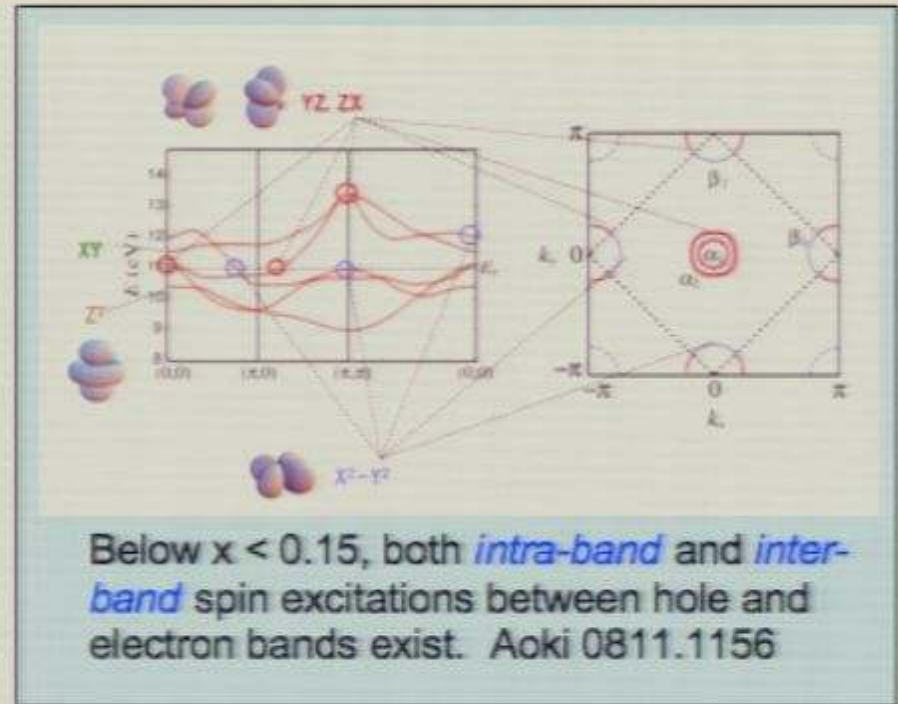
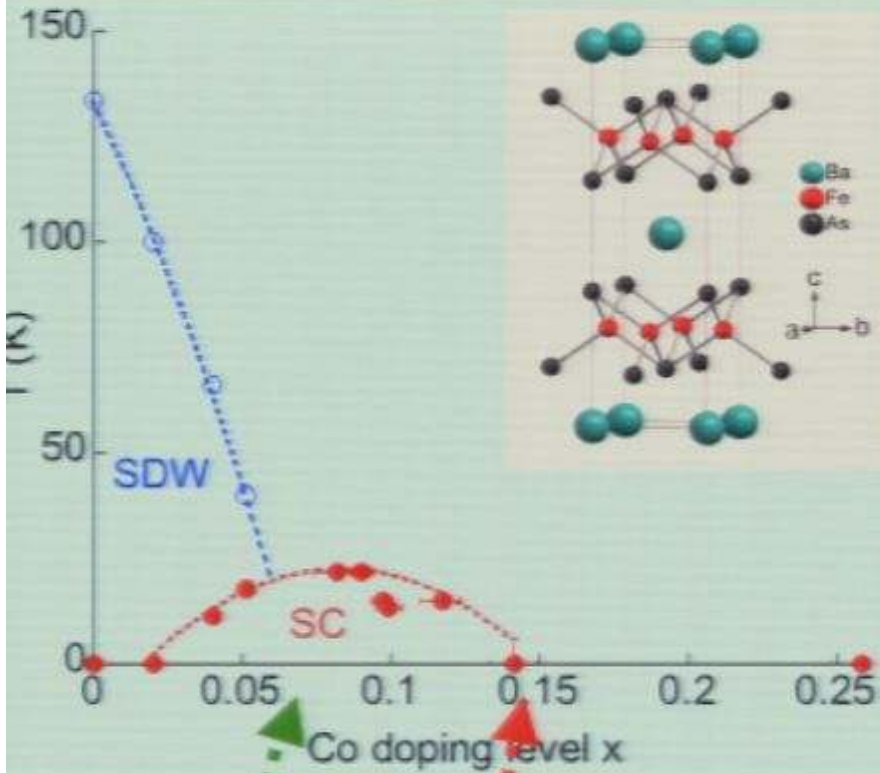
Sponsors at McMaster : NSERC, CFI, CIFAR



Ning *et al.* PRL 104 (2010) 037001.

Imai *et al.* PRL 102 (2009) 177005.

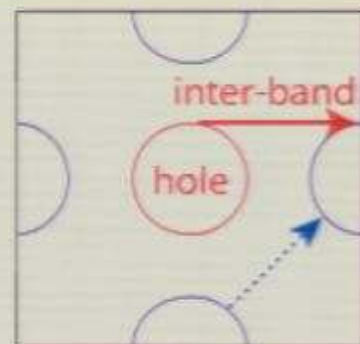
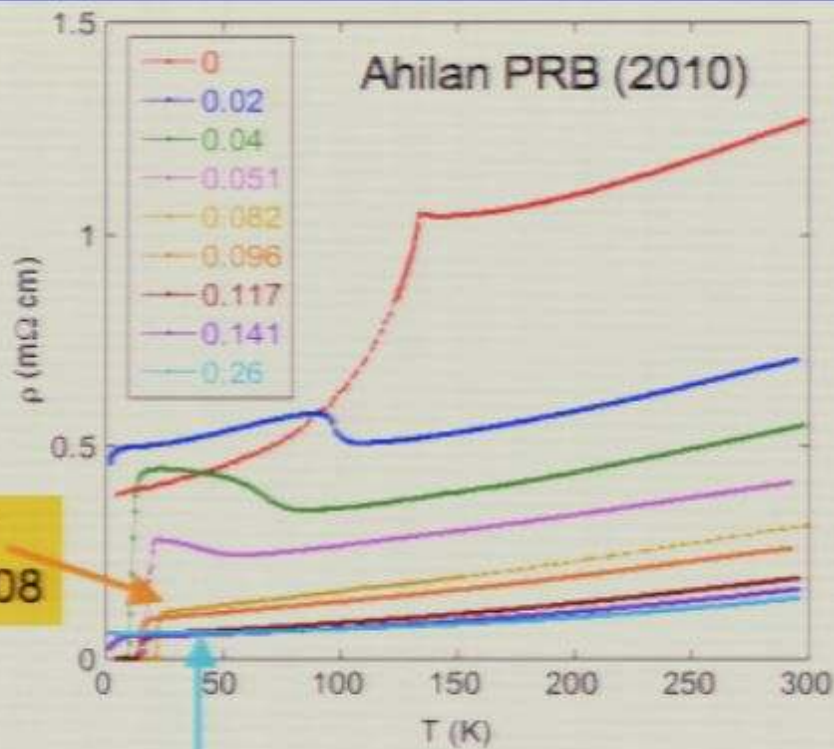
# Electronic Phase Diagram of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



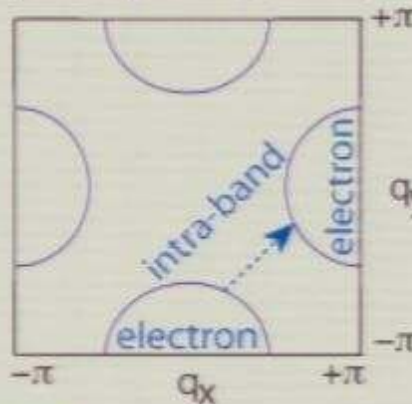
Hole pockets near the  $\Gamma$  point (almost) disappear in the overdoped non-superconducting regime  $x > 0.15$

Sekiba *et al.* NJP 2009

# Contrasting behavior between underdoped and overdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



$x < 0.15$  (superconducting)  
Nested with  $\Delta\mathbf{q} \sim (\pi/a, 0)$



$0.15 < x$   
(non-superconducting)

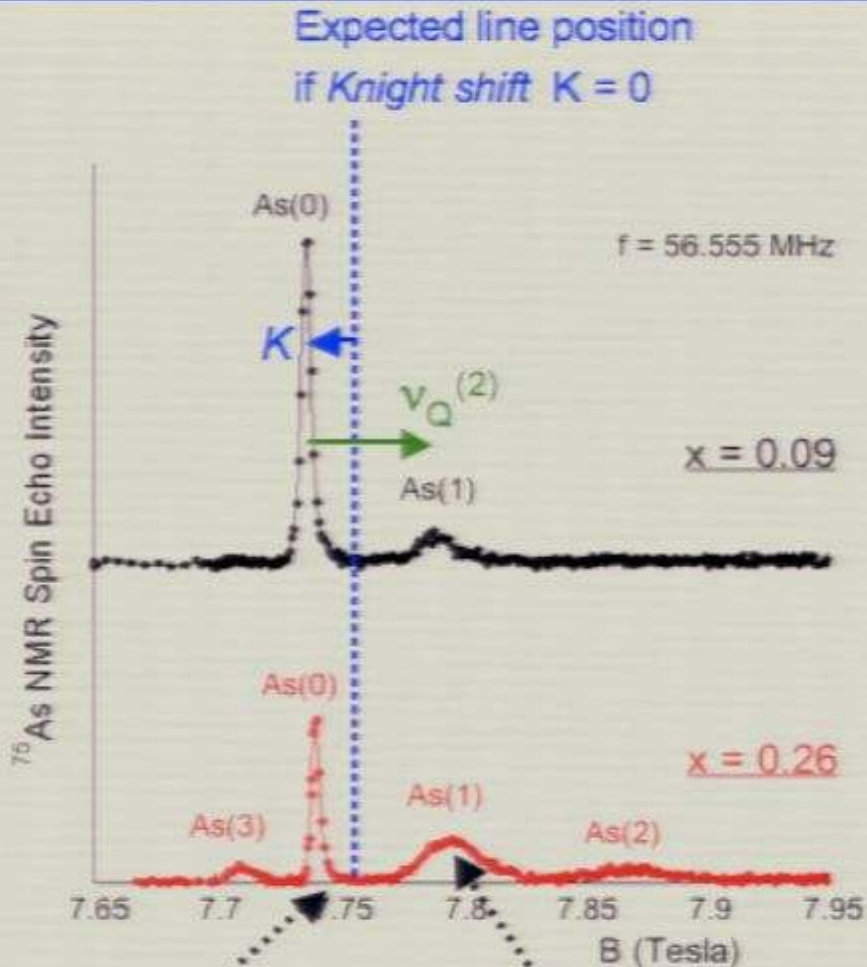
$x = 0.26$  :  
Non-superconducting, paramagnetic metal;  $\rho_{ab} \sim T^2$

## Key Questions (and our Answers based on NMR measurements) :

- 1)  $\rho_{ab} \sim T$  in the normal state above  $T_c$  for  $x=0.08$  ; spin fluctuations enhanced? ----- Yes.
- 2)  $\rho_{ab} \sim T^2$  for  $x=0.26$ ; Fermi liquid ? ----- Maybe.
- 3) How does the change of Fermi surface geometry affect spin fluctuations? Any correlation with the emergence of superconductivity? ----- Clear correlation.

# $^{75}\text{As}$ NMR Lineshapes for $I_z = +1/2$ to $-1/2$ central transition : multiple As sites depending on Co occupancy at n.n. sites

Ning PRL (2010)



- NMR resonance frequency

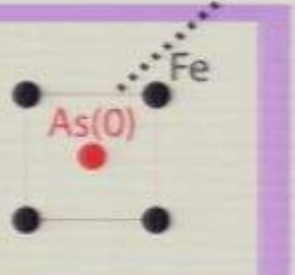
$$f = \gamma_n B(1 + K) + \nu_Q^{(2)}$$

where Knight shift,

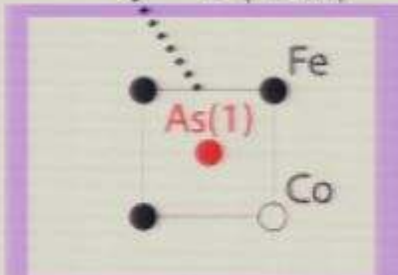
$$K(T) = K_{\text{spin}}(T) + K_{\text{chem}} = A_{\text{hf}} \chi_{\text{spin}}(\mathbf{q}=0) + K_{\text{chem}}$$

- The line splitting between As(N) sites is caused primarily by different **second order nuclear quadrupole effects**,  $\nu_Q^{(2)}$ , in different nearest neighbor site configurations.

- **Knight shift  $K$**  is identical between different As(N) sites, *i.e.* Co does not induce localized moments in their vicinity. This finding is very different from the case of Zn doped high  $T_c$  cuprates.



All 4 n.n. sites



One n.n. site

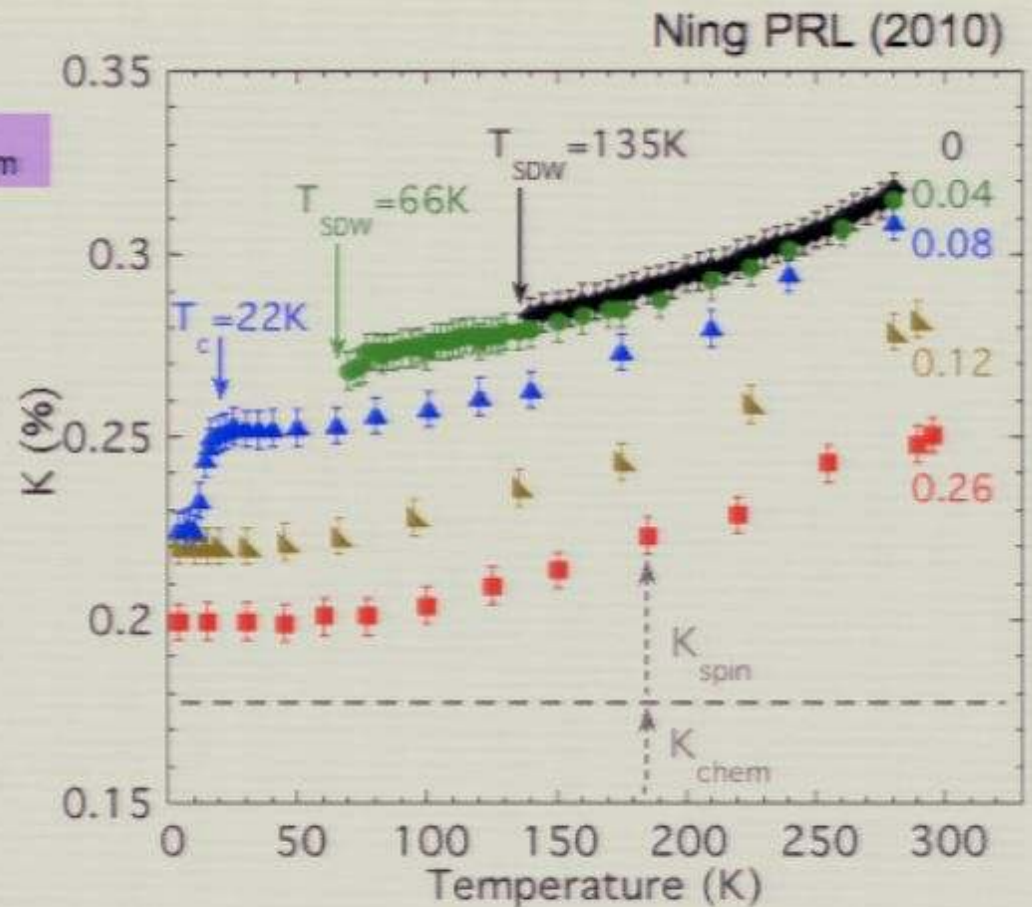
# $^{55}\text{As}$ NMR Knight shift measurements of local uniform spin susceptibility $\chi_{\text{spin}}(\mathbf{q}=0)$ in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

"Knight shift"

$$K(T) \equiv K_{\text{spin}}(T) + K_{\text{chem}} = A_{\text{hf}} \chi_{\text{spin}}(\mathbf{q}=0) + K_{\text{chem}}$$

Hyperfine coupling constant

Chemical shift  
Temperature independent  
(Concentration dependent)



The uniform spin susceptibility  $\chi_{\text{spin}}(\mathbf{q}=0)$  decreases with  $T$ , then levels off below  $\sim 100\text{K}$ .

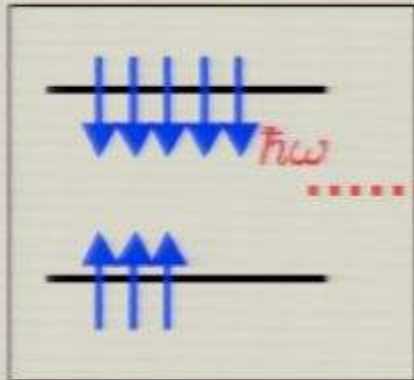
Consistent with AF short range order and/or pseudo-gap ( $\Delta/k_B \sim 450\text{K}$ ) behavior.

Qualitatively the same behavior for all compositions regardless of the nature of the ground state.

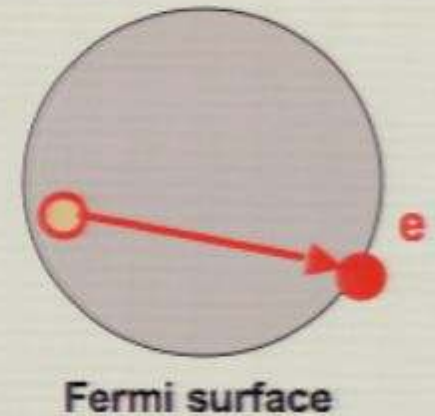
Notes:  $\text{LaFeAs}(\text{O},\text{F})$  and  $\text{FeSe}$  show qualitatively the same behavior as well (Ahilan PRB2009, Imai PRL2009)

# $1/T_1$ (spin-lattice relaxation rate) probes low energy excitations / fluctuations

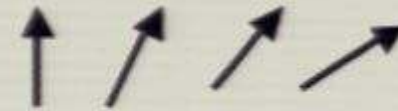
Excited nuclear spins damp excess energy to....



conduction electrons  
(electron-hole pair excitations)



Magnons,  
Spin fluctuations  
etc.

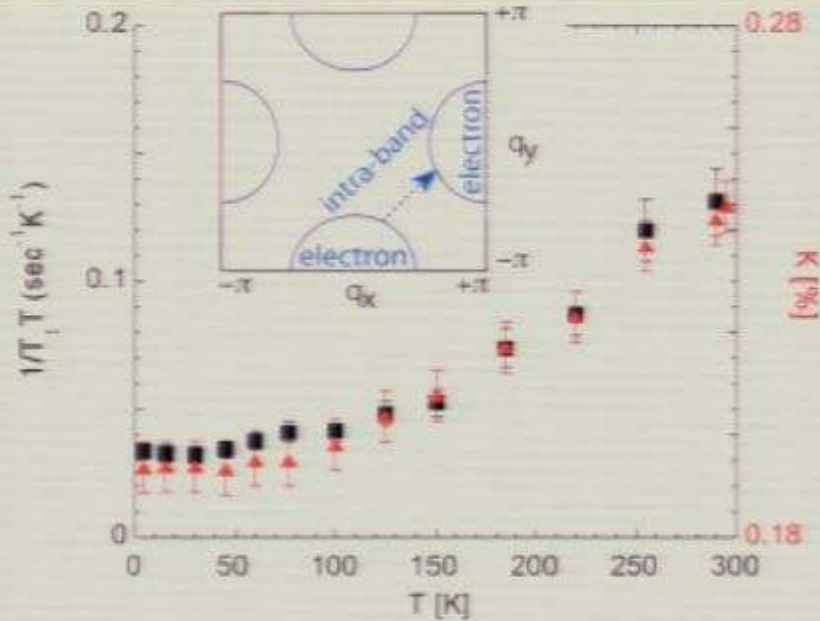


$$\frac{1}{T_1 T} \propto \sum_{q \in 1st B.Z.} |A(q)|^2 \chi''(q, f)$$

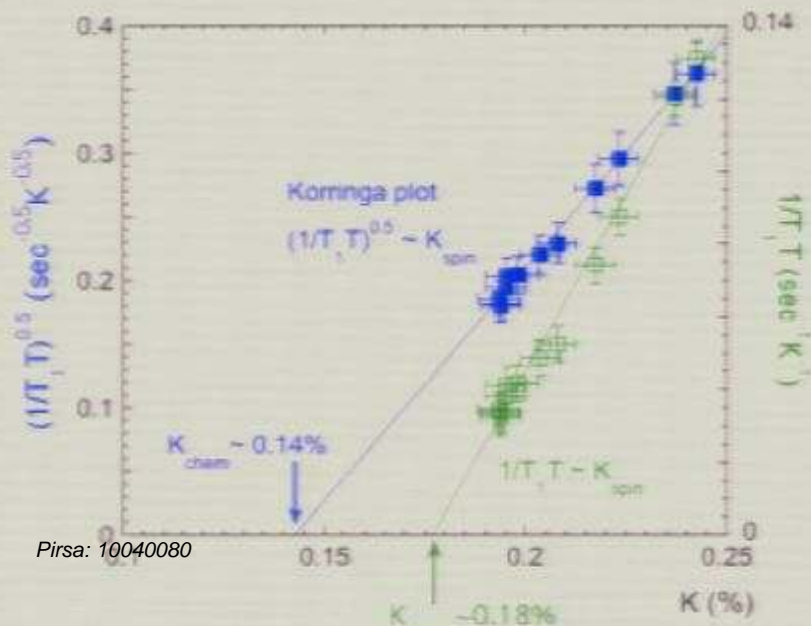
“Hyperfine form factor”

$1/T_1 T$  probes the  $q$ -integral in the B.Z. of the low frequency component of spin fluctuations,  $\chi''$

# Overdoped Ba(Fe<sub>0.74</sub>Co<sub>0.26</sub>)<sub>2</sub>As<sub>2</sub> non-superconductor : Fermi liquid?



- $1/T_1T$  and  $K$  show qualitatively the same  $T$ -dependence, *i.e.* Low energy components of spin excitations decrease with temperature, then level off in the entire  $q$ -space.



- Consistent with the “Korringa relation” for canonical Fermi liquids,

$$K_{\text{spin}} \sim \chi_{\text{Pauli}} \sim N(E_F),$$

$$1/T_1T \sim N(E_F)^2,$$

hence

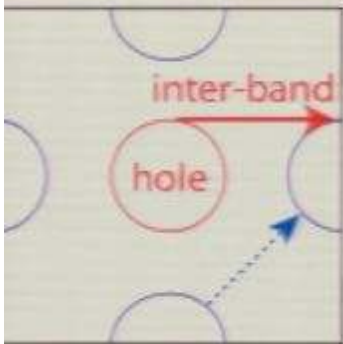
$$(1/T_1T)^{0.5} \sim K_{\text{spin}} + K_{\text{chem}}$$

although we can't rule out overdamped magnons,

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# Spin fluctuations in superconducting and underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

Ning *et al.* PRL (2010)



$$\Delta\mathbf{q} \sim (\pi/a, 0)$$

**Underdoped regime ( $x < 0.08$ ):**

$1/T_1T$  shows divergent behavior at  $T_{\text{SDW}}$  due to the critical slowing down of spin fluctuations with  $\Delta\mathbf{q} \sim (\pi/a, 0)$ .

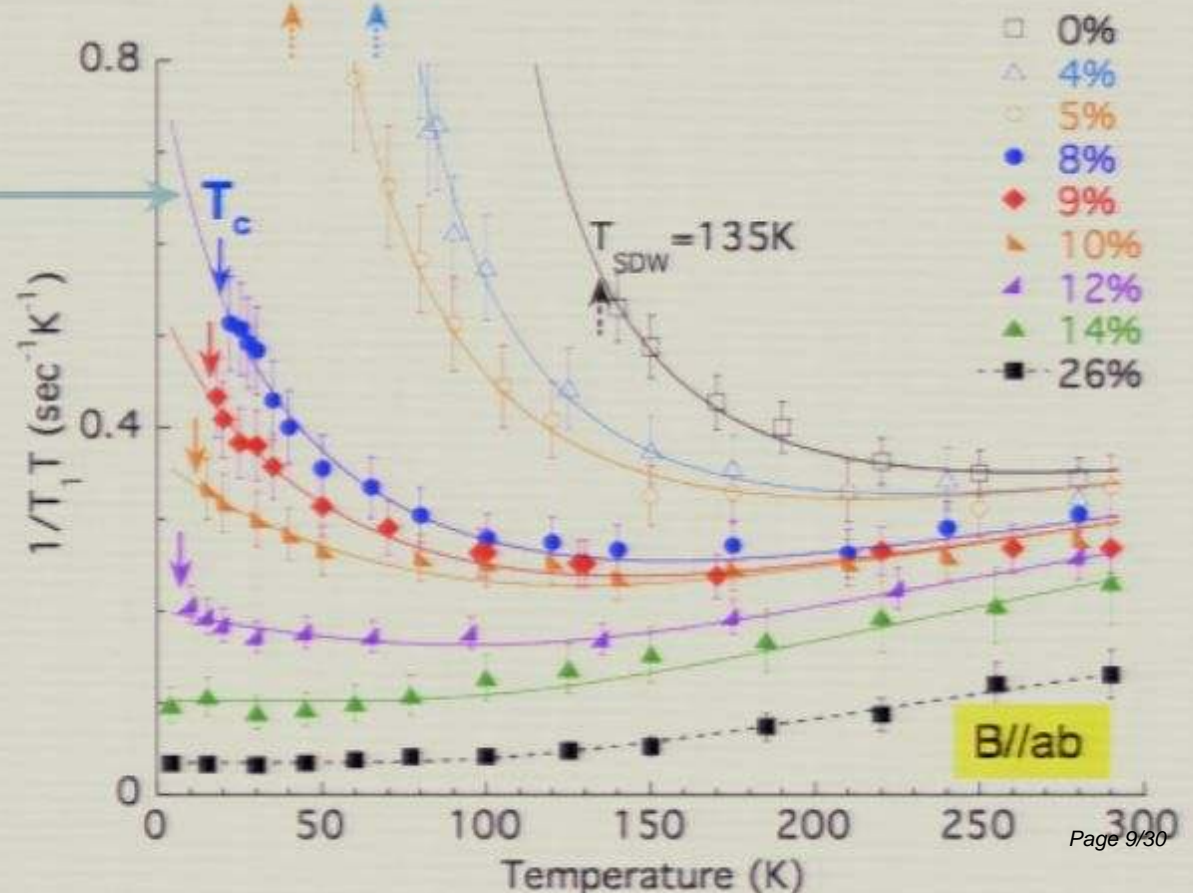
**Superconducting regime ( $0.08 < x < 0.12$ ):**

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**Solid curves: Curie-Weiss fit with a background term**

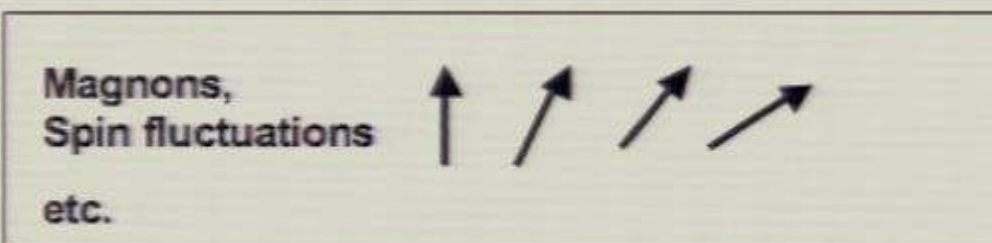
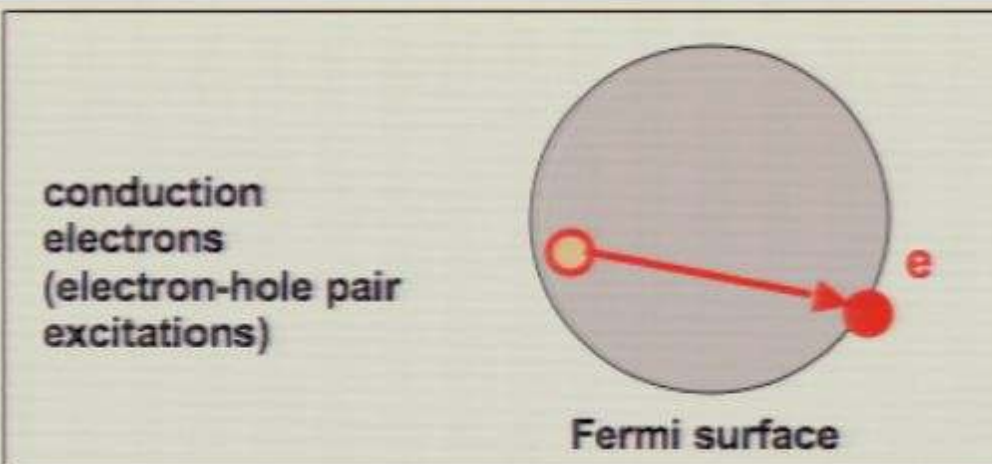
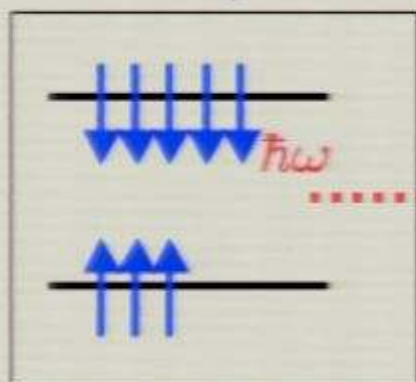
$$\frac{1}{T_1T} = \frac{C}{T + \theta} + A \cdot \exp\left(-\frac{\Delta}{k_B T}\right)$$

Pirsa: 10040080



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Excited nuclear spins damp excess energy to....

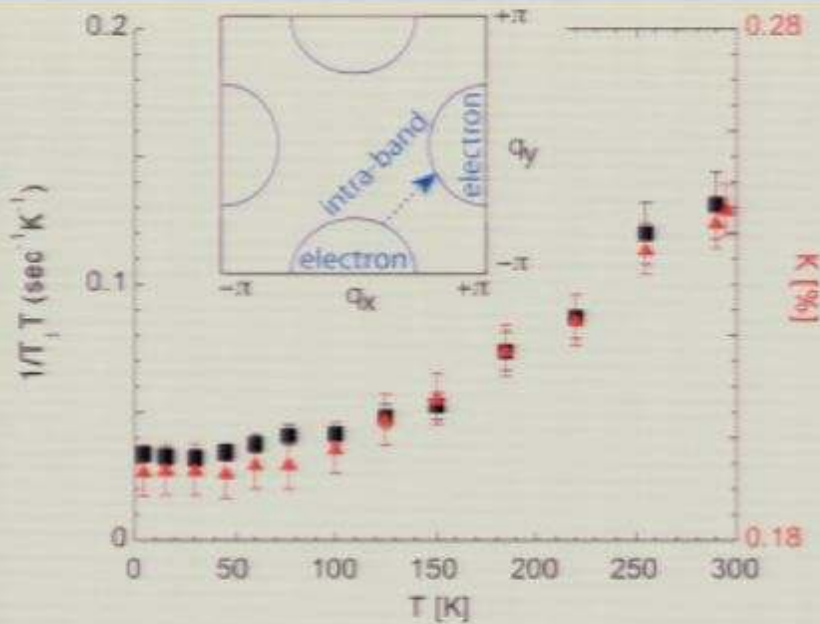


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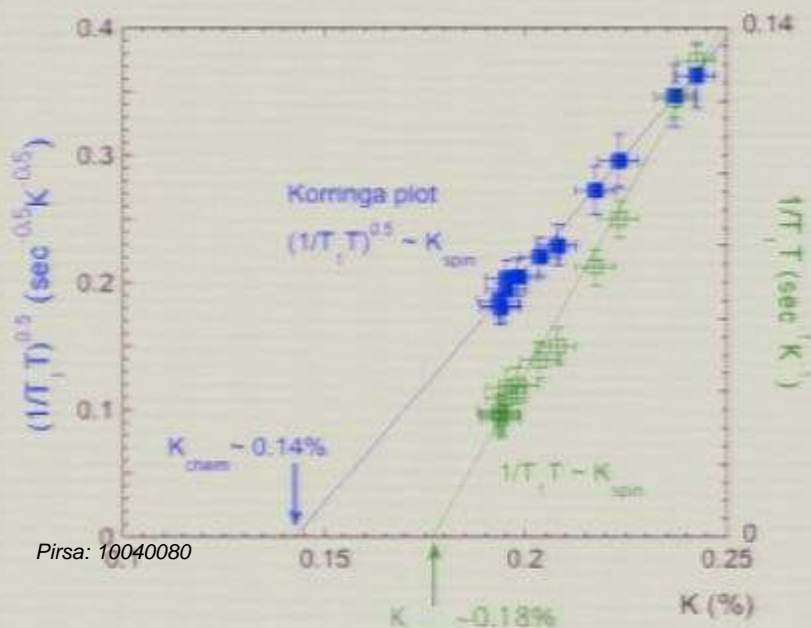
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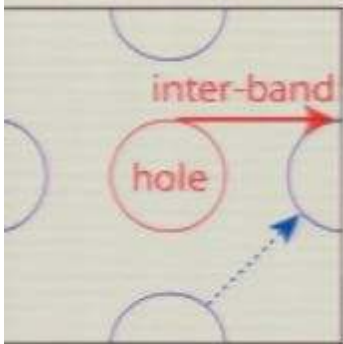
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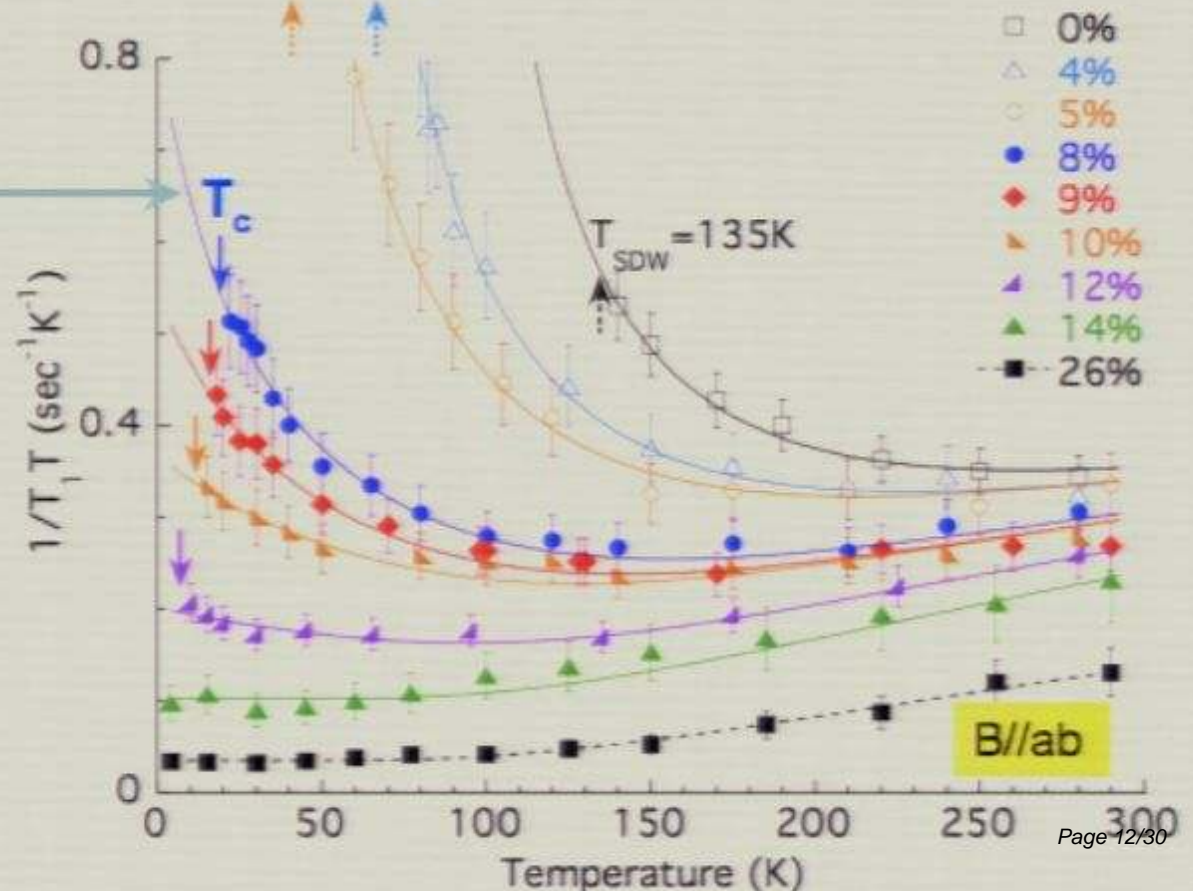
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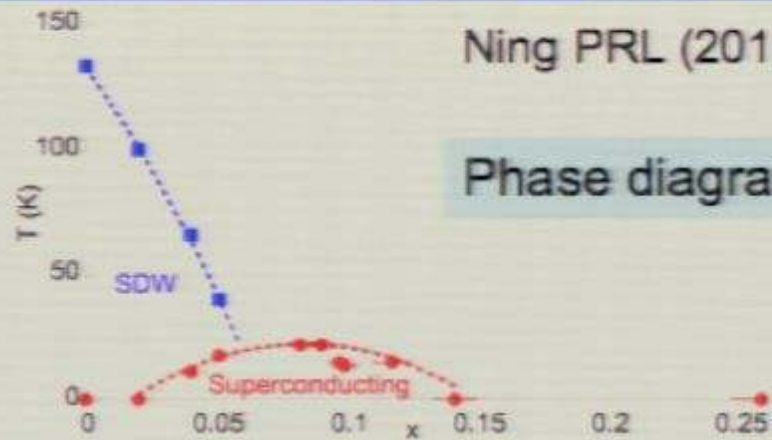
Pirsa: 10040080



# Correlation between $T_c$ , antiferromagnetic spin fluctuations, and the Fermi surface geometry in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (Hole band emerges below $x \sim 0.15$ )

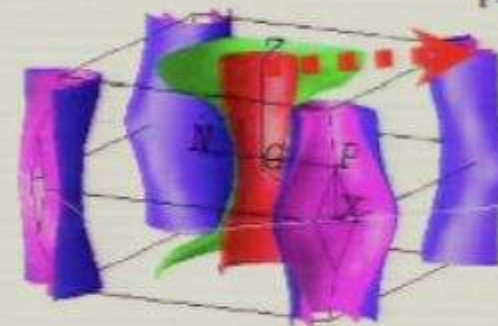
Ning PRL (2010)

Phase diagram

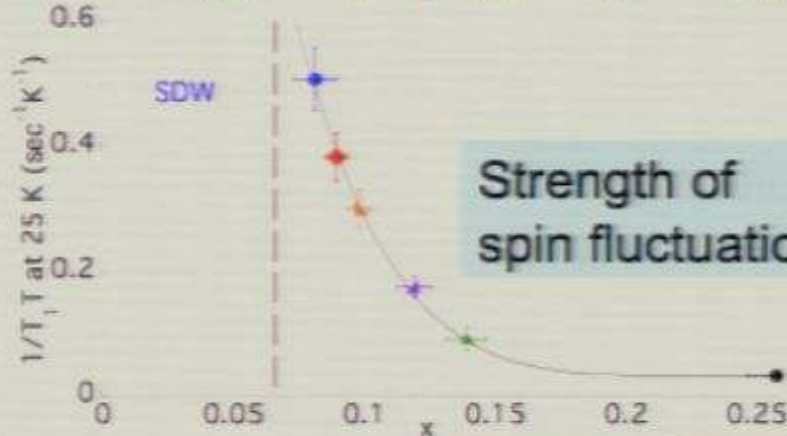


Fermi surface geometry of  $\text{BaFe}_2\text{As}_2$  and "nesting"

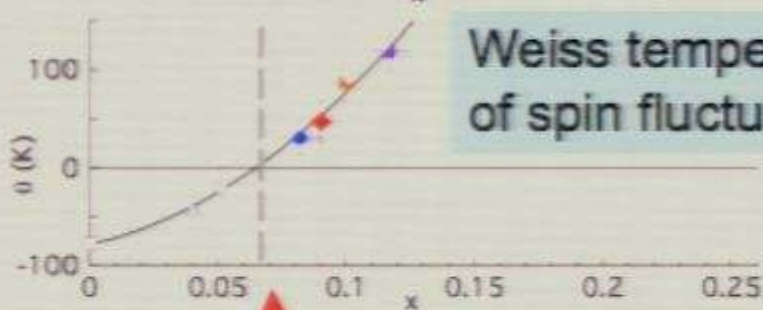
Kaminski



Strength of spin fluctuations at 25K

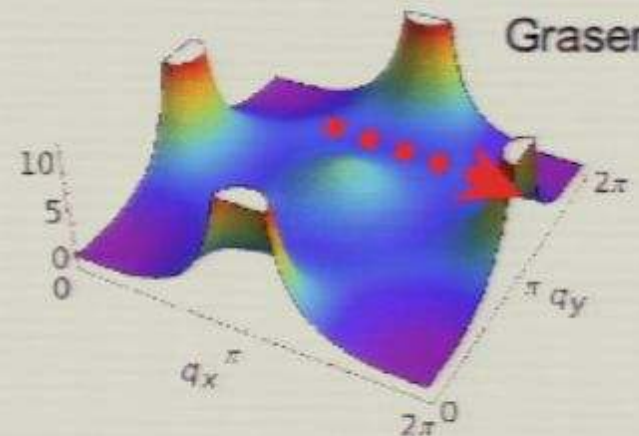


Weiss temperature  $\theta$  of spin fluctuations



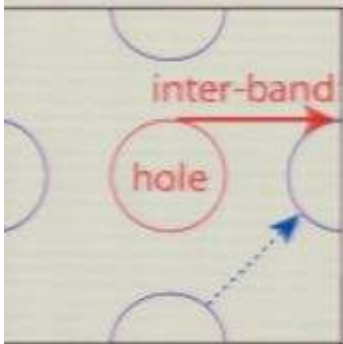
$$\chi_{\text{RPA}}(q_x, q_y)|_{k_z=\pi}$$

Graser



# Spin fluctuations in superconducting and underdoped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

Ning *et al.* PRL (2010)



$$\Delta\mathbf{q} \sim (\pi/a, 0)$$

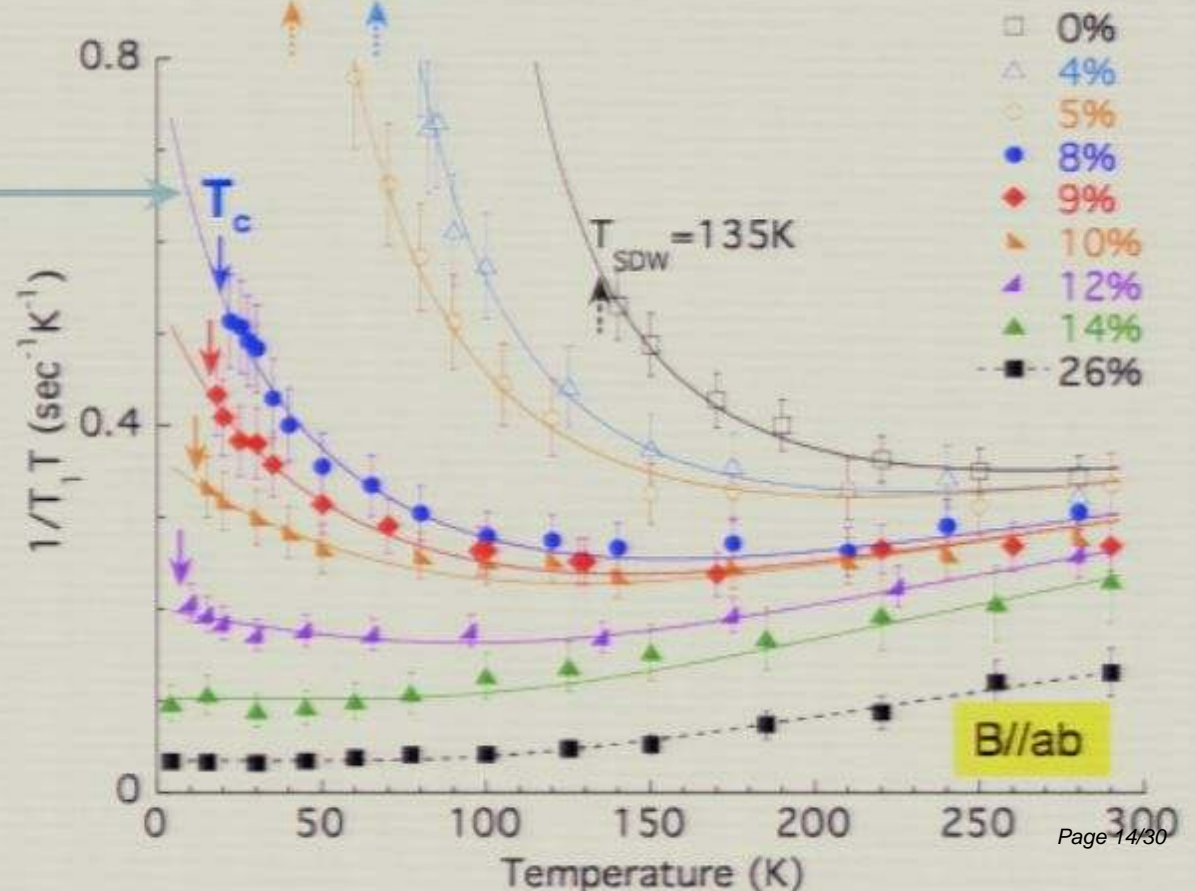
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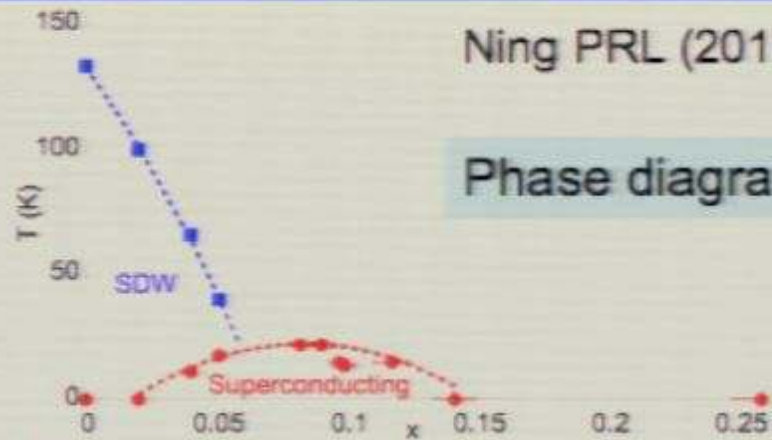
Pirsa: 10040080



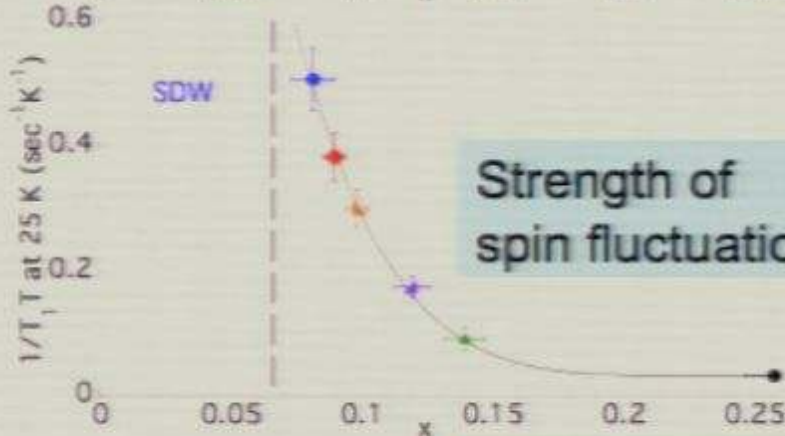
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Ning PRL (2010)

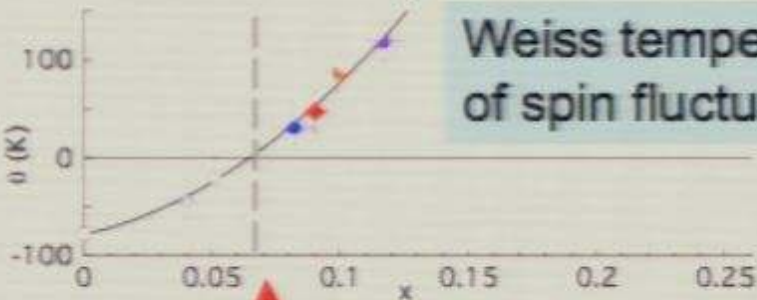
Phase diagram



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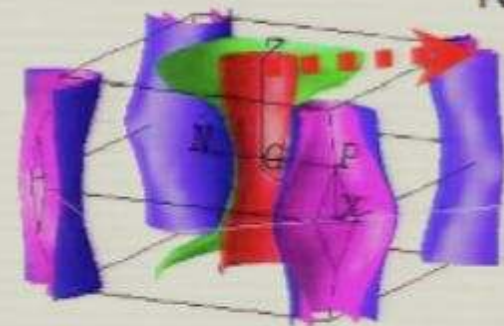


Weiss temperature  $\theta$  of spin fluctuations



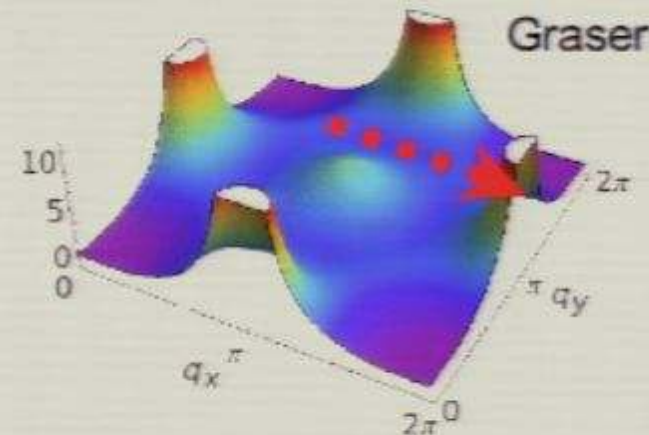
Fermi surface geometry of  $\text{BaFe}_2\text{As}_2$  and "nesting"

Kaminski



$$\chi_{\text{RPA}}(q_x, q_y) |_{k_z=\pi}$$

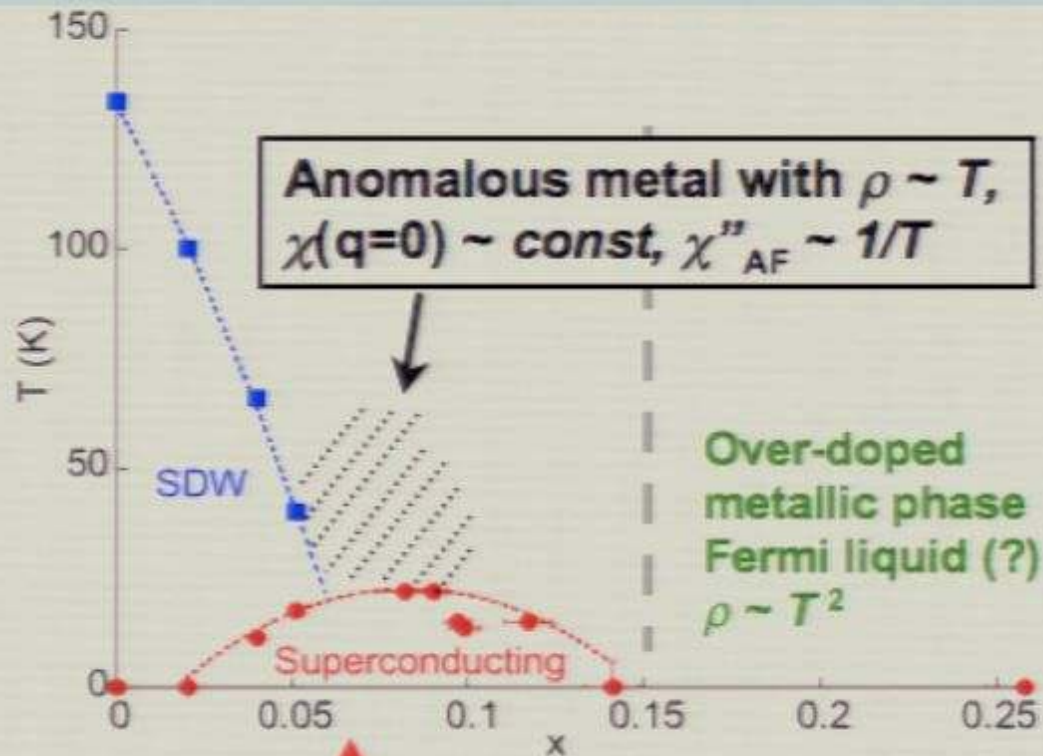
Graser



# Spin fluctuations mediate superconductivity in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (?)

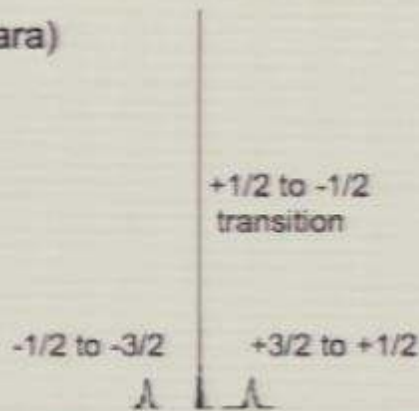
**Superconductivity** is optimized when **SDW** is barely suppressed.

FeSe show very similar behavior (see below).



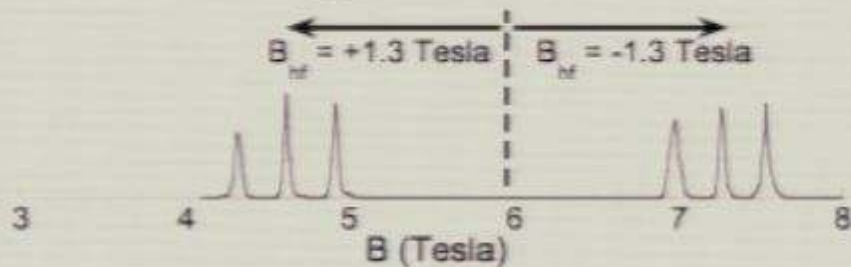
# SDW ordered state under the presence of Co=2%

x=0 at 145 K (para)



Ning *et al.*, PRB 79 (2009) 140506 (R)

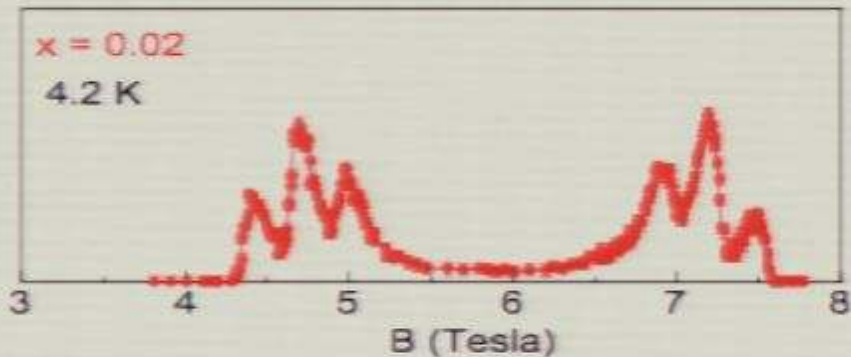
x=0 at 77 K ( $< T_{SDW}$ )



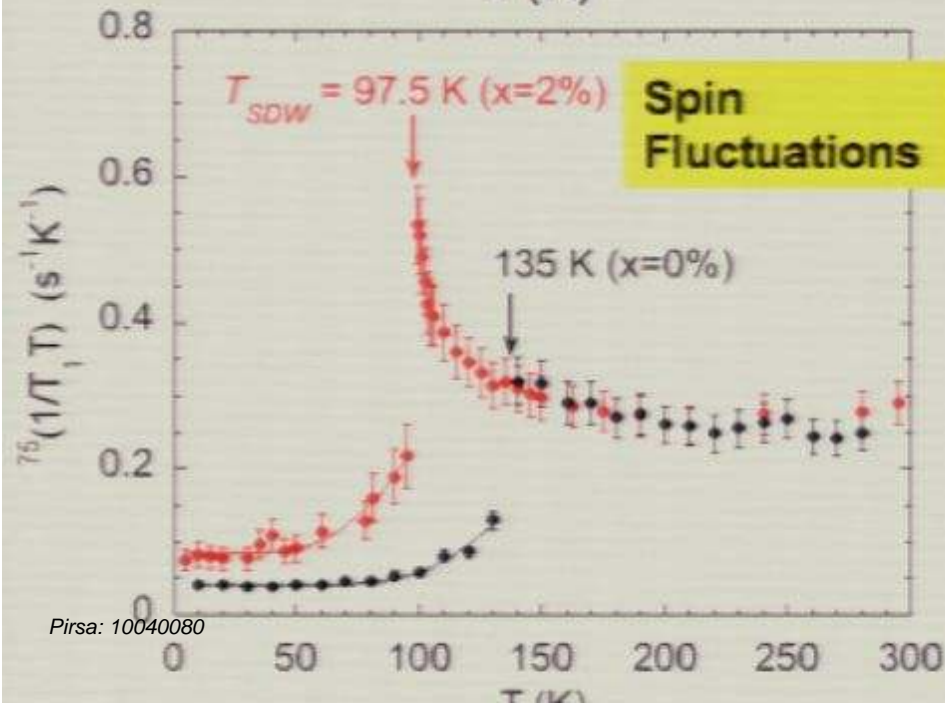
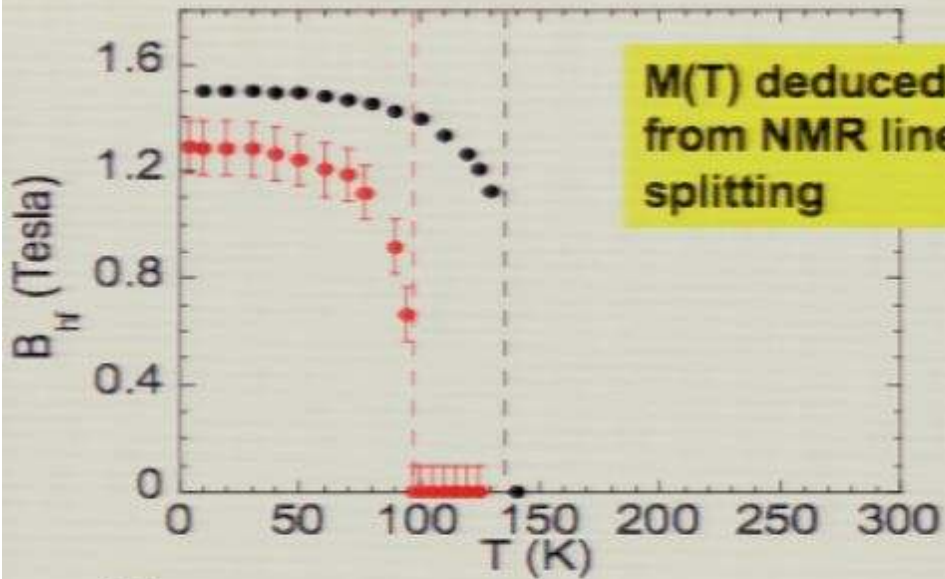
**x=0** : Commensurate SDW below  $T_{SDW}=135$ K.  
 $^{75}\text{As}$  NMR shows bi-modal splitting due to two discrete values of static hyperfine magnetic field

$$B_{hf} \sim M(T)/A_{hf}$$

**x=0.02**: Continuum between the peaks, i.e. continuous distribution of  $M(T)$ . Note that some  $^{75}\text{As}$  nuclear spins see zero hyperfine fields (i.e. locally  $M=0$ ). **Consistent with incommensurate SDW and/or disorder.**



# Spin fluctuations in the SDW ordered state with Co = 2%



## • Low temperature limit

Spin fluctuations die out, and Korringa law is approximately valid;

$$\frac{(1/T_1 T)_{2\%}}{(1/T_1 T)_{0\%}} \approx \left( \frac{\tilde{N}(E_F)_{2\%}}{\tilde{N}(E_F)_{0\%}} \right)^2 \approx 2$$

$\tilde{N}(E_F)$ : DOS below  $T_{SDW}$  from reconstructed Fermi surface

## • Finite temperatures below $T_{SDW}$

Fit with activation law

$$\frac{1}{T_1 T} \approx a + b \exp\left(-\frac{\Delta}{k_B T}\right)$$

with

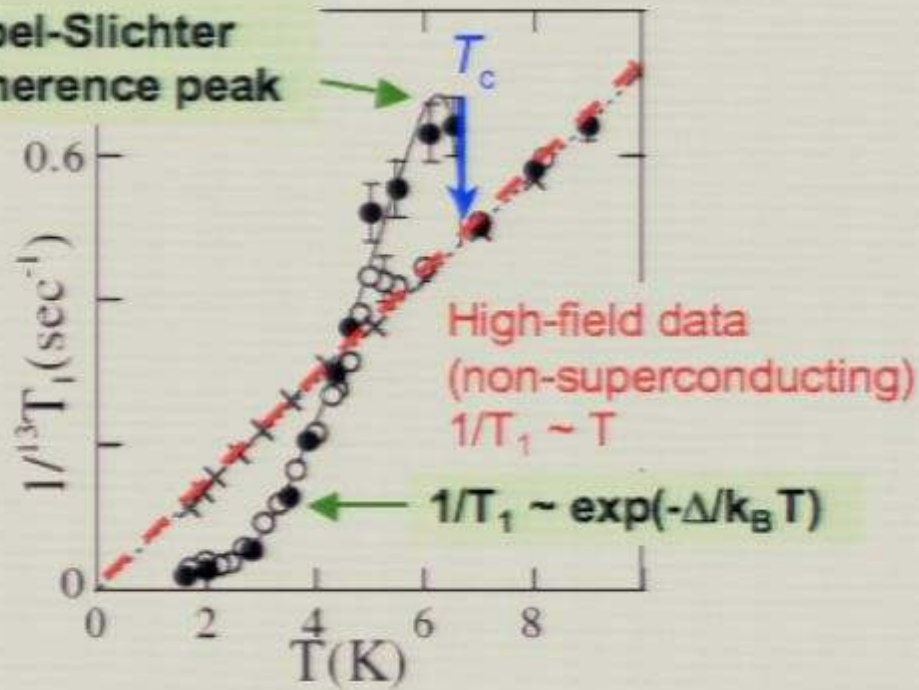
$$\Delta/k_B \sim 330\text{K} \quad \text{for } x = 2\%$$

$$640\text{K} \quad \text{for } x = 0\%$$

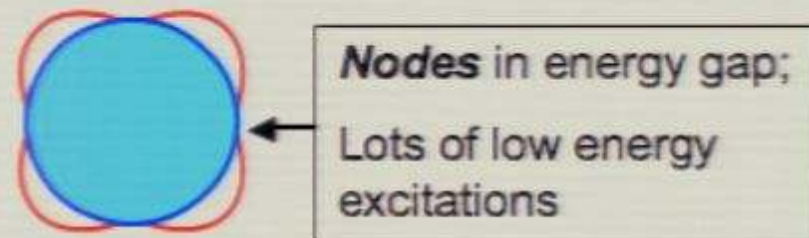
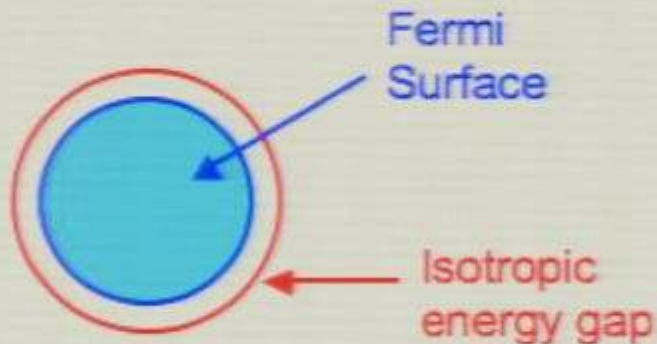
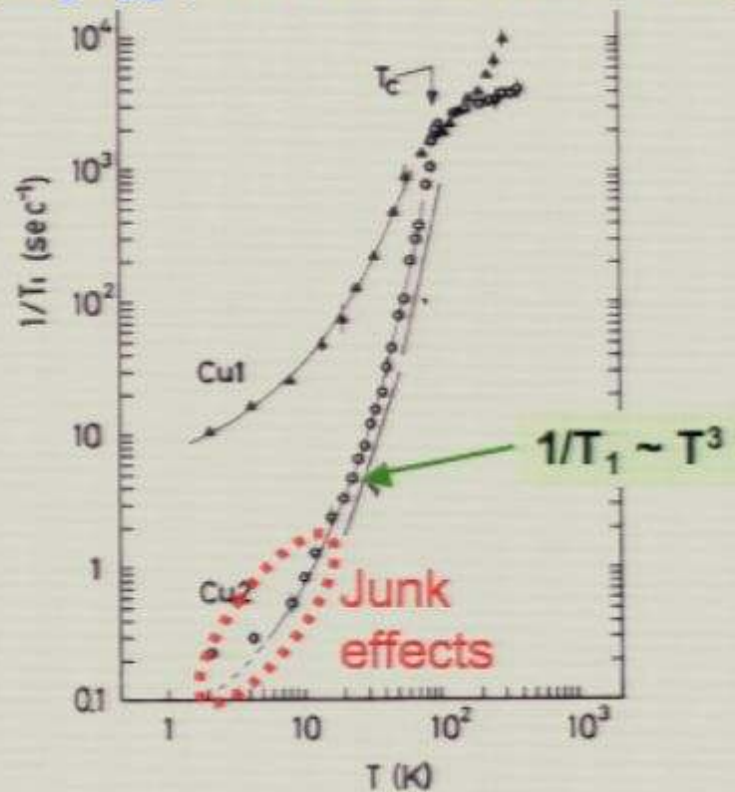
# Example of $1/T_1$ in superconductors

**MgCNi<sub>3</sub>** (Singer, Imai, Cava PRL 2001)

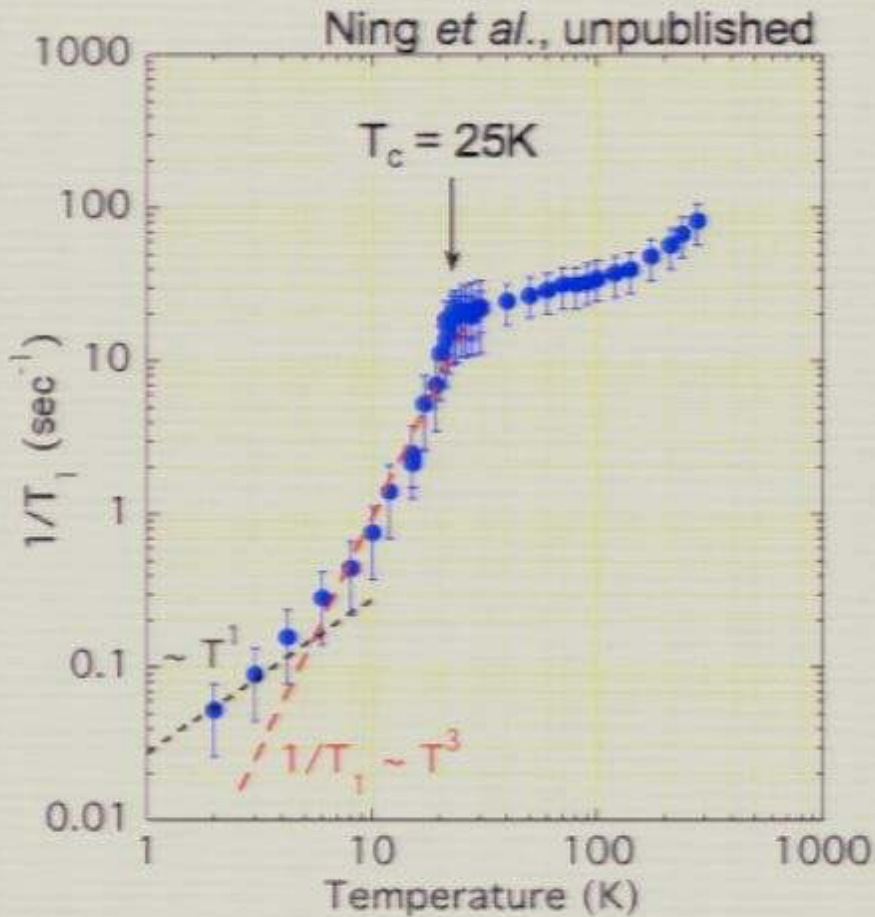
Hebel-Slichter  
Coherence peak



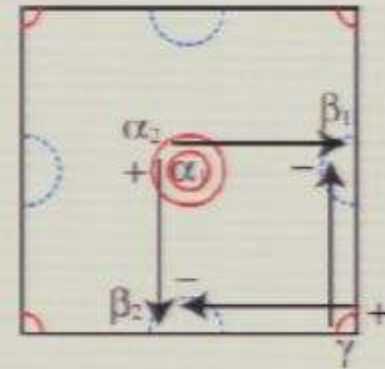
**YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.9</sub>** (Imai, Yasuoka JPSJ 1988)



# Symmetry of the superconducting energy gap in $\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2$

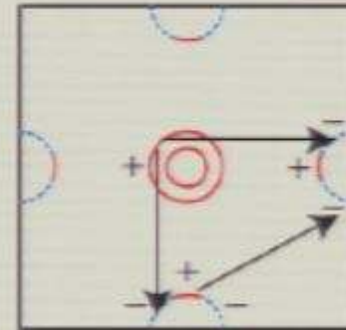


fully gapped  $s \pm$  wave



Kuroki *et al.*  
PRB 79(2009)  
244511

nodal  $s \pm$  wave

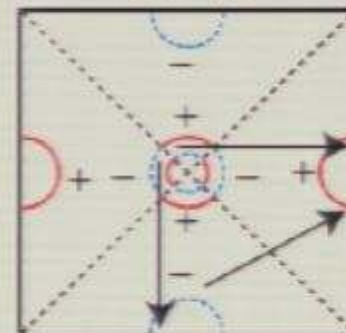


Mazin, Singh  
*et al.*  
PRL(2008)

Ikeda *et al.*  
JPSJ (2008)

And many  
others

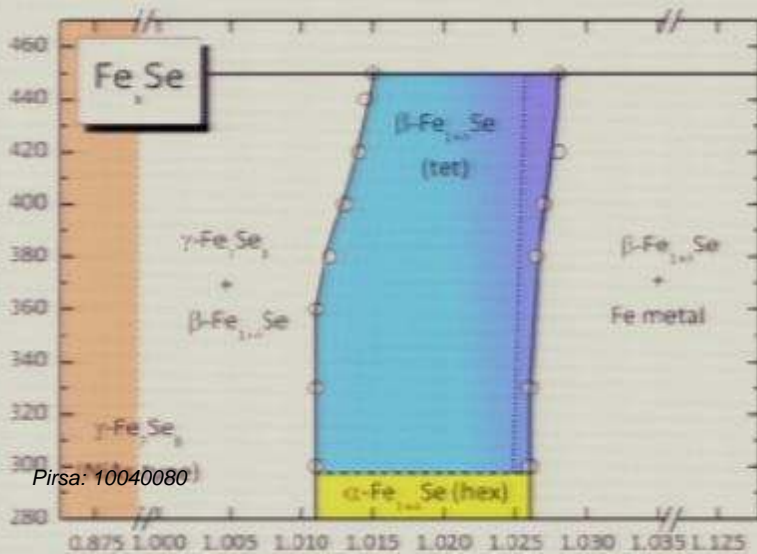
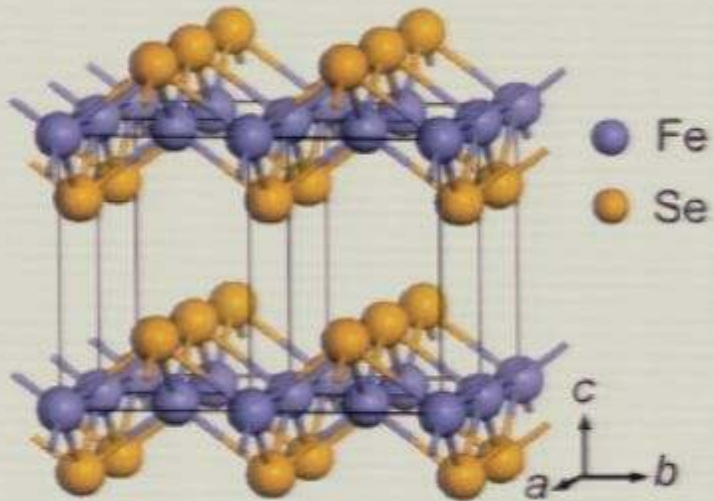
d-wave



- 1) No Hebel-Slichter coherence peak expected for conventional BCS  $s$ -wave systems.
- 2) Consistent with a power-law (but inconclusive).
- 3) Similar to 1111 (Nakai *et al.* JPSJ 2008, Grafe *et al.* PRL 2008)

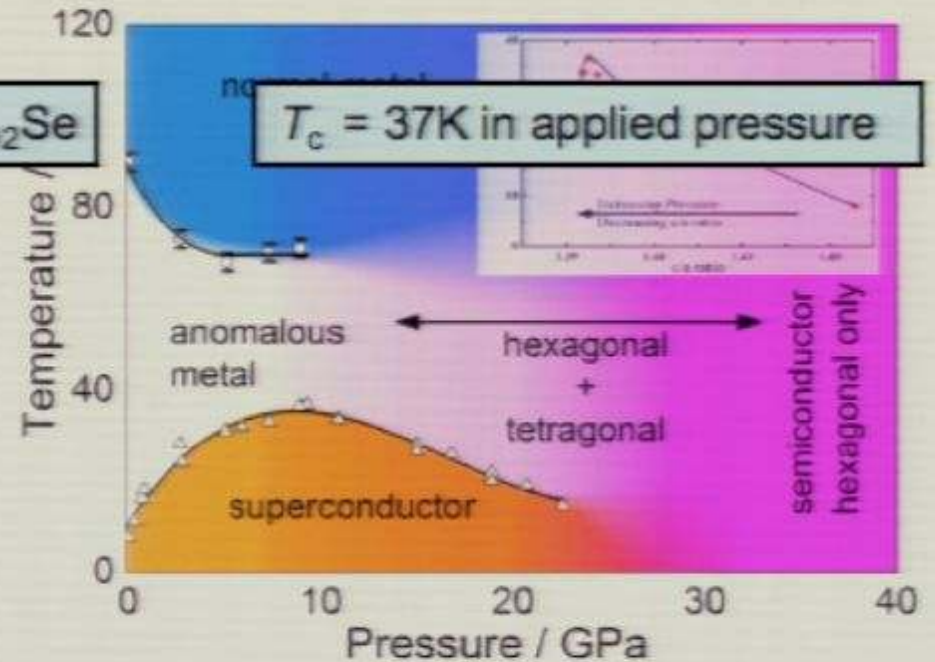
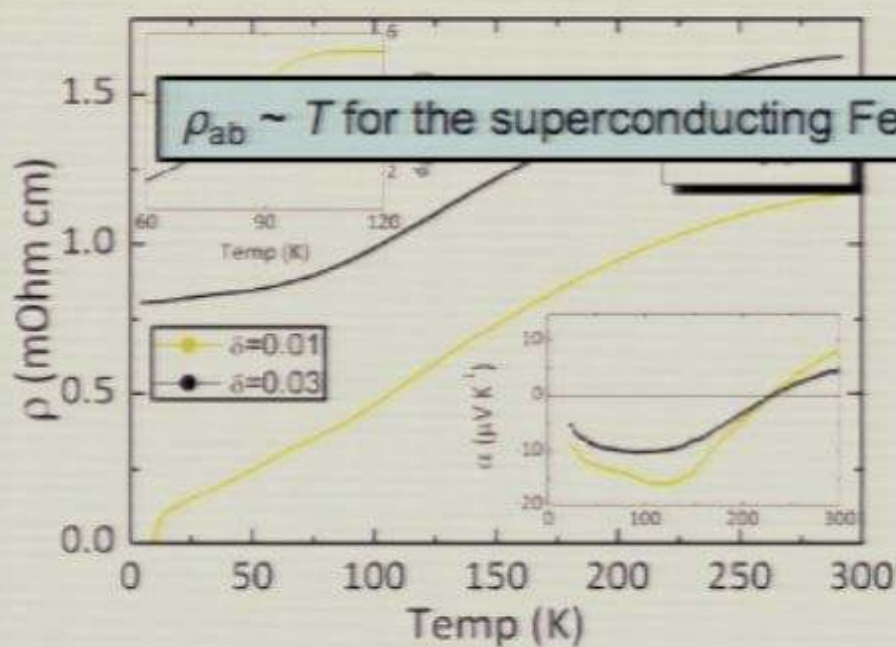
## Comparison with the case of defect-free FeSe

Discovery of superconductivity in nominal  $\text{FeSe}_{1-d}$  with  $T_c \sim 9 \text{ K}$   
Hsu, Wu et al. PNAS 105 (2008)14262



Defect-free FeSe is the clean superconducting phase  
McQueeney, Cava *et al.* PRB (2009)

## Properties of the defect-free FeSe



Medvedev, Cava *et al.* Nature Materials (2009)

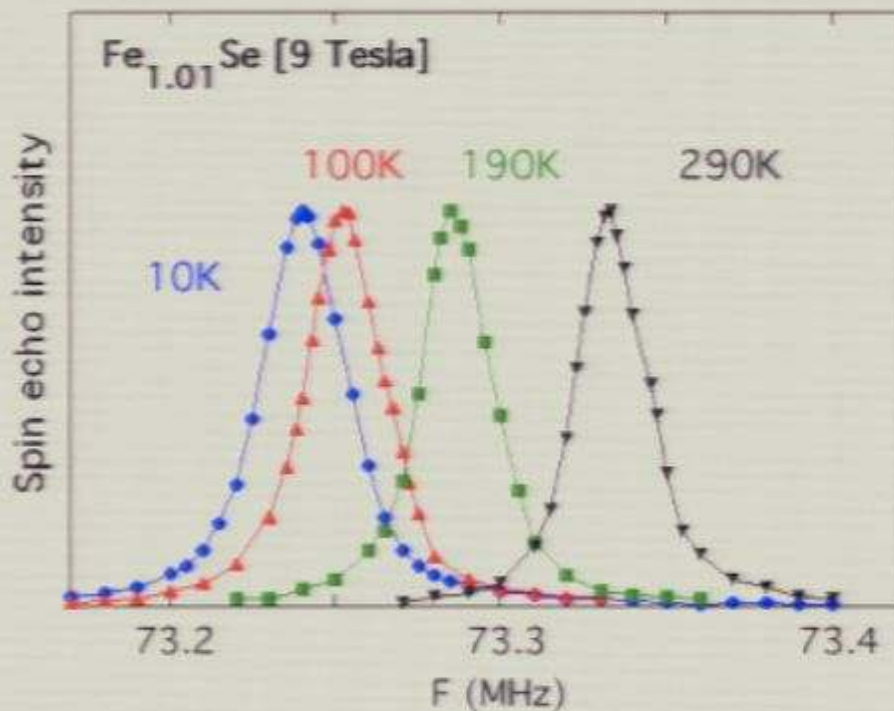
### Key Questions (and answers from NMR)

1. Is FeSe fundamentally different from FeAs superconductors? ---- **No.**
2. Are spin fluctuations enhanced near  $T_c$  in superconducting  $\text{Fe}_{1.01 \pm 0.02}\text{Se}$  as well? ---- **Yes.**
3. Does applied pressure enhance spin fluctuations as well as  $T_c$ ? ---- **Yes.**

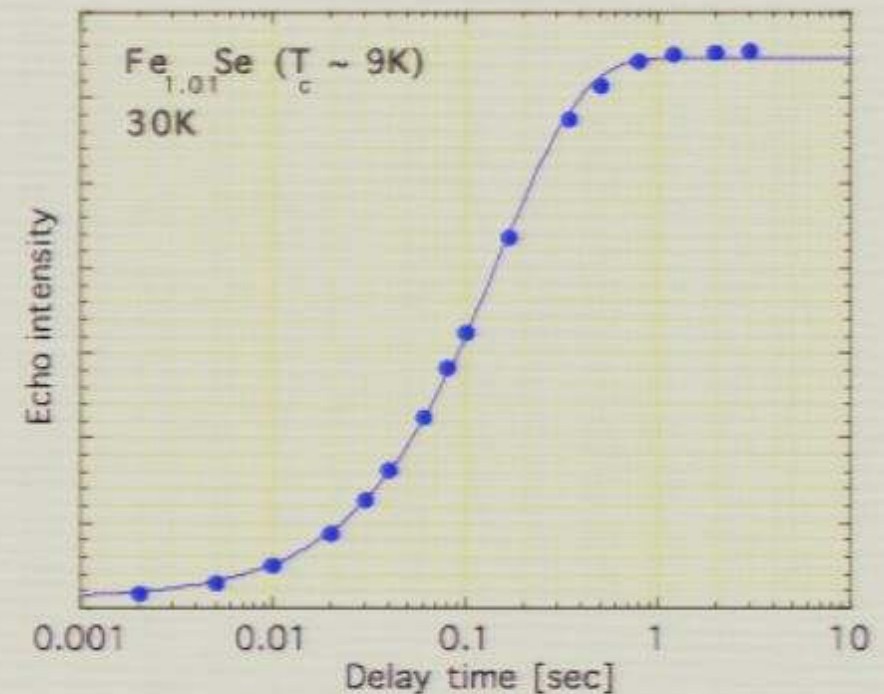
# Very narrow $^{77}\text{Se}$ NMR lineshapes in defect-free Princeton samples

Imai et al. PRL (2009).

Narrow NMR line



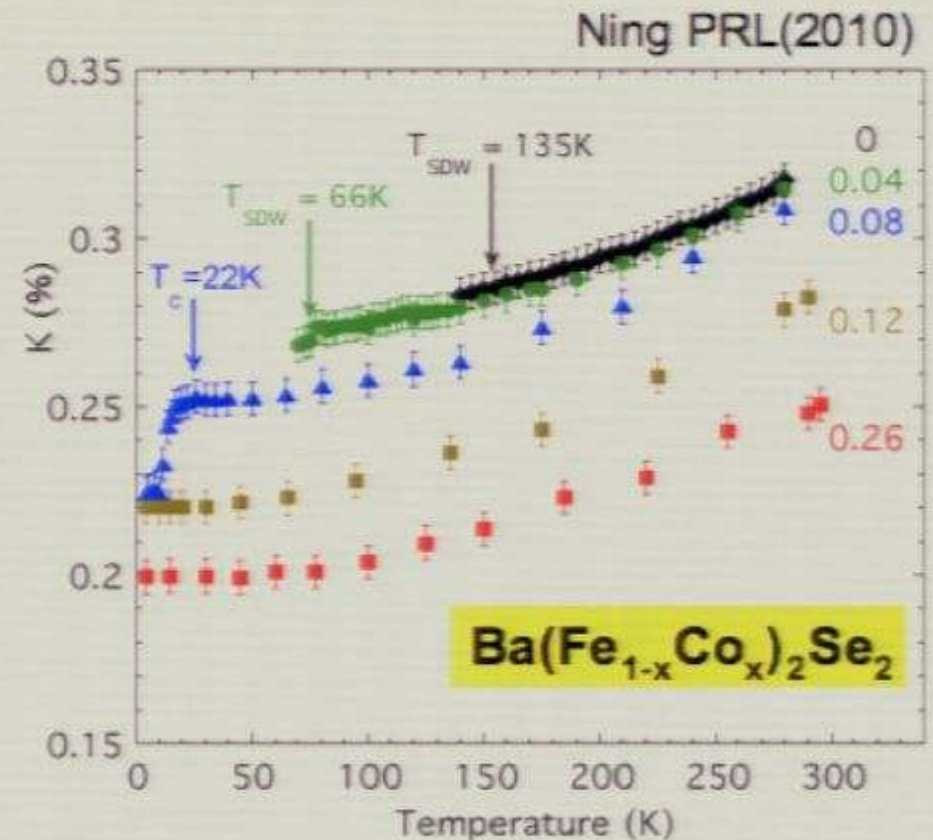
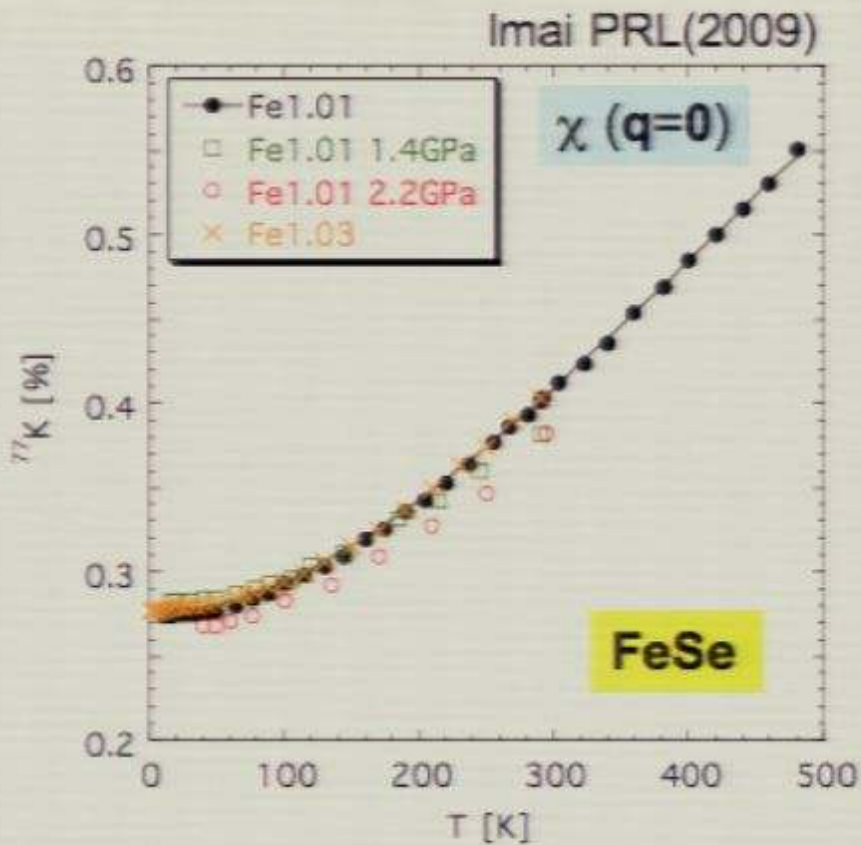
Well-defined T1 with no distribution



Narrower than the NMR lines observed for typical  $\text{FeSe}_{1-d}$  by a factor of  $\sim 4$ ; **Very clean sample.**

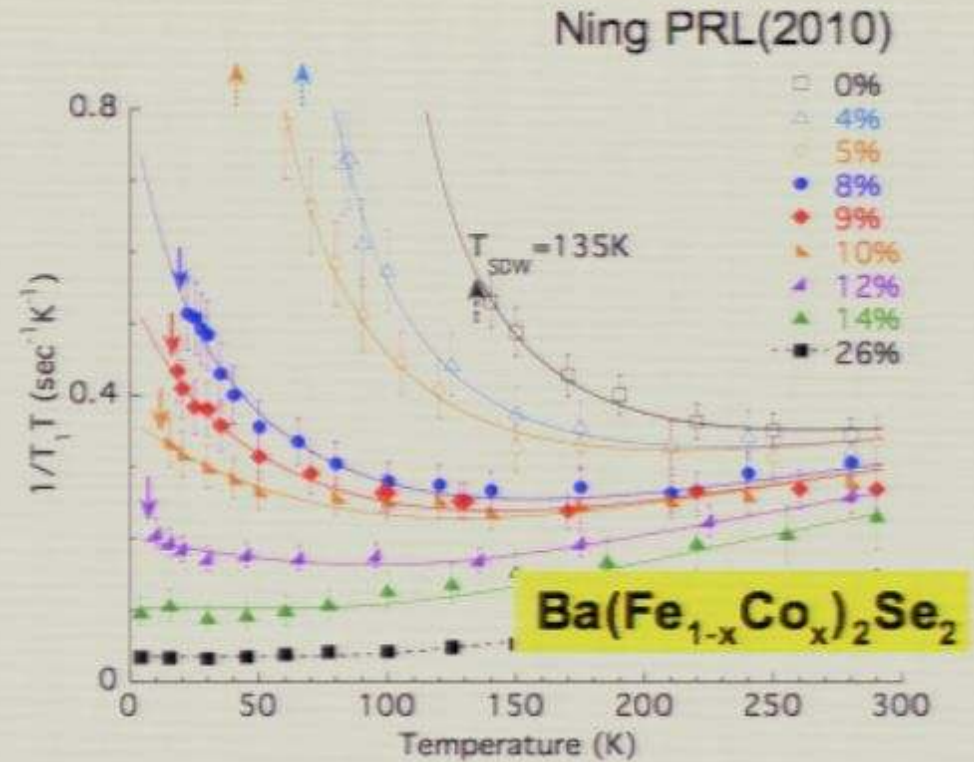
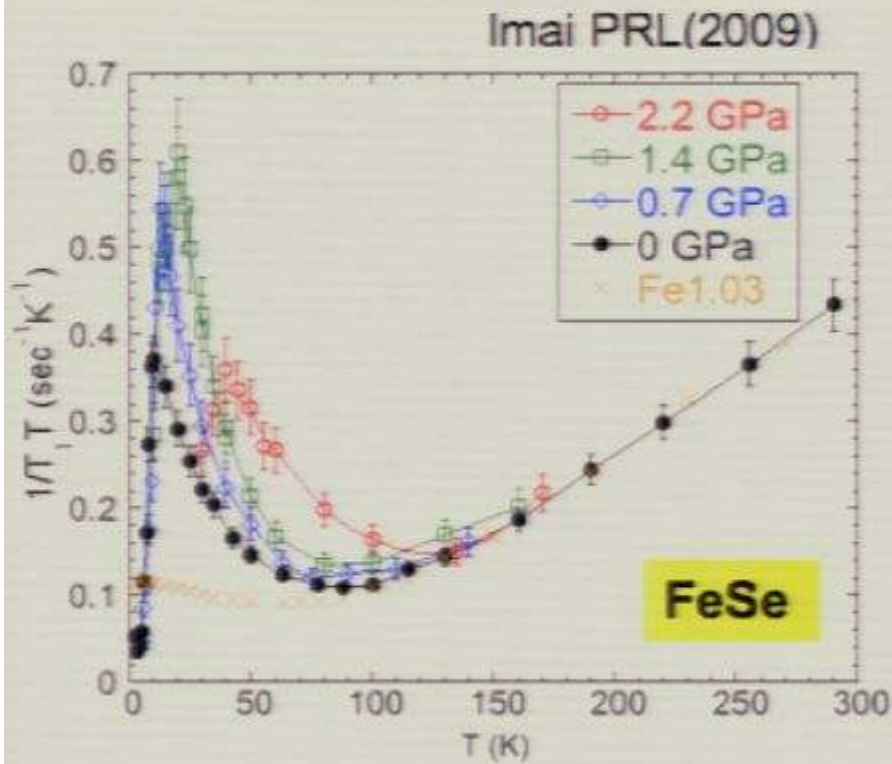
- (Advantage 1) Narrow NMR lines allow us to carry out **accurate Knight shift measurements.**
- (Advantage 2) Narrow NMR lines allow us to carry out accurate measurements of **intrinsic  $1/T_1$**  of the superconducting phase, without distributions of  $T_1$  and/or hole burning.

# Intrinsic spin susceptibility $\chi(q=0)$ as measured by $^{77}\text{Se}$ NMR Knight shift



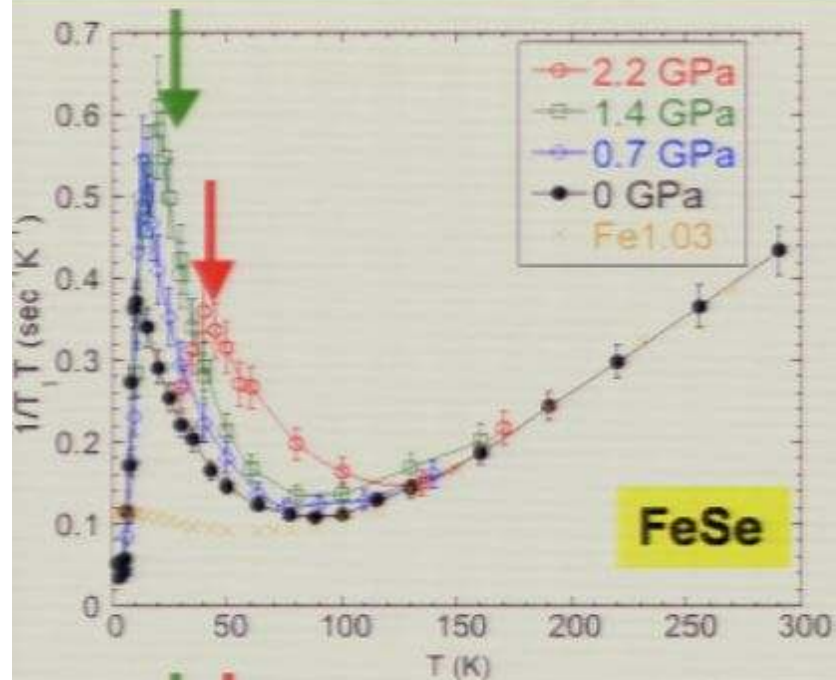
- $\text{FeSe}$  and  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  show qualitatively the same behavior;  $\chi(q=0)$  decreases with  $T$ , then levels off where  $\rho \sim T$ .
- Little pressure or concentration dependencies, if any.

# Spin fluctuations $\chi''(q, \omega)$ as measured by $^{77}\text{Se}$ NMR $1/T_1T$

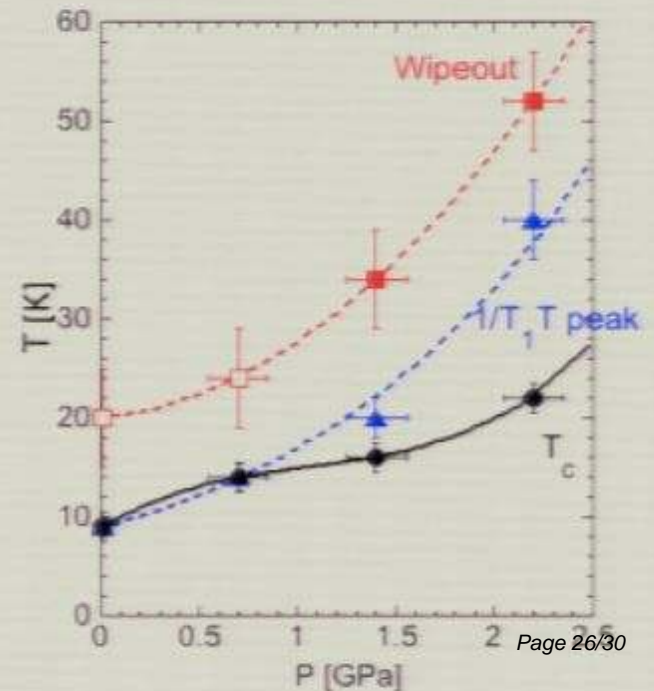
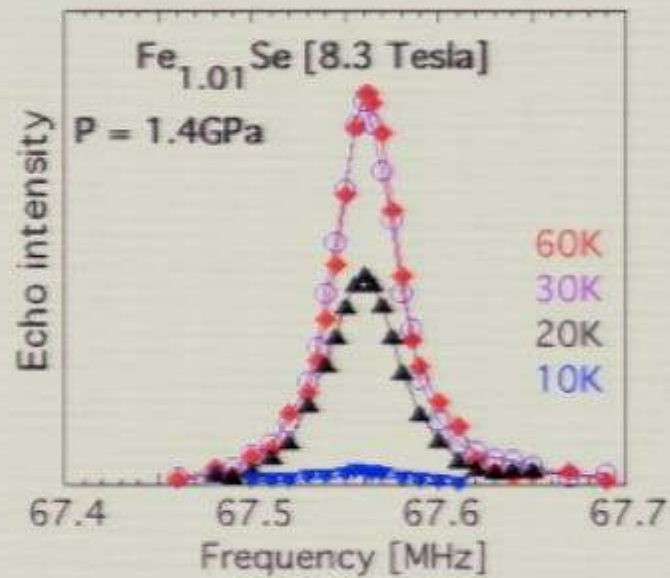
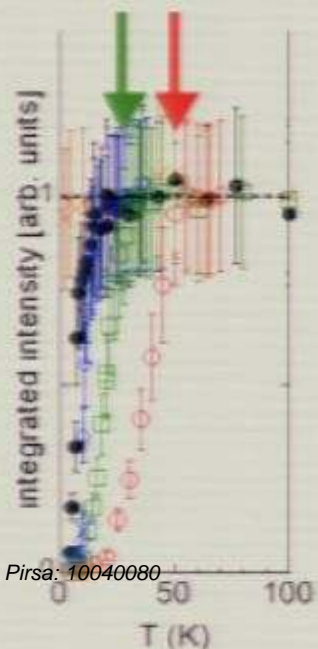


- 1)  $\text{Fe}_{1.01}\text{Se}$  ( $T_c = 9\text{K}$ ): Qualitatively the same behavior as superconducting  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ .
- 2)  $\text{Fe}_{1.03}\text{Se}$  (Non-SC): No enhancement of AFSF at low T; qualitatively the same behavior as overdoped non-SC  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ .
- 3) Low energy spin excitations initially decrease below 300K down to  $\sim 100\text{K}$ , then increase toward  $T_c$ . Curie-Weiss fit below  $\sim 100\text{K}$  gives  $\theta = 30\text{K}$  (0 GPa)  $\sim 10\text{K}$  (0.7GPa) (i.e. on the verge of magnetic order).
- 4) Applied pressure enhances spin fluctuations AND  $T_c$ .

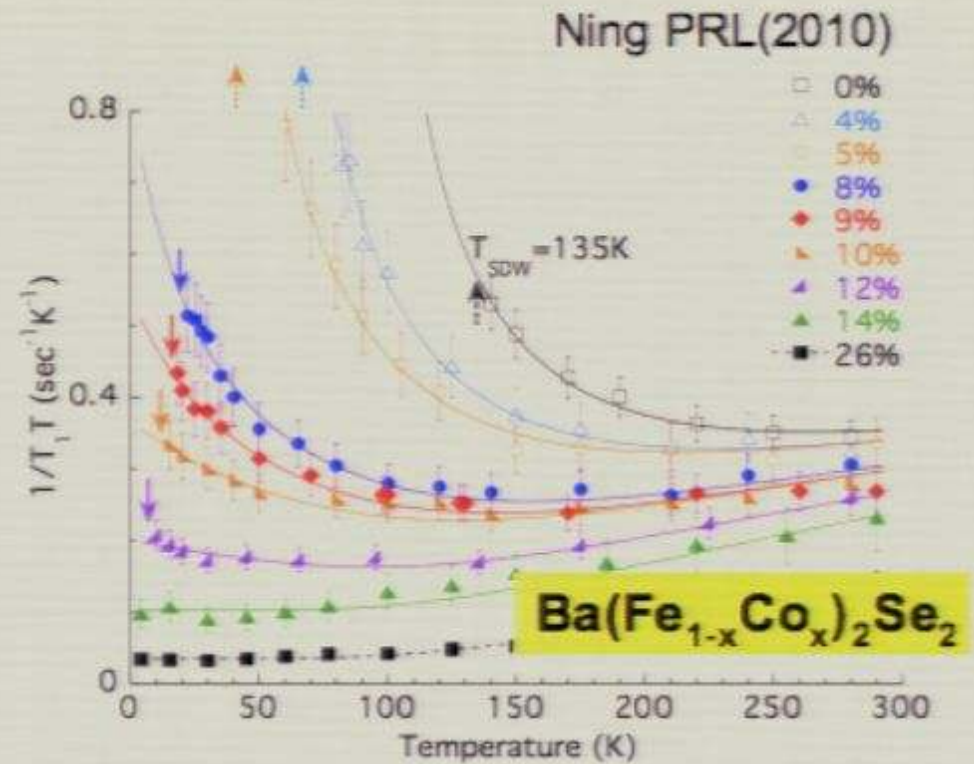
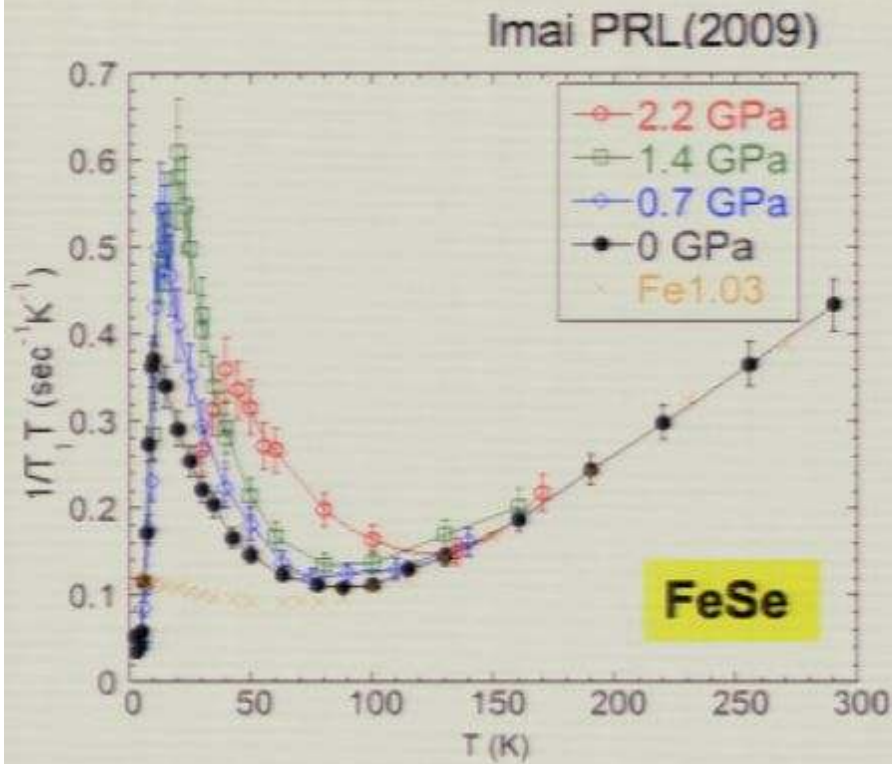
# Complications: NMR signal intensity wipeout; **spin freezing** and/or **phase separation** under pressure $P > 1$ GPa?



- 1)  $1/T_1 T$  shows a peak above  $T_c$  in  $P > 1$  GPa.
- 2) NMR signal intensity decreases below the peak temperature; implying *divergently large  $1/T_1$* , or *line broadening* for unobservable signals
- 3) Non-monotonic increase of  $T_c$  (as emphasized by Kotegawa *et al.* JPSJ 2008)

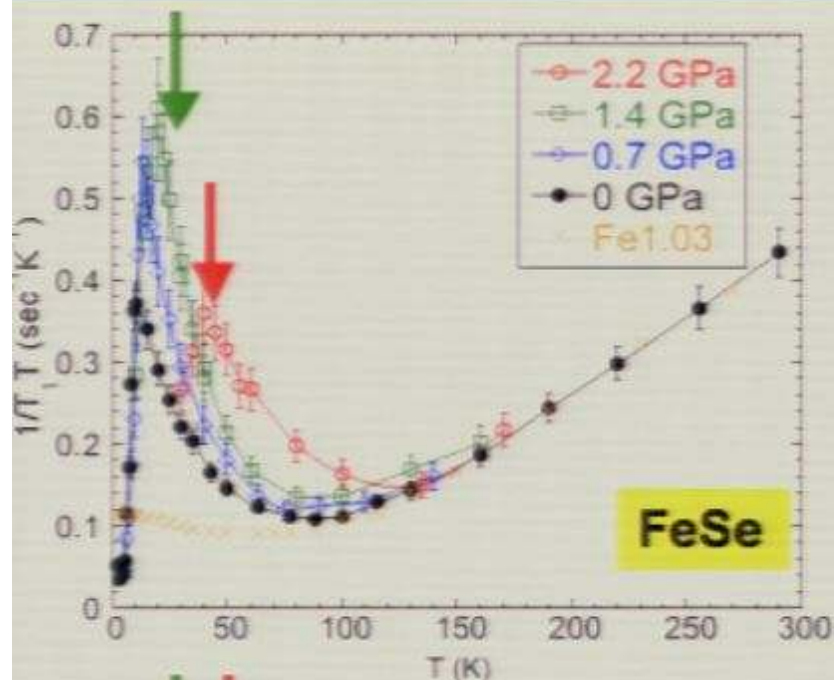


# Spin fluctuations $\chi''(q, \hbar)$ as measured by $^{77}\text{Se}$ NMR $1/T_1T$

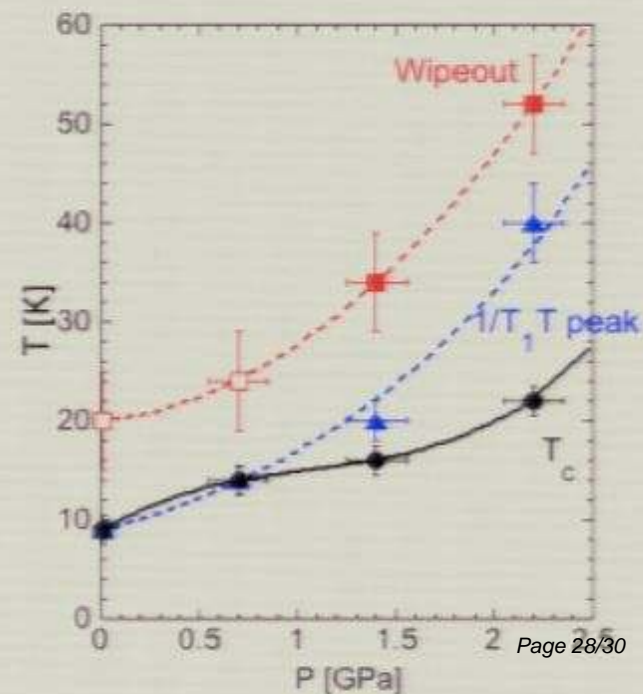
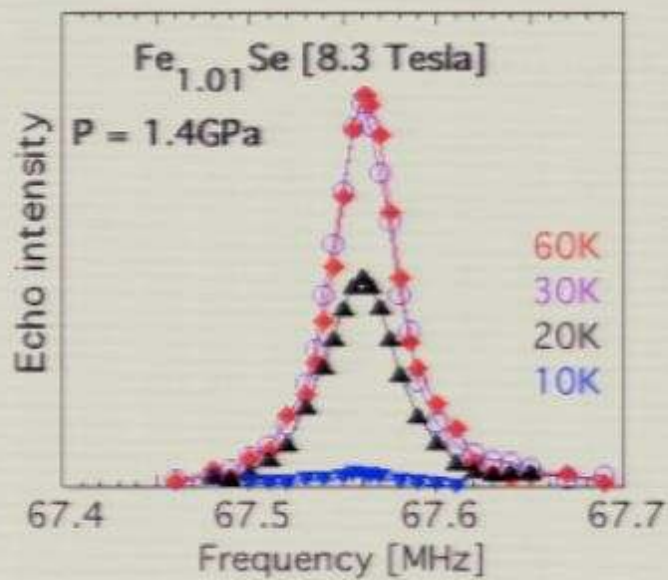
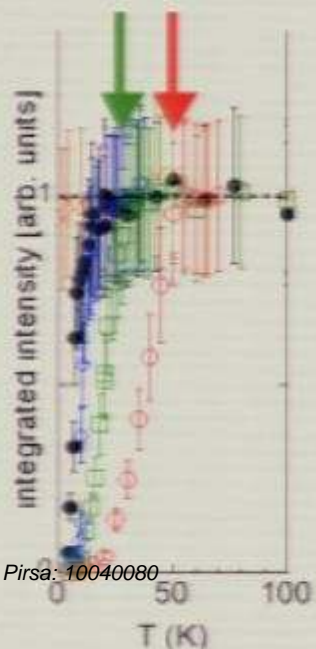


- 1) **Fe<sub>1.01</sub>Se ( $T_c = 9\text{K}$ )**: Qualitatively the same behavior as superconducting Ba(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>As<sub>2</sub>.
- 2) **Fe<sub>1.03</sub>Se (Non-SC)**: No enhancement of AFSF at low T; qualitatively the same behavior as overdoped non-SC Ba(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>As<sub>2</sub>.
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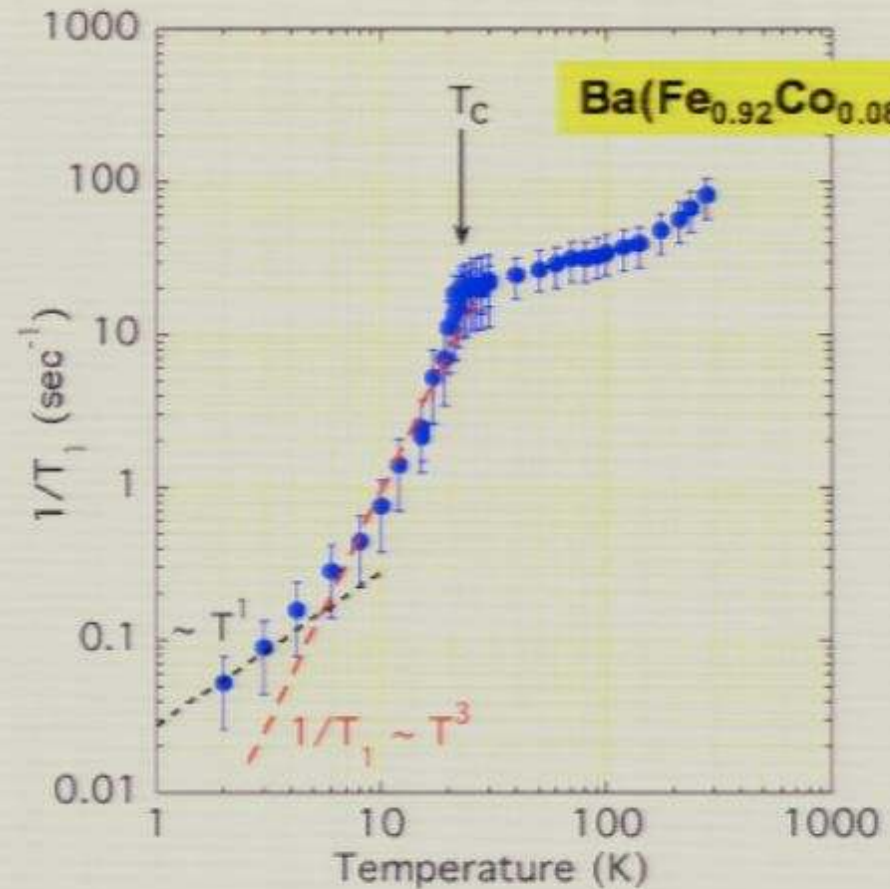
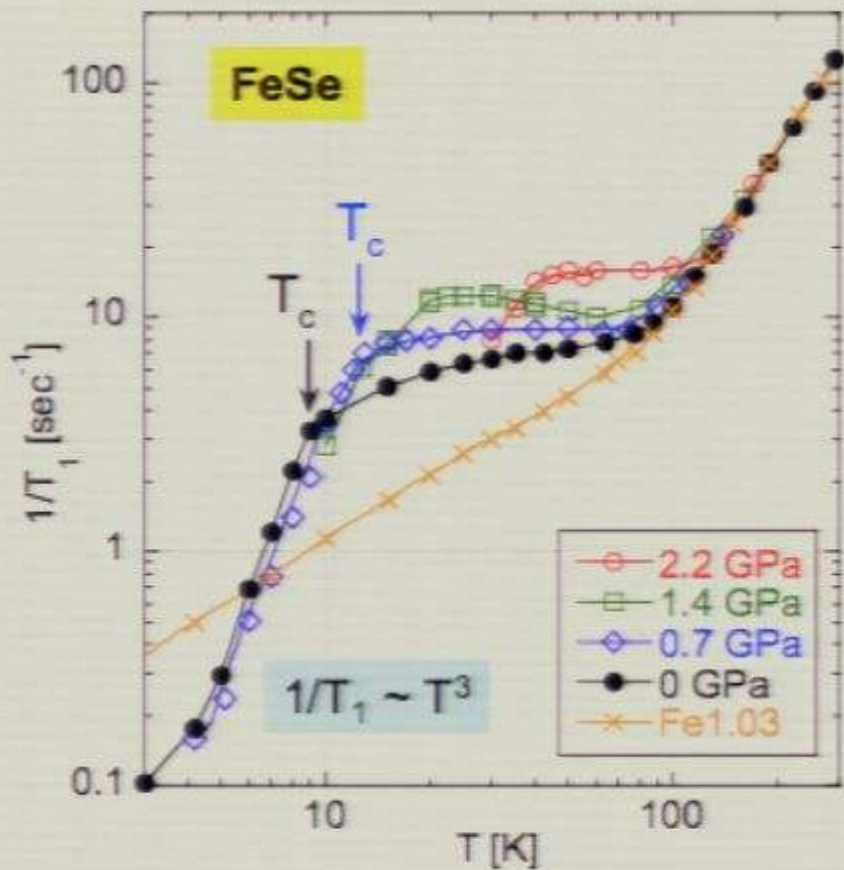
# Complications: NMR signal intensity wipeout; **spin freezing** and/or **phase separation** under pressure $P > 1$ GPa?



- 1)  $1/T_1 T$  shows a peak above  $T_c$  in  $P > 1$  GPa.
- 2) NMR signal intensity decreases below the peak temperature; implying *divergently large  $1/T_1$* , or *line broadening* for unobservable signals
- 3) Non-monotonic increase of  $T_c$  (as emphasized by Kotegawa *et al.* JPSJ 2008)



# Symmetry of the superconducting energy gap in FeSe; Similarity with $\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2$



- No BCS coherence peak just below  $T_c$ .  $1/T_1 \sim T^3$  for  $T \ll T_c$ .
- Very similar to the case of  $\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2$
- Analogous to unconventional pairing in YBCO etc.

• Similar results observed also for disordered  $\text{FeSe}_{1-d}$  in  $P=0$ . Kotegawa *et al.* JPSJ 77 (2008) 113703.

## Summary

1. The mechanism of the pseudo-gap like behavior of  $\chi(q=0)$  is still a big mystery.  $\chi(q=0)$  levels off to a constant when  $\rho \sim T$ .
2. Robust AF spin fluctuations even for optimally superconducting  $\text{Ba}(\text{FeCo})_2\text{As}_2$  and FeSe.
3. Superconductivity optimized when AF spin fluctuations obey a Curie law  $\chi''_{\text{AF}} \sim 1/T$ , i.e. quantum critical.
4. Pairing state still murky;  $1/T_1$  similar to early, dirty samples of YBCO.
5. SDW state under the presence of doping is not consistent with homogeneous, commensurate SDW.