

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 Ba(Fe,Co)2As2 and stoichiometric 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

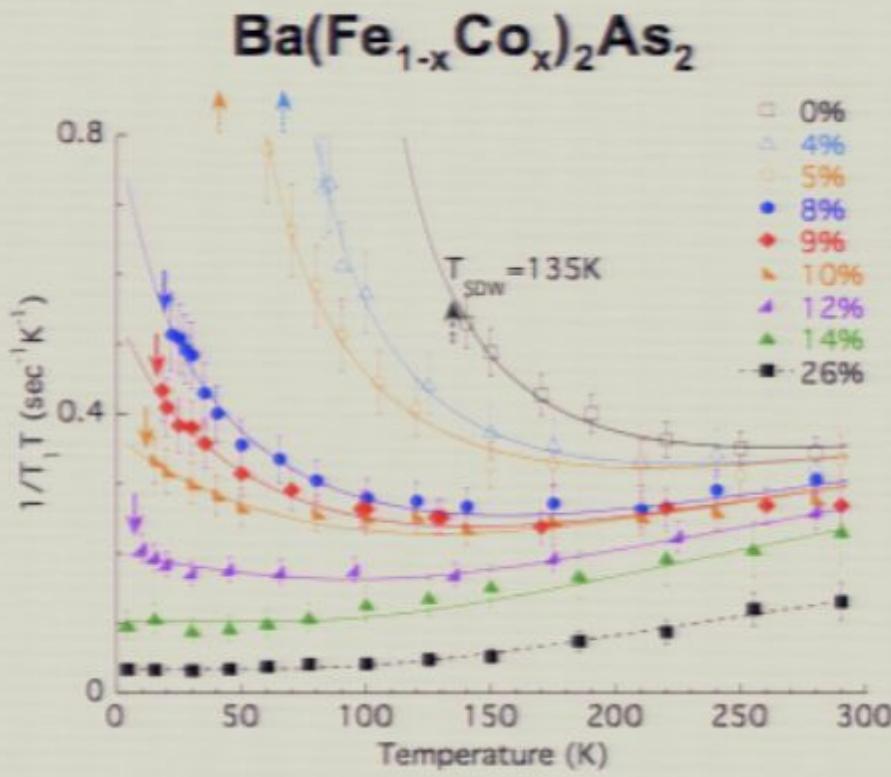
J. Ning, K. Ahilan, T.I. McMaster University and Canadian Institute for Advanced Research

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

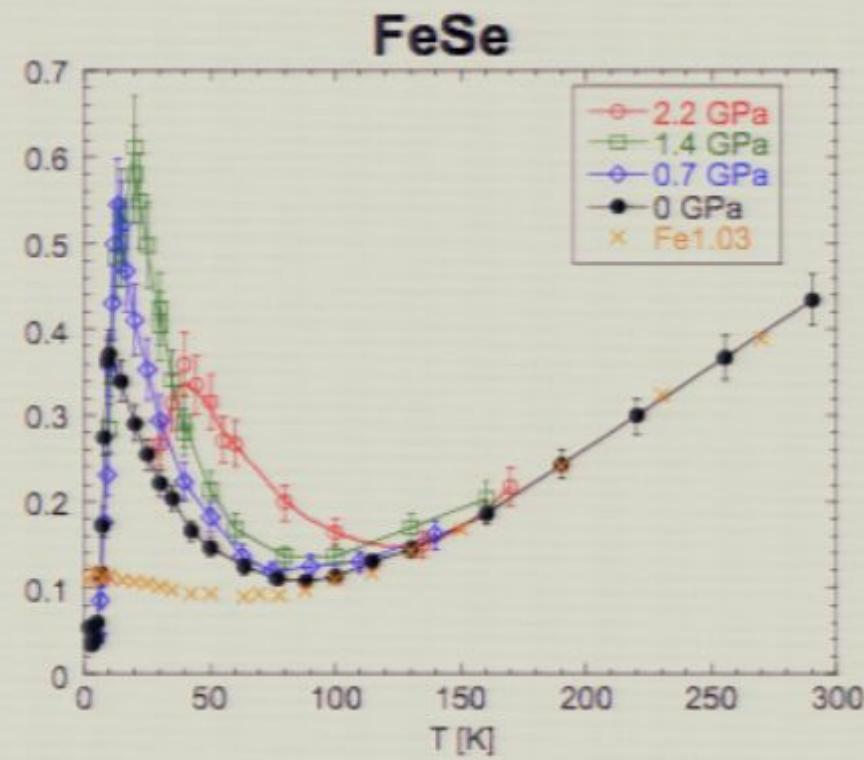


Ning et al. PRL 104 (2010) 037001.

Pirsa: 10040080

Ning et al. JPSJ 78 (2009) 013711.

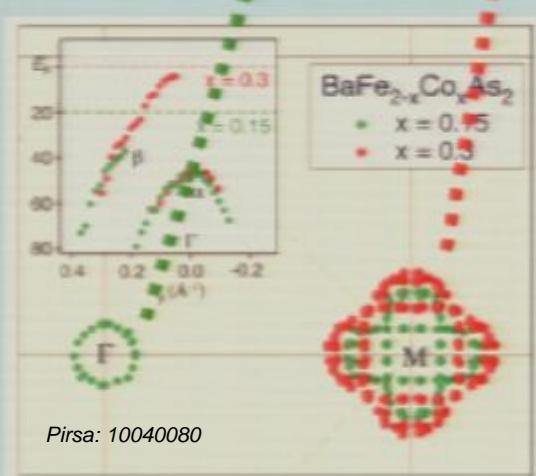
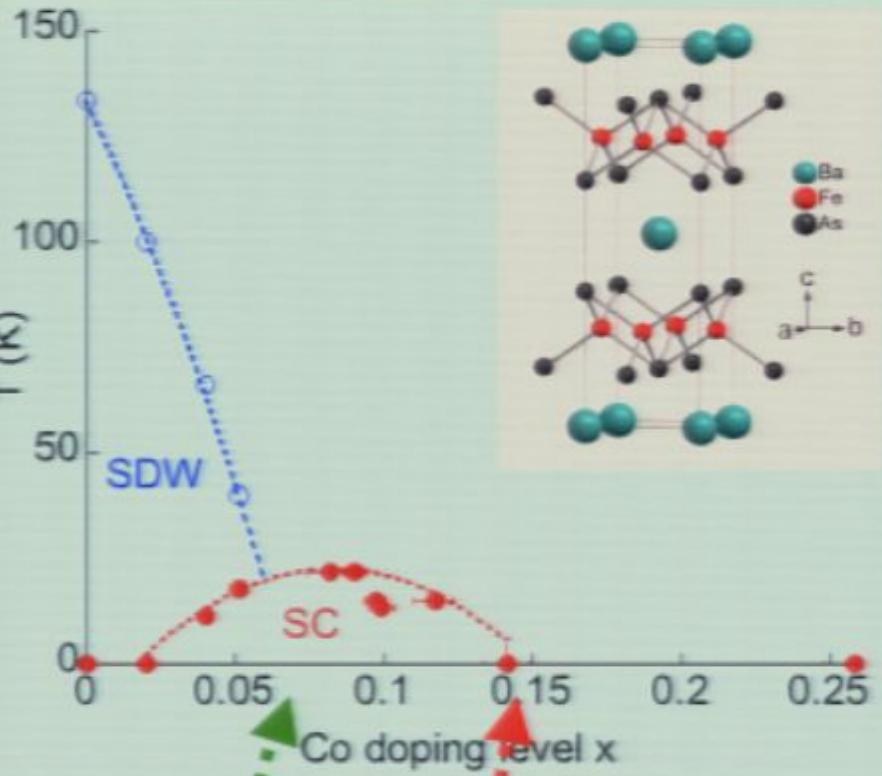
Ahilan et al. PRR 80 (2009) 134423



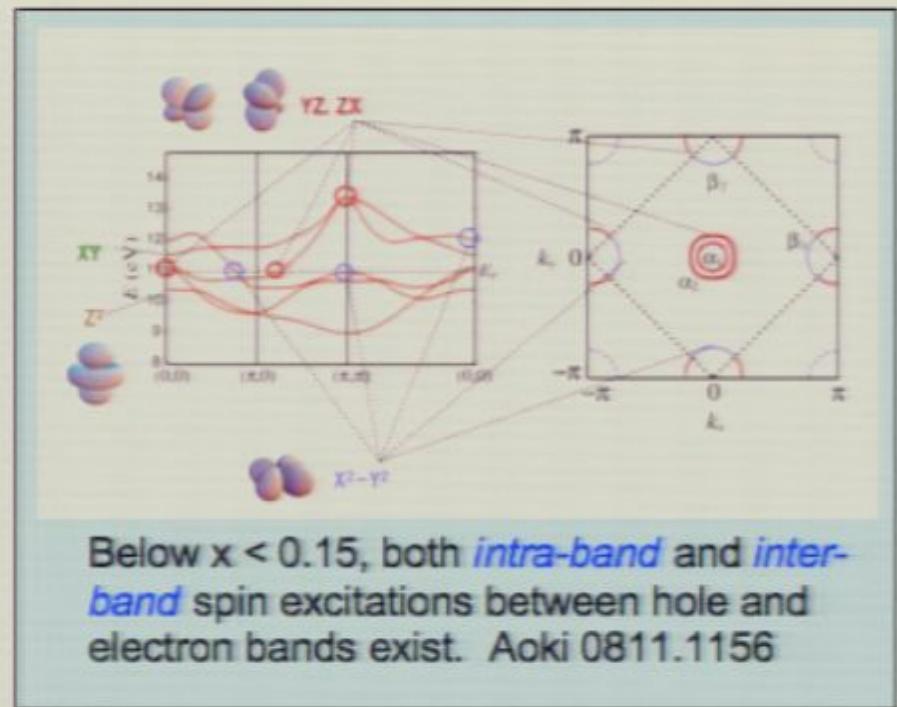
Imai et al. PRL 102 (2009) 177005.

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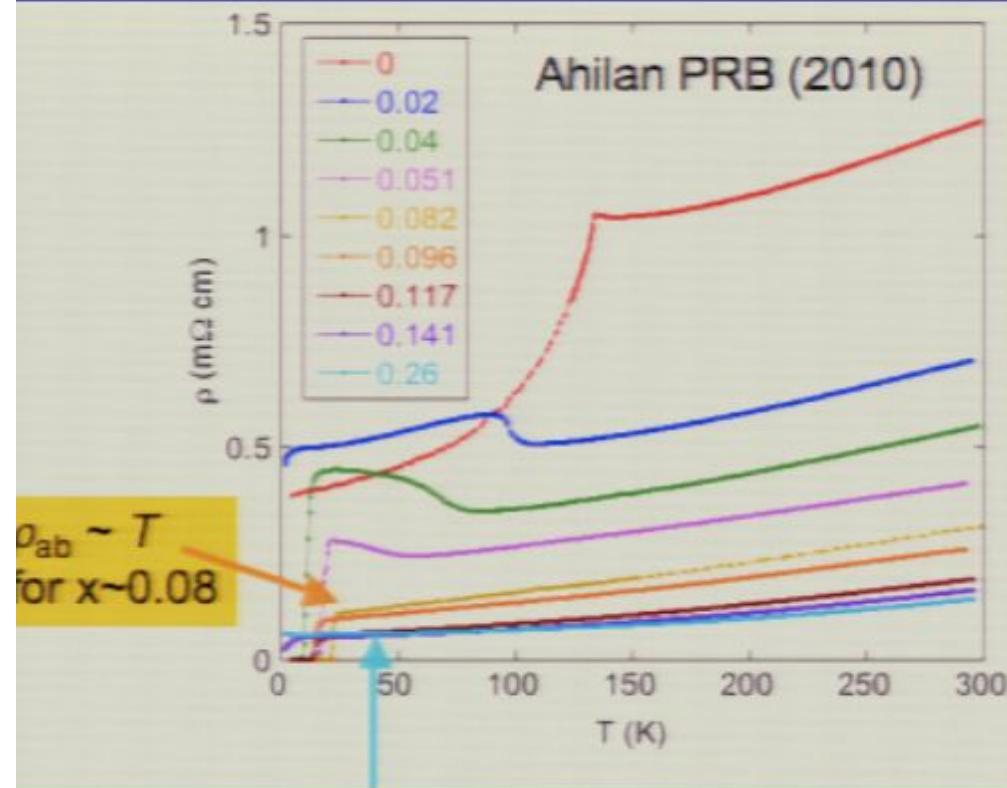
# Electronic Phase Diagram of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



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;  $\rho_{ab} \sim T^2$

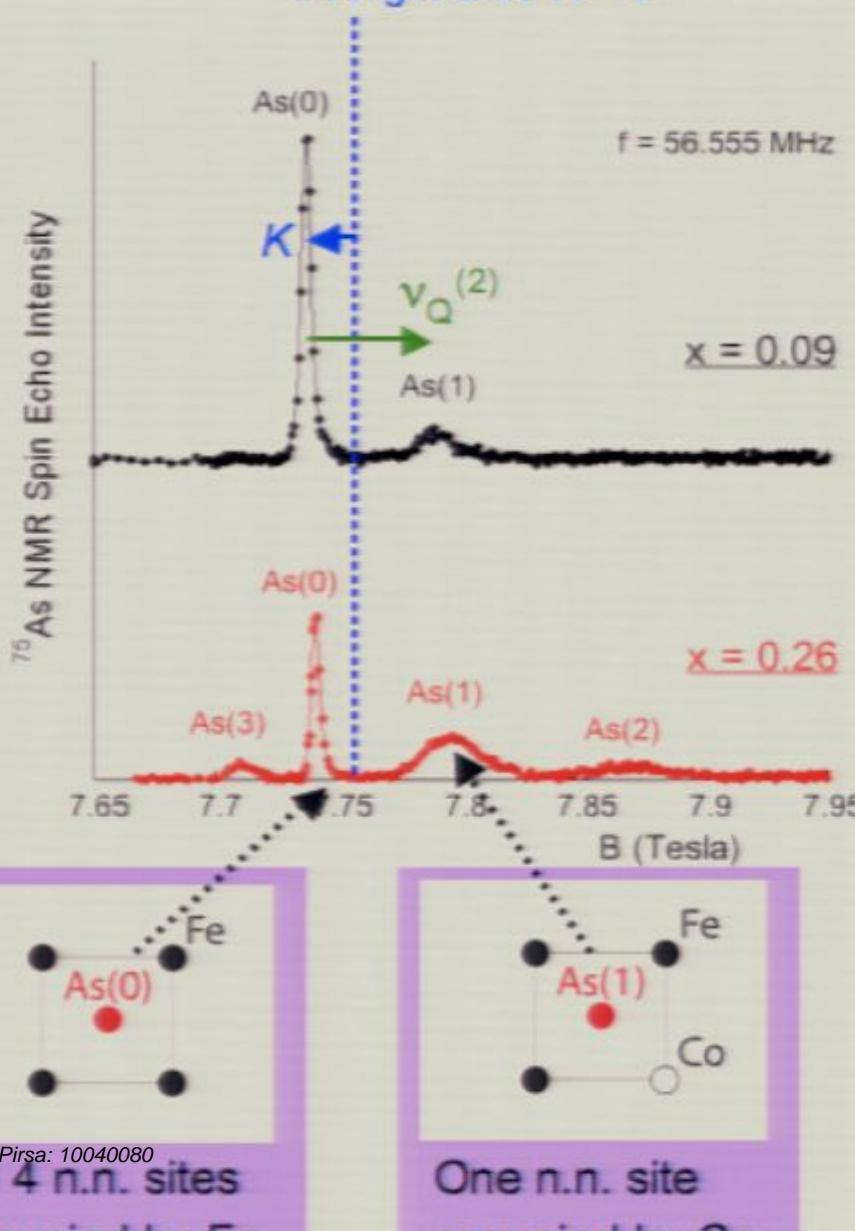
**Key Questions (and our Answers based on NMR measurements) :**

- 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

Expected line position  
if Knight shift  $K = 0$

Ning PRL (2010)



- NMR resonance frequency

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

where Knight shift,

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

- The line splitting between As(N) sites is caused primarily by different second order nuclear quadrupole effects,  $v_Q^{(2)}$ , 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.

## $^{57}\text{As}$ NMR Knight shift measurements of local uniform spin susceptibility $\chi_{\text{spin}}(\mathbf{q}=0)$ in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

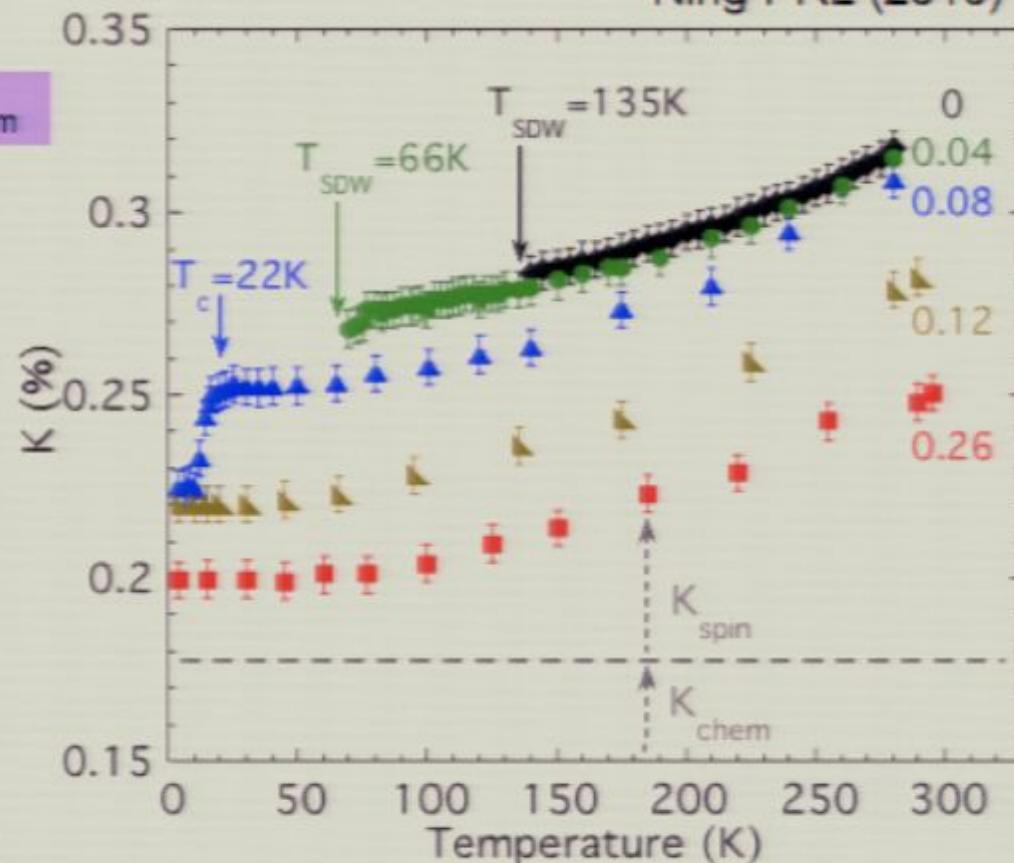
Knight shift"

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

Hyperfine coupling constant

Chemical shift  
Temperature independent  
(Concentration dependent)

Ning PRL (2010)



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

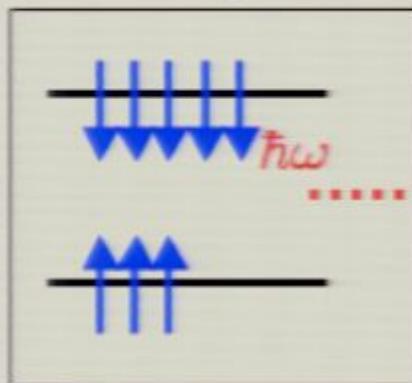
Consistent with AF short range order and/or pseudo-gap ( $\Delta/k_B \sim 450\text{ K}$ ) behavior.

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

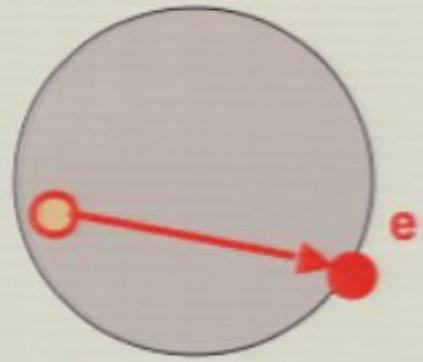
Note: LaFeAs(O,F) and FeSe show qualitatively the same behavior as well (Ahilan PRB2008, Imai PRL2009)

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

Excited nuclear spins damp excess energy to....



conduction  
electrons  
(electron-hole pair  
excitations)



Fermi surface

Magnons,  
Spin fluctuations  
etc.

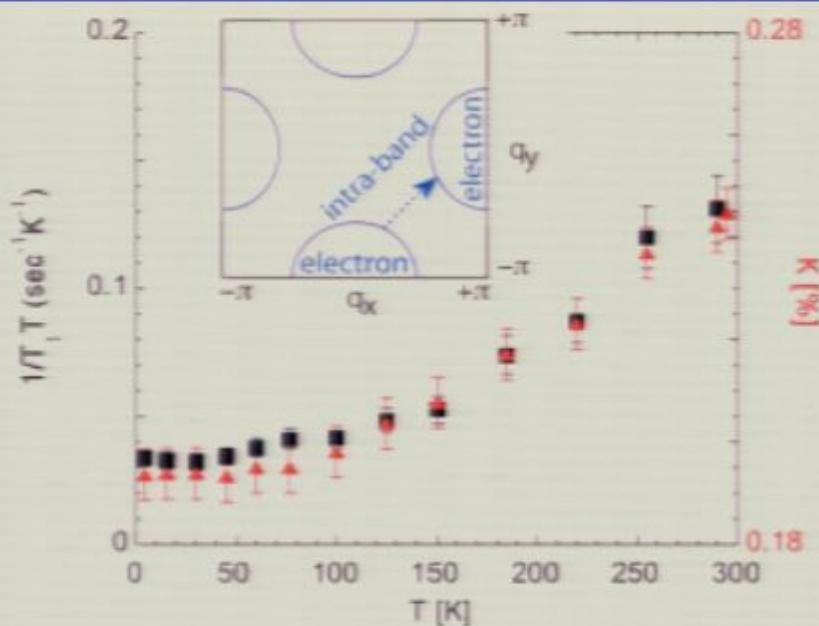


$$\frac{1}{T_1 T} \propto \sum_{q \in 1st B.Z.} |A(q)|^2 \chi''(q, f)$$

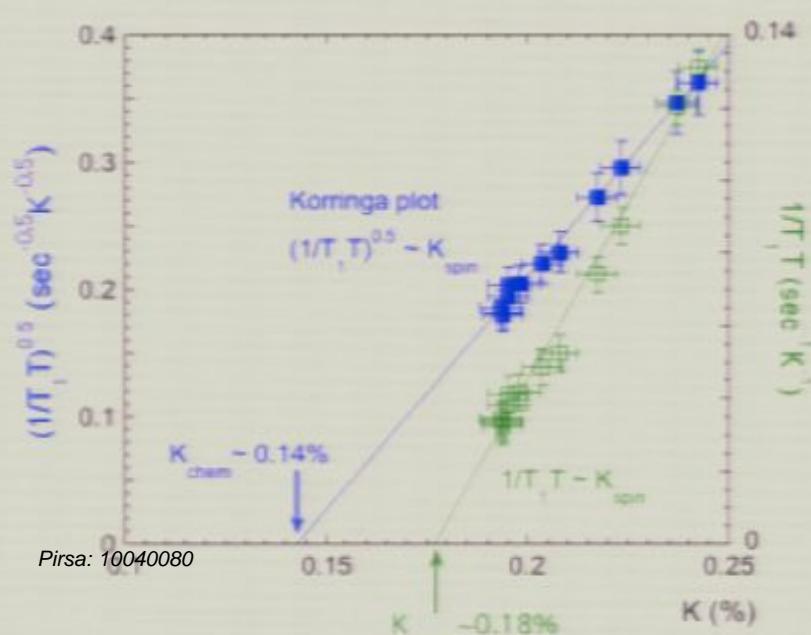
"Hyperfine form factor"

$1/T_1 T$  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?



- $1/T_1 T$  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  $\mathbf{q}$ -space.



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

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

$$1/T_1 T \sim N(E_F)^2,$$

hence

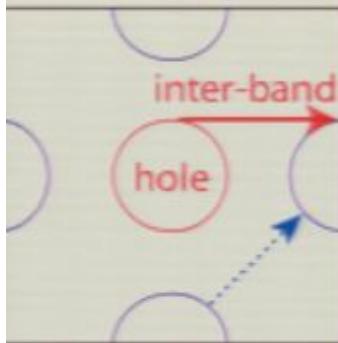
$$(1/T_1 T)^{0.5} \sim K_{\text{spin}} + K_{\text{chem}}$$

although we can't rule out overdamped magnons,

$$1/T_1 T \sim K_{\text{spin}} + K_{\text{chem}}.$$

# Spin fluctuations in superconducting and underdoped Ba(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>As<sub>2</sub>

Ning et al. PRL (2010)



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

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

Robust enhancement of spin fluctuations with  $\Delta q \sim (\pi/a, 0)$

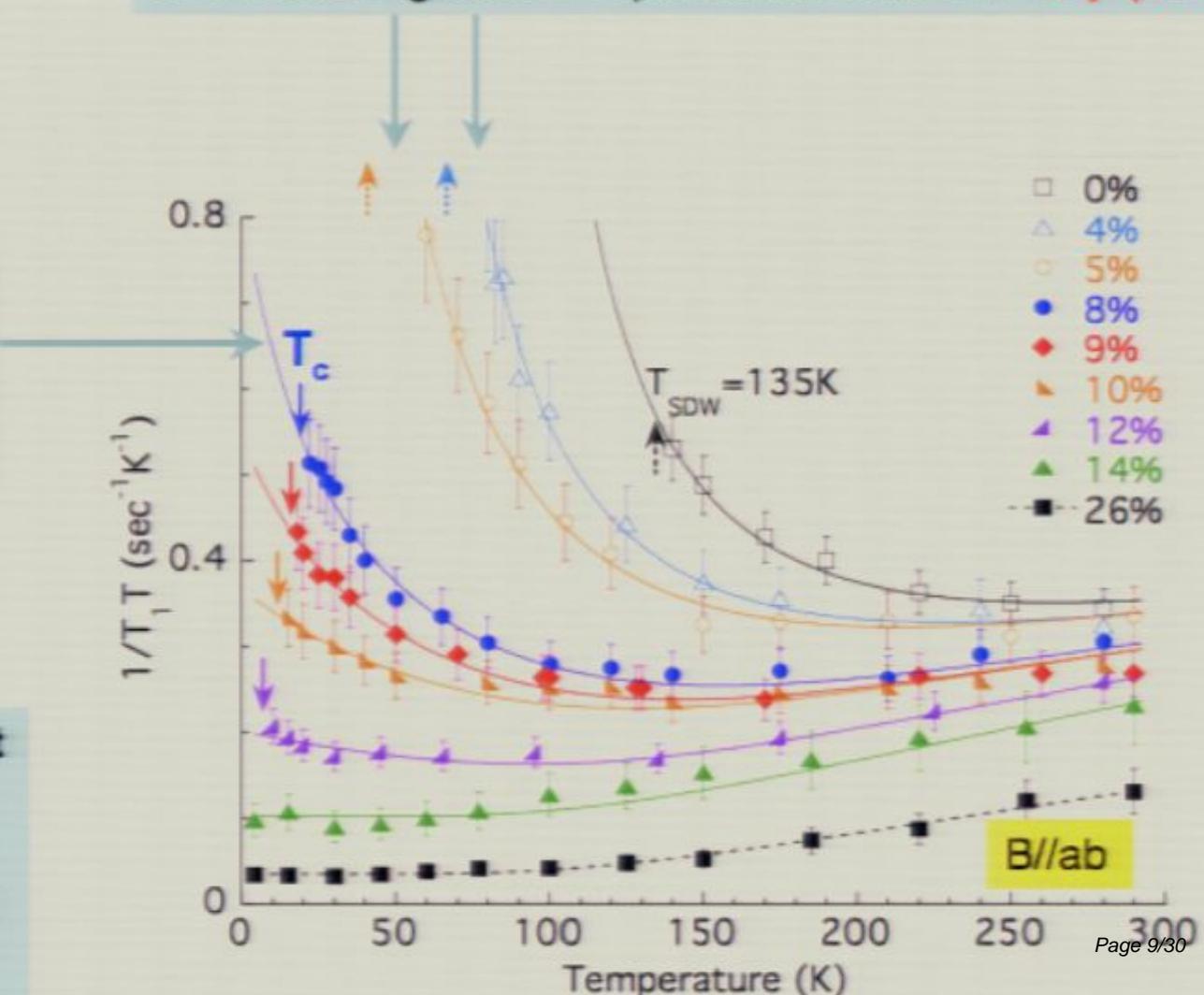
**Solid curves:** Curie-Weiss fit with a background term

$$\frac{1}{T_1 T} = \frac{C}{T + \theta} + A \cdot \exp\left(-\frac{\Delta}{k_B T}\right)$$

with  $\Delta = 450$  K

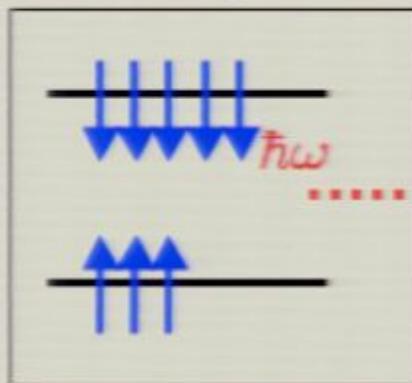
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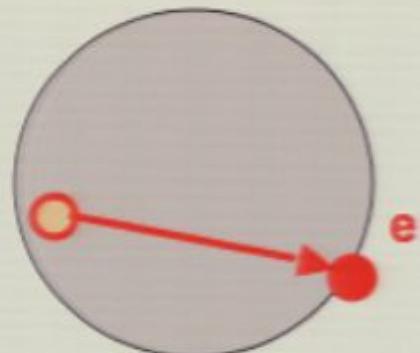


## $1/T_1$ (spin-lattice relaxation rate) probes low energy excitations / fluctuations

Excited nuclear spins damp excess energy to....



conduction  
electrons  
(electron-hole pair  
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Fermi surface

Magnons,  
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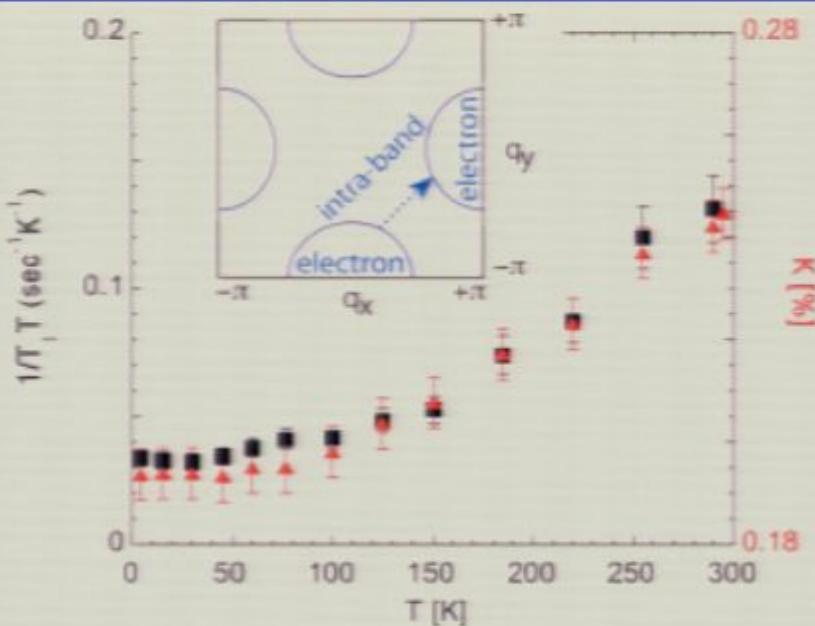


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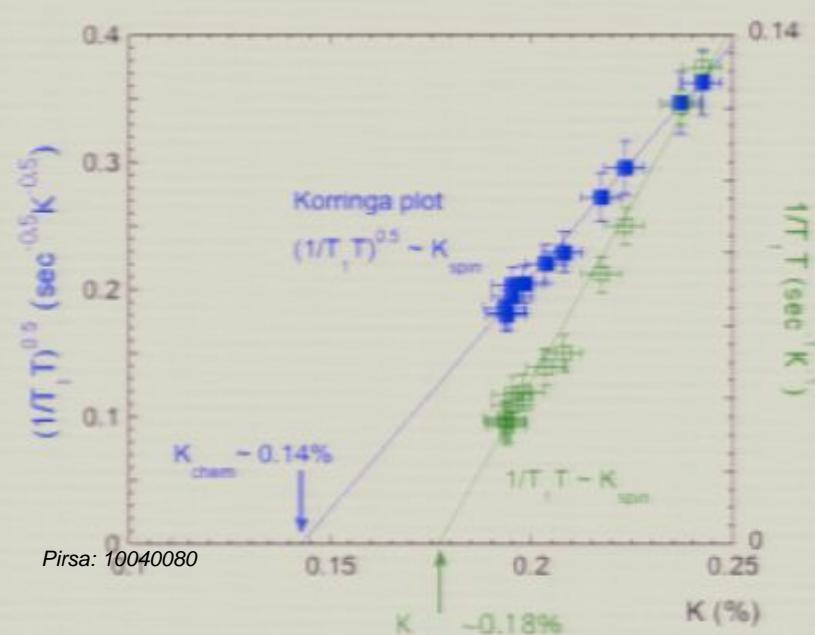
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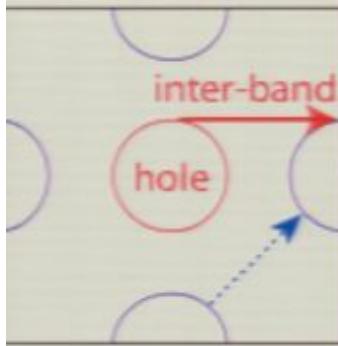
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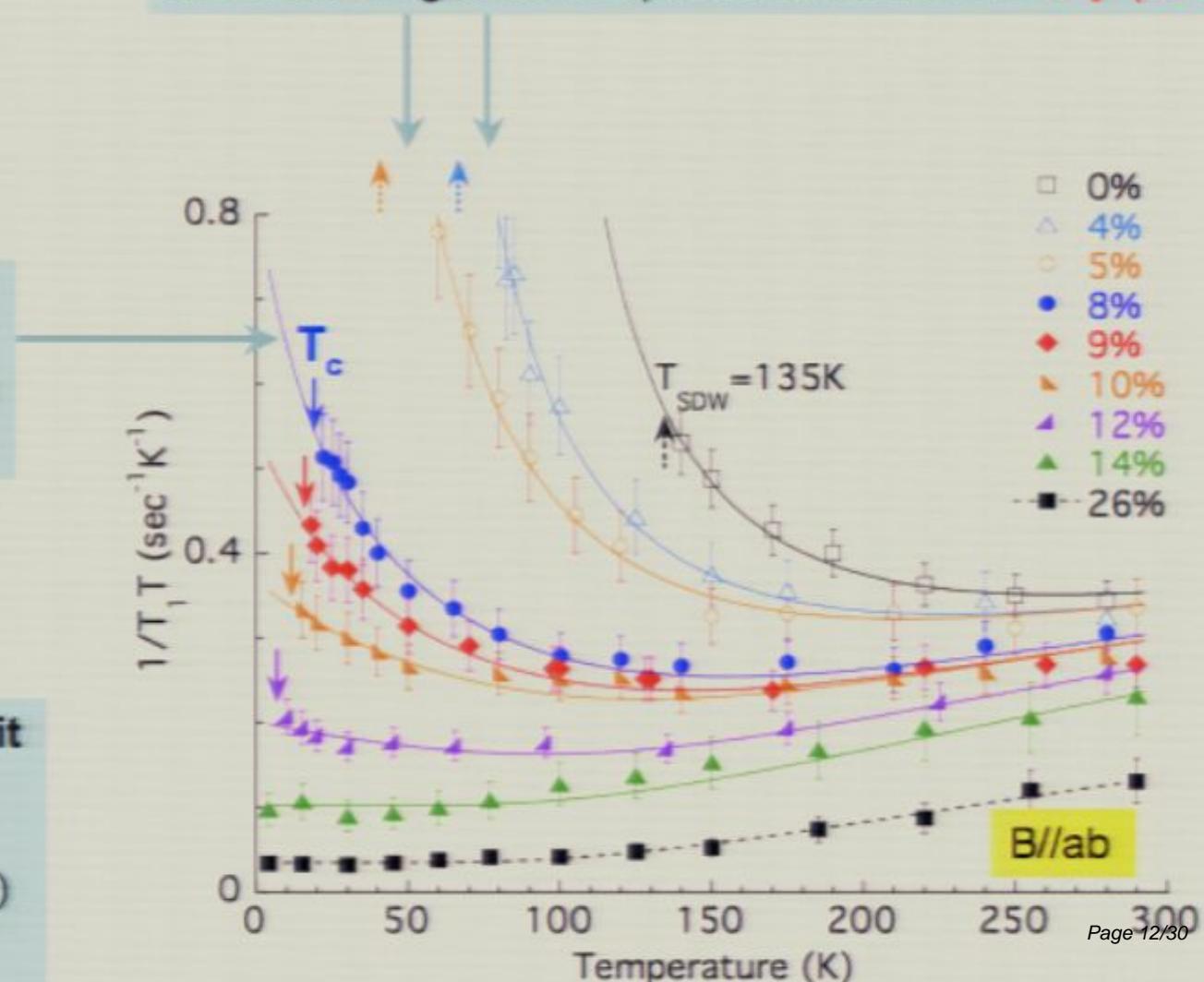
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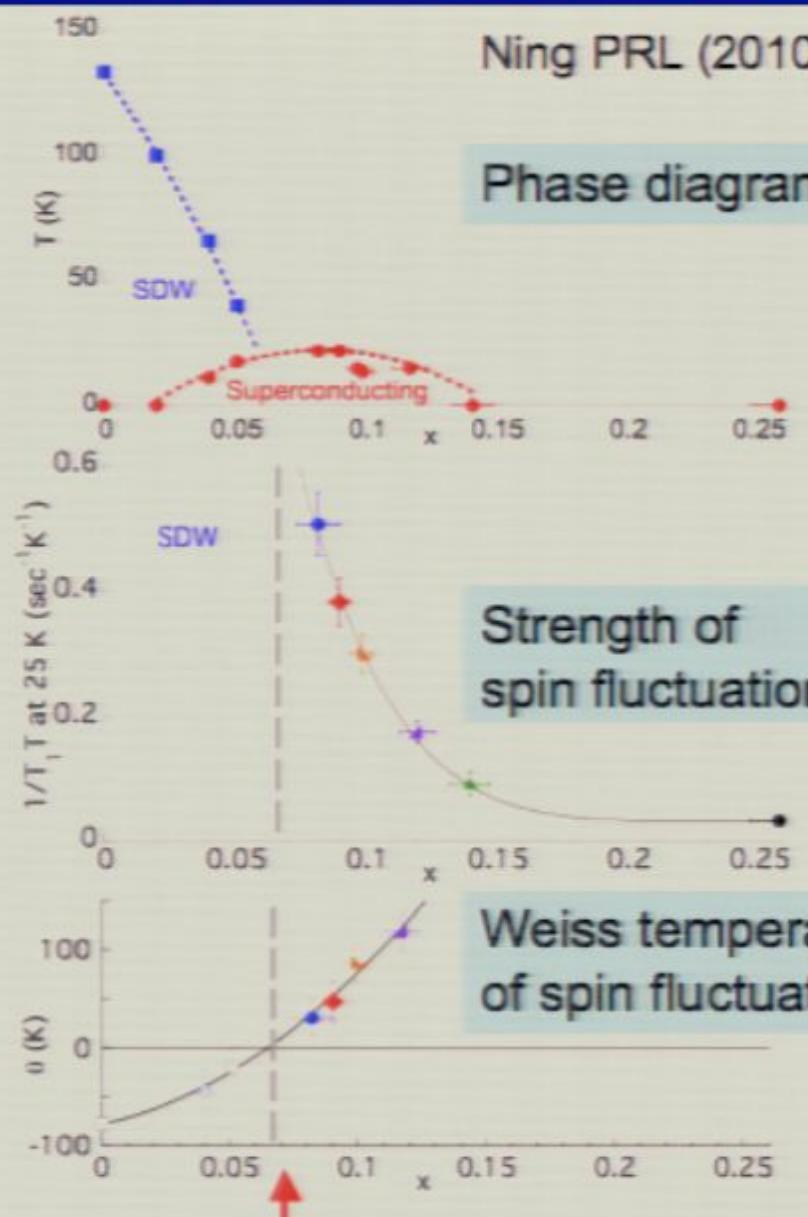
with  $\Delta = 152\text{K}$

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

$1/T_1 T$  shows divergent behavior at  $T_{SDW}$  due to the critical slowing down of spin fluctuations with  $\Delta q \sim (\pi/a, 0)$ .

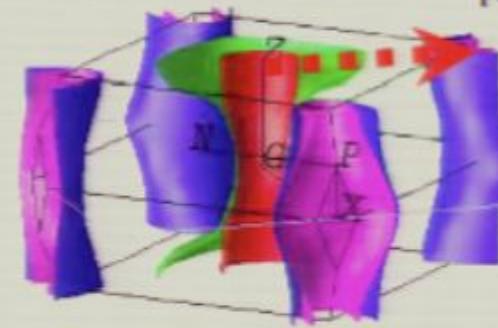


# Correlation between $T_c$ , antiferromagnetic spin fluctuations, and the Fermi surface geometry in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (Hole band emerges below $x \sim 0.15$ )



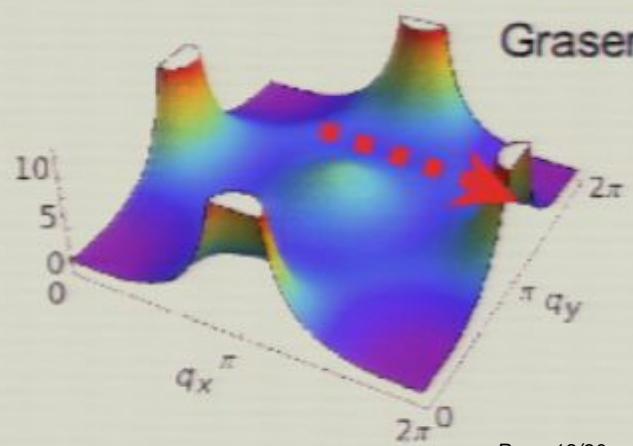
Fermi surface geometry of  $\text{BaFe}_2\text{As}_2$  and “nesting”

Kaminski



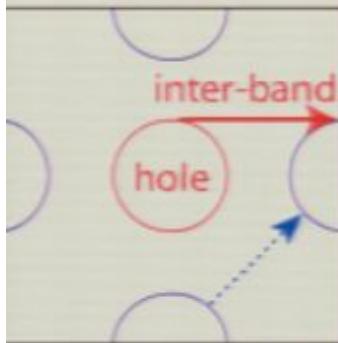
$$\chi_{\text{RPA}}(q_x, q_y)|_{k_z=0}$$

Graser



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Ning et al. PRL (2010)



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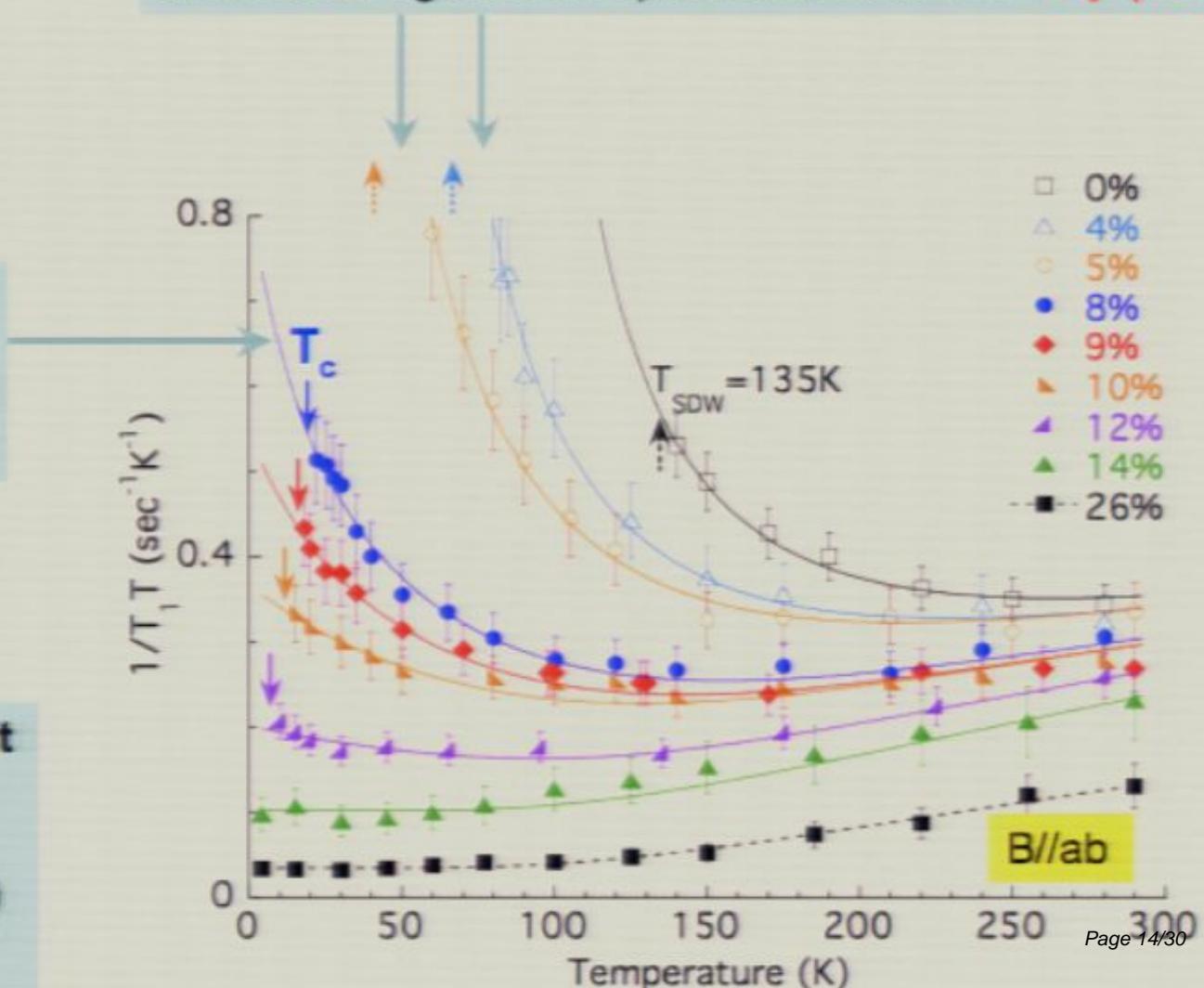
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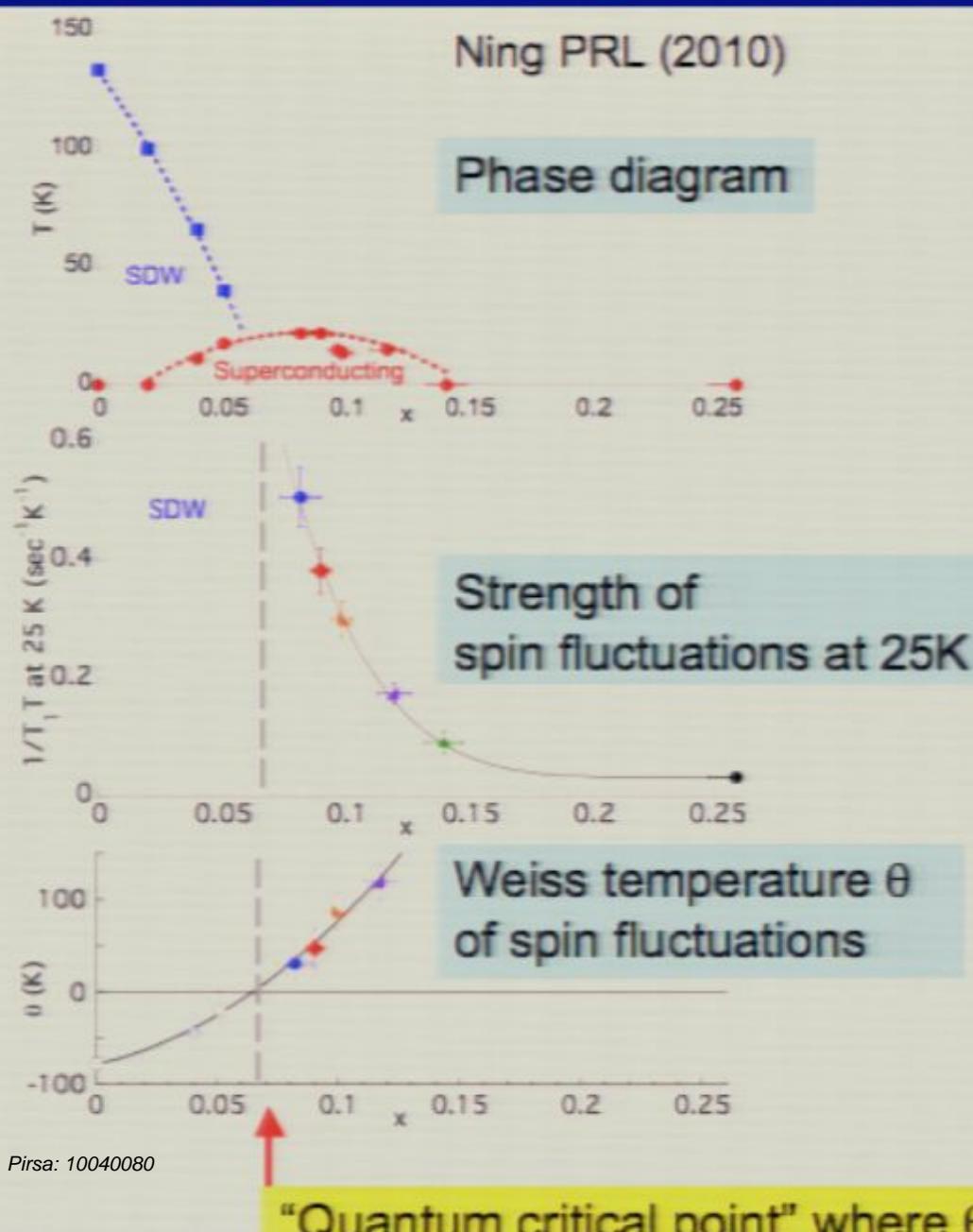
with  $\Delta = 450\text{K}$

Underdoped regime (x < 0.08) :

$1/T_1 T$  shows divergent behavior at  $T_{SDW}$  due to the critical slowing down of spin fluctuations with  $\Delta q \sim (\pi/a, 0)$ .

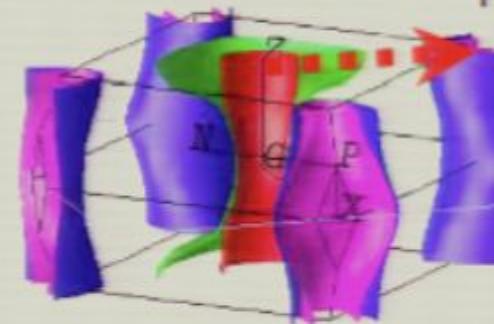


# Correlation between $T_c$ , antiferromagnetic spin fluctuations, and the Fermi surface geometry in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (Hole band emerges below $x \sim 0.15$ )



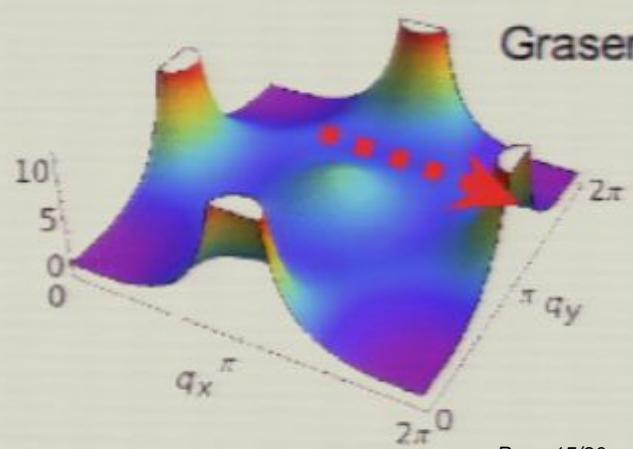
Fermi surface geometry of  $\text{BaFe}_2\text{As}_2$  and “nesting”

Kaminski



$$\chi_{\text{RPA}}(q_x, q_y)|_{k_z=0}$$

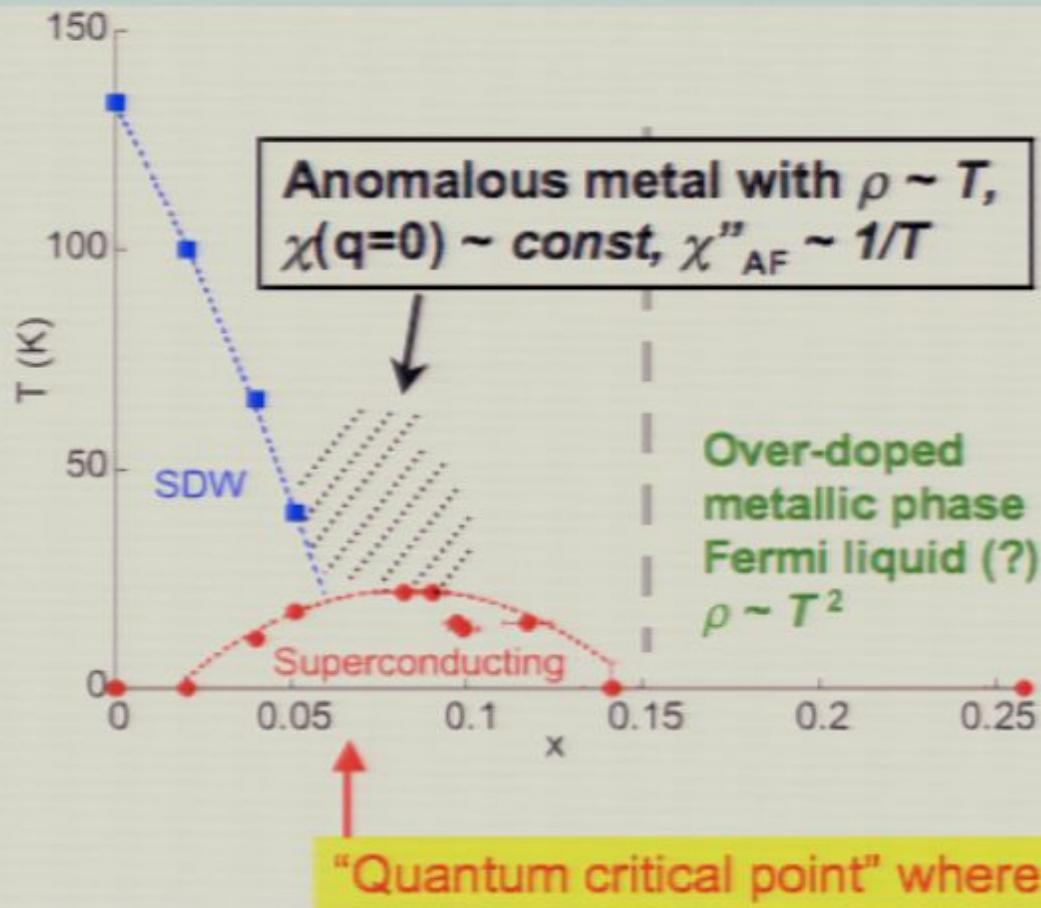
Graser



## 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.

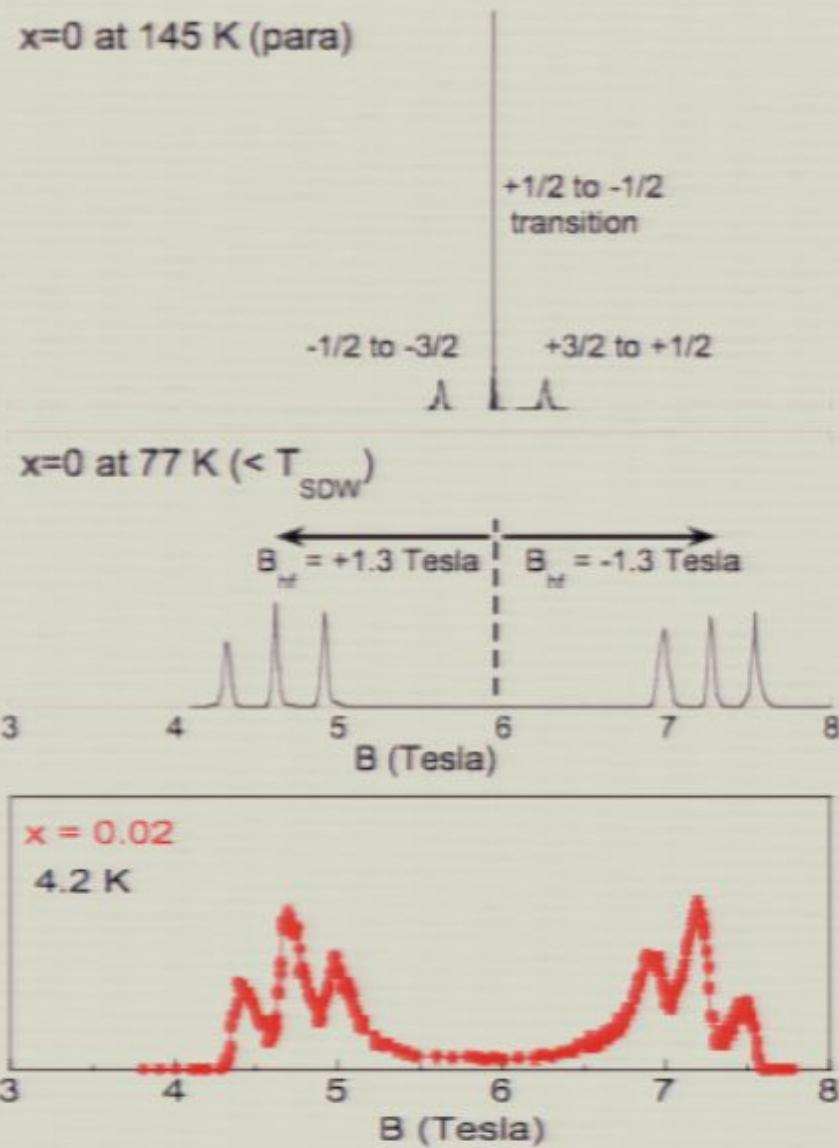
FeSe show very similar behavior (see below).



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

$x=0$  at 145 K (para)

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

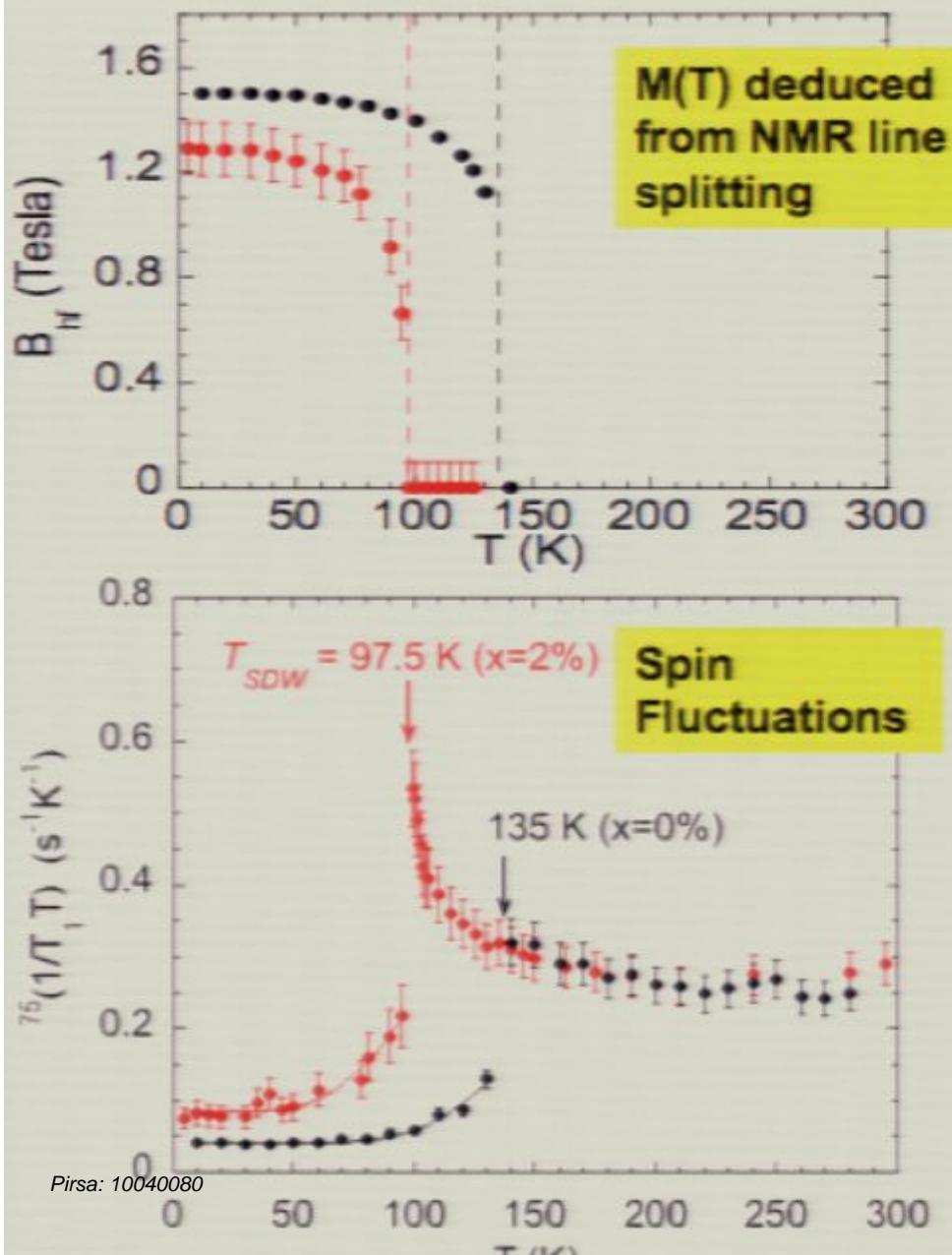


$x=0$  : Commensurate SDW below  $T_{SDW}=135K$ .  
 $^{75}\text{As}$  NMR shows bi-modal splitting due to two discrete values of static hyperfine magnetic field

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

$x=0.02$ : 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;

$$\frac{(1/T_1T)_{2\%}}{(1/T_1T)_{0\%}} \approx \left( \frac{\tilde{N}(E_F)_{2\%}}{\tilde{N}(E_F)_{0\%}} \right)^2 \approx 2$$

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

- Finite temperatures below  $T_{SDW}$

Fit with activation law

$$\frac{1}{T_1T} \approx a + b \exp\left(-\frac{\Delta}{k_B T}\right)$$

with

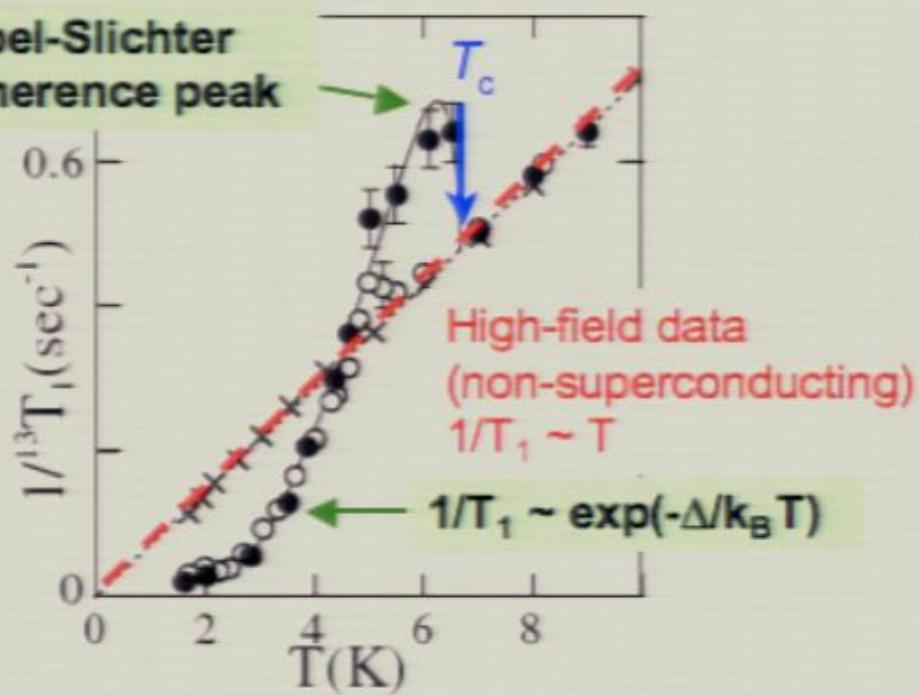
$$\Delta/k_B \sim 330\text{K} \quad \text{for } x = 2\%$$

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

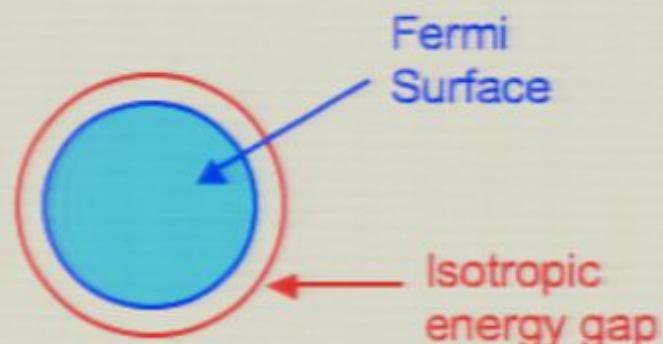
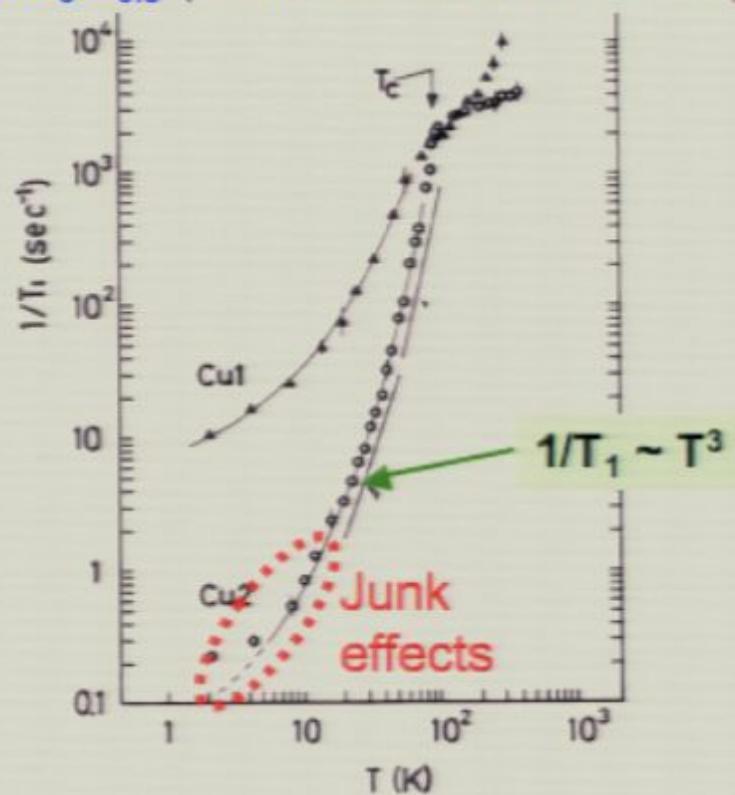
## Example of $1/T_1$ in superconductors

$\text{MgCNi}_3$  (Singer, Imai, Cava PRL 2001)

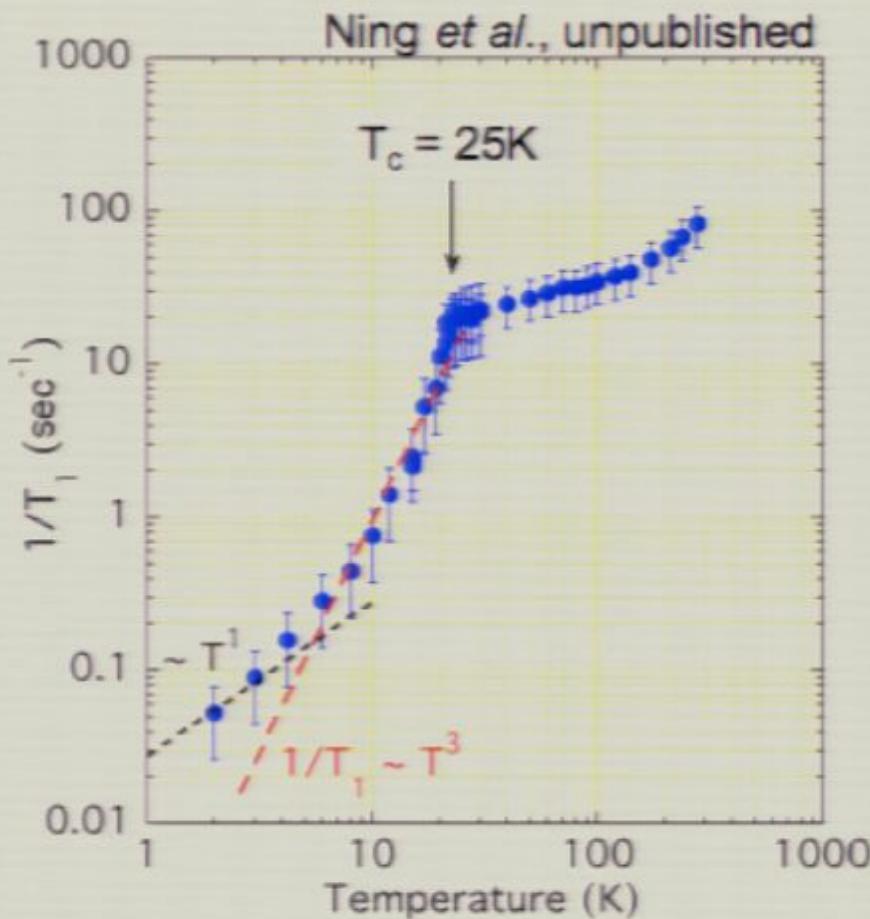
Hebel-Slichter  
Coherence peak



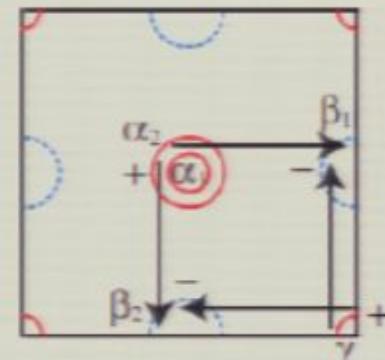
$\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  (Imai, Yasuoka JPSJ 1988)



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

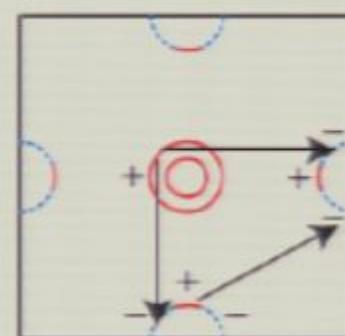


fully gapped  $s\pm$  wave



Kuroki et al.  
PRB 79(2009)  
244511

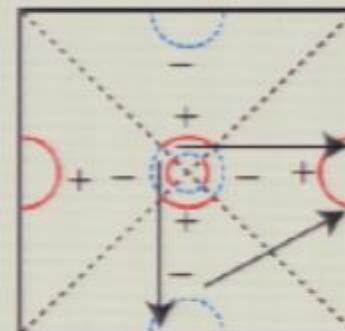
nodal  $s\pm$  wave



Ikeda e al.  
JPSJ (2008)

And many  
others

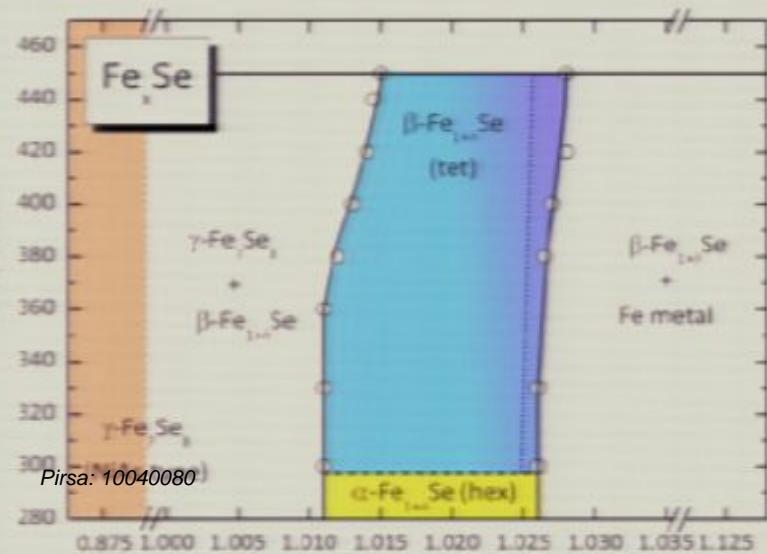
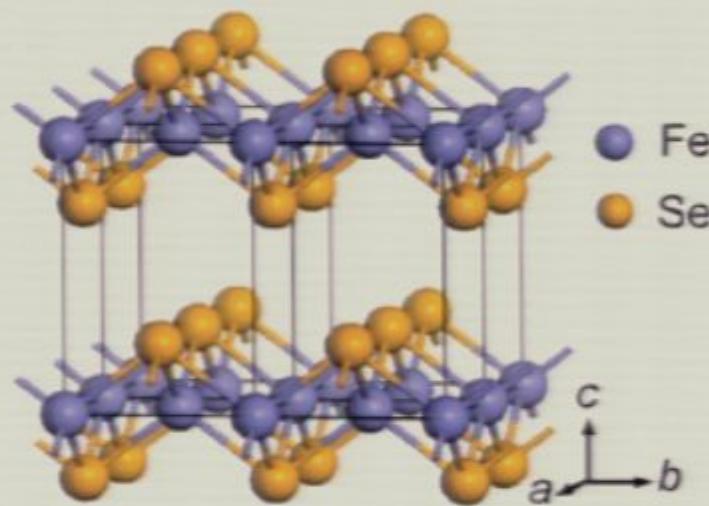
d-wave



- 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, Gafe et al. PRL 2008)

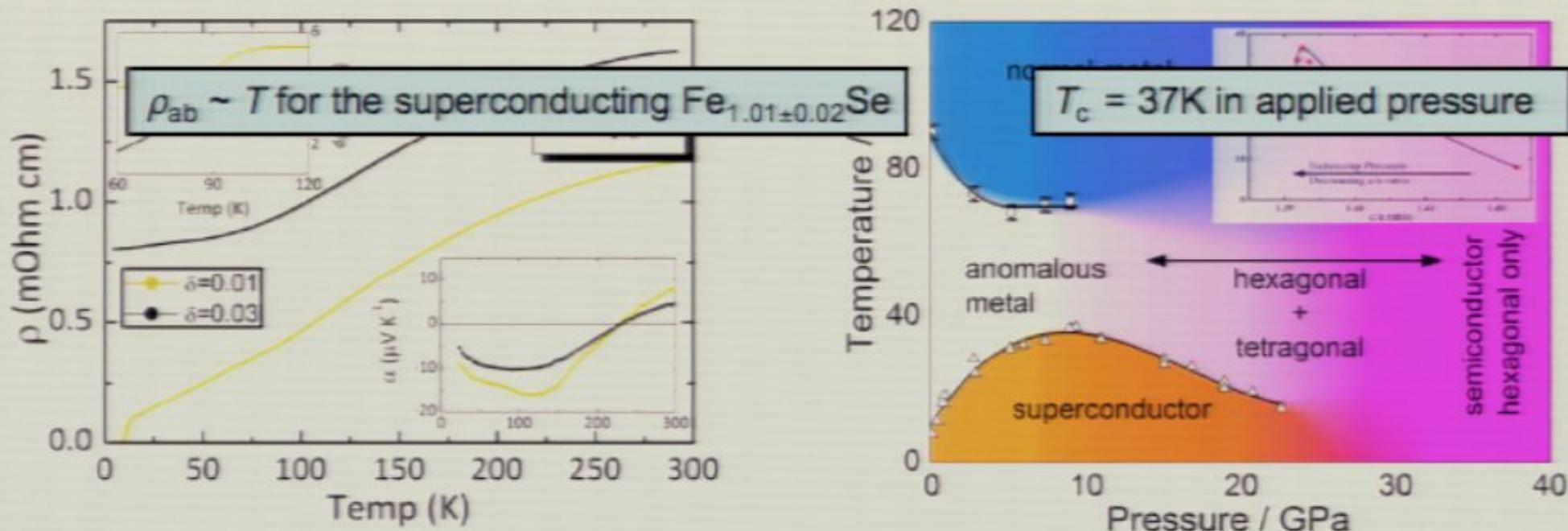
## Comparison with the case of defect-free FeSe

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  
McQueeny, Cava et al. PRB (2009)

## Properties of the defect-free FeSe



Medvedev, Cava et al. Nature Materials (2009)

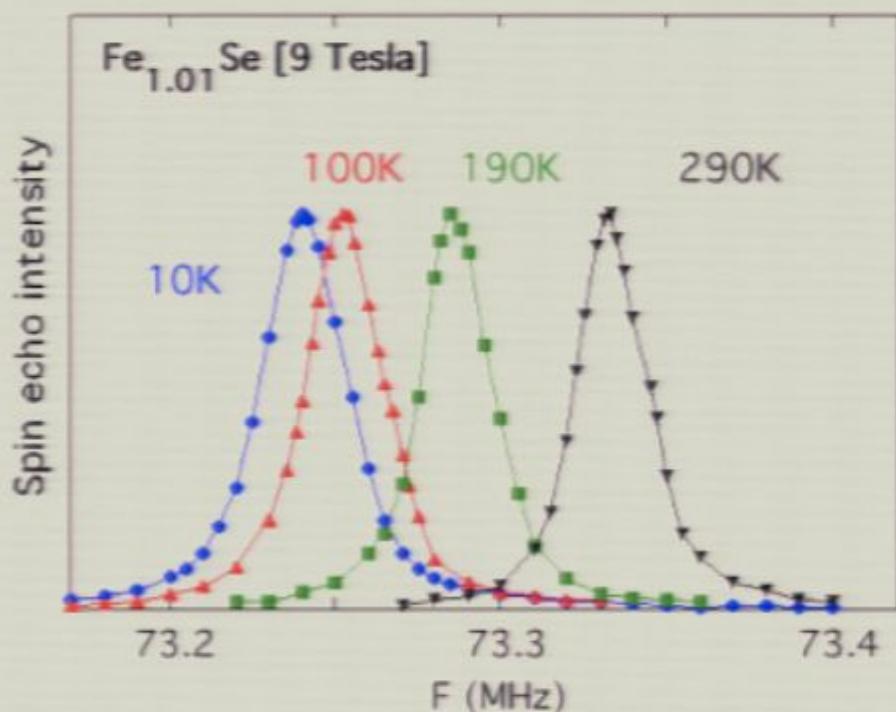
### Key Questions (and answers from NMR)

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.

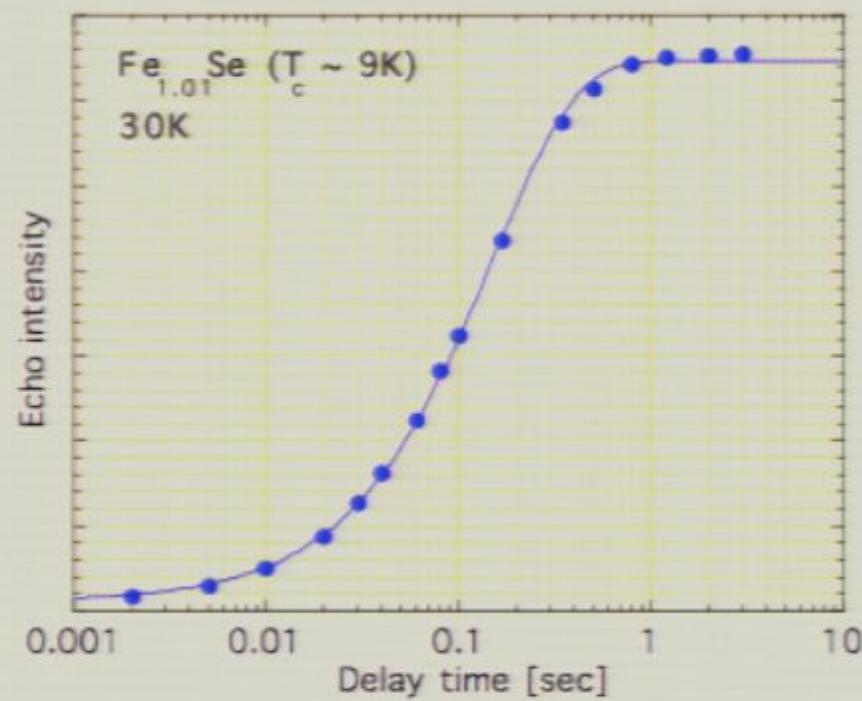
# Very narrow $^{77}\text{Se}$ NMR lineshapes in defect-free Princeton samples

Imai et al. PRL (2009).

Narrow NMR line



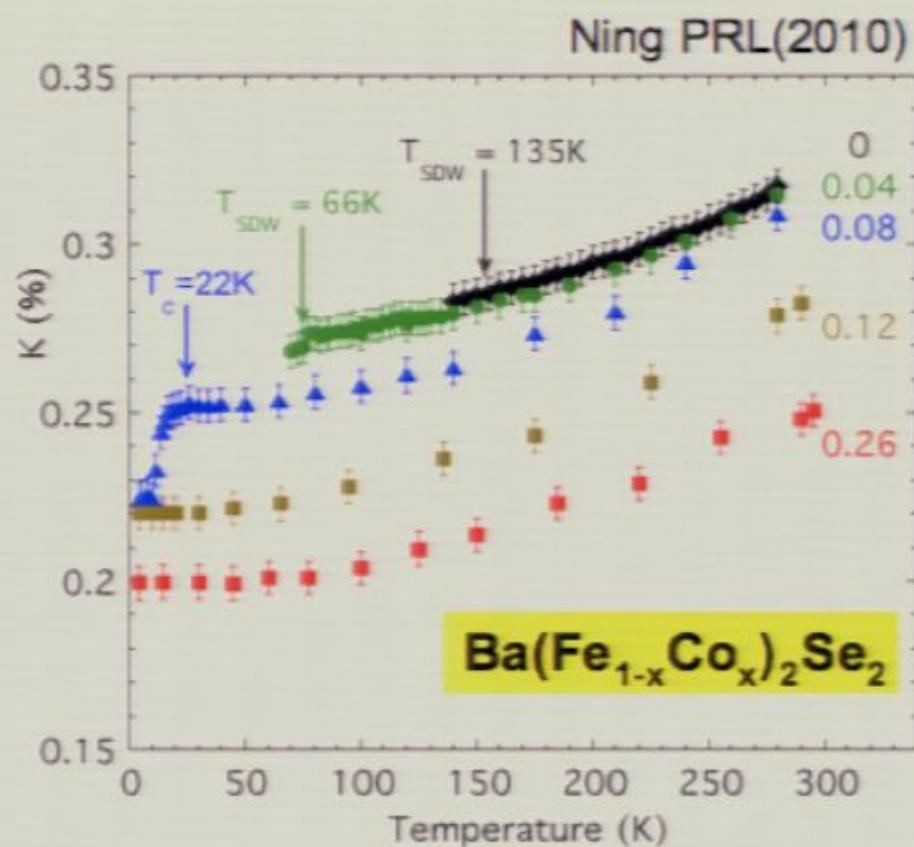
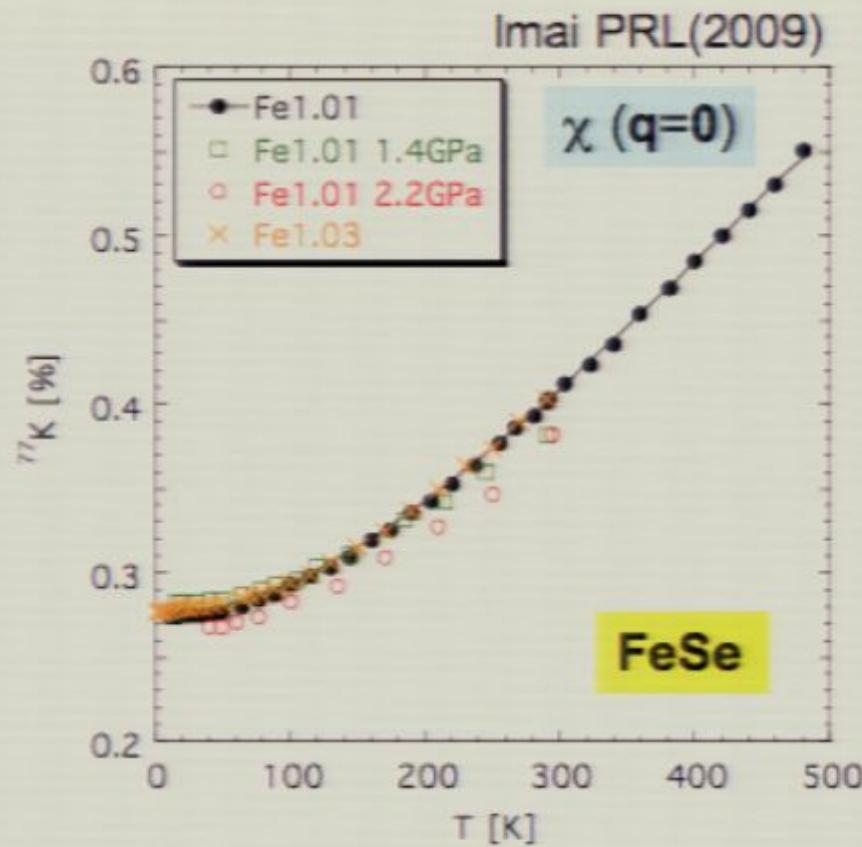
Well-defined  $T_1$  with no distribution



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

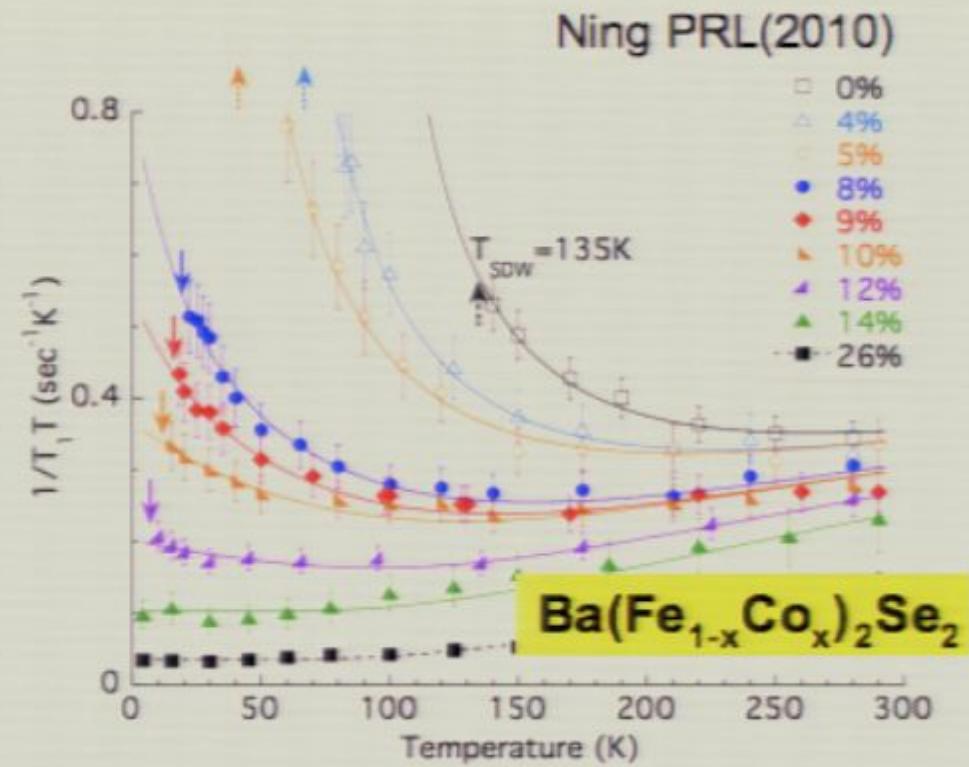
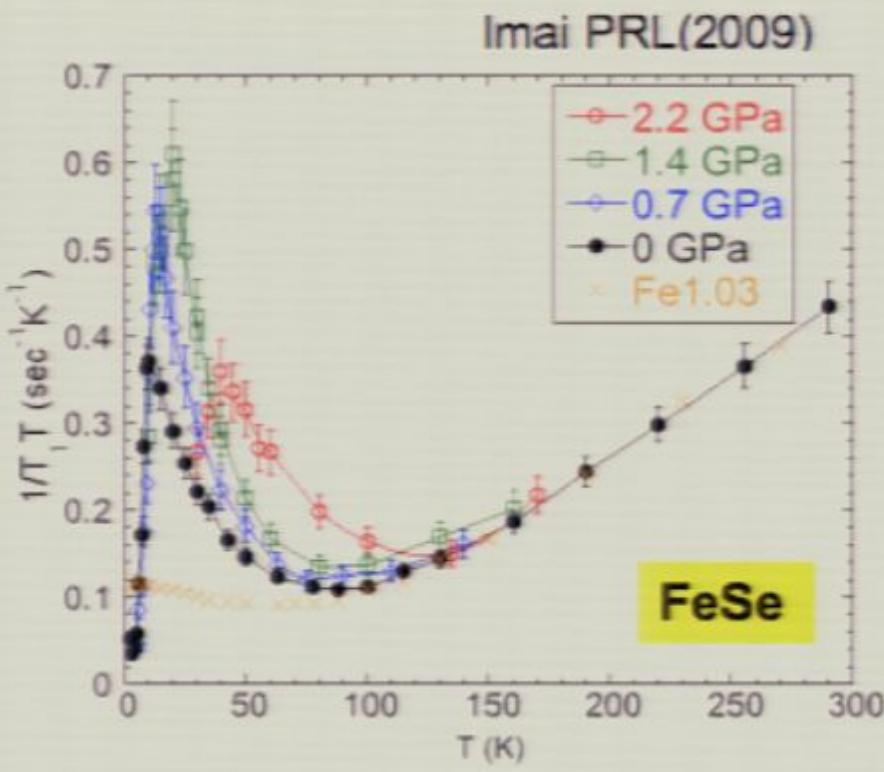
- (Advantage 1) Narrow NMR lines allow us to carry out accurate Knight shift measurements.
- (Advantage 2) Narrow NMR lines allow us to carry out accurate measurements of intrinsic  $1/T_1$  of the superconducting phase, without distributions of  $T_1$  and/or hole burning.

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



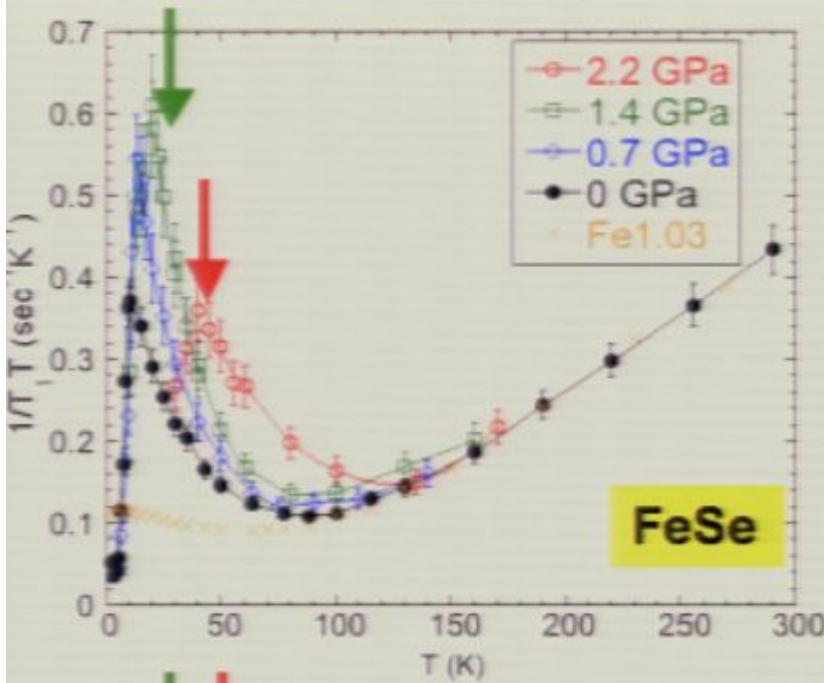
- FeSe and  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  show qualitatively the same behavior;  $\chi(q=0)$  decreases with  $T$ , then levels off where  $\rho \sim T$ .
- Little pressure or concentration dependencies, if any.

## Spin fluctuations $\chi''(\mathbf{q}, \mathbf{f})$ as measured by $^{77}\text{Se}$ NMR $1/T_1 T$

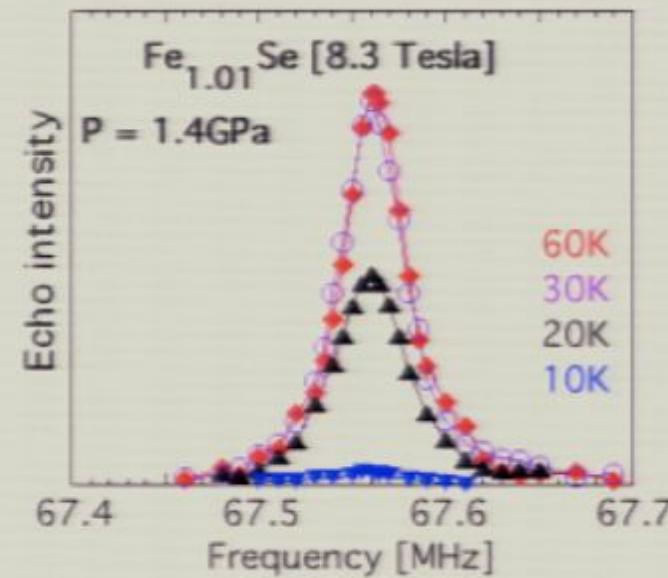
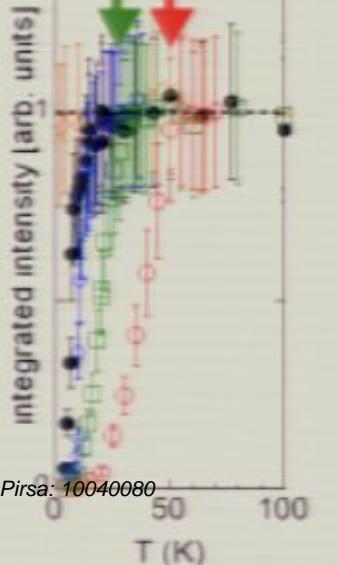


- 1)  $\text{Fe}_{1.01}\text{Se}$  ( $T_c = 9\text{K}$ ): Qualitatively the same behavior as superconducting  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ .
- 2)  $\text{Fe}_{1.03}\text{Se}$  (Non-SC): No enhancement of AFSF at low T; qualitatively the same behavior as overdoped non-SC  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ .
- 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  $T_c$ .

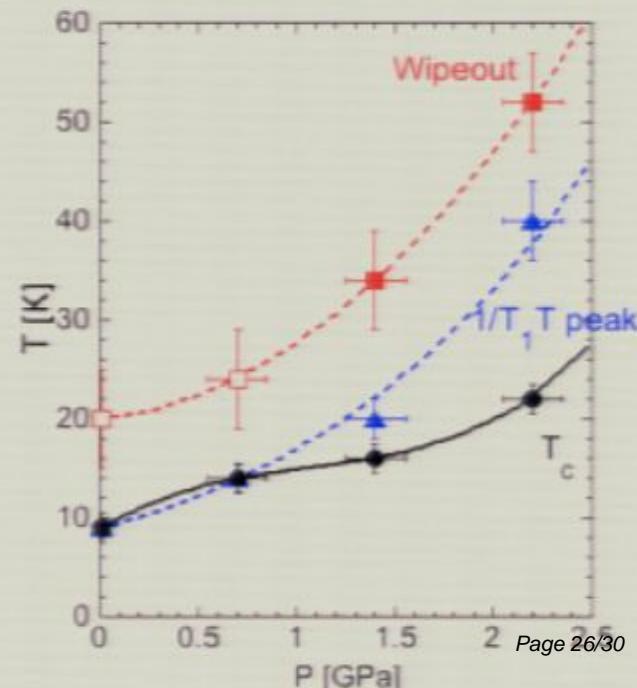
## Complications: NMR signal intensity wipeout; spin freezing and/or phase separation under pressure $P > 1$ GPa?



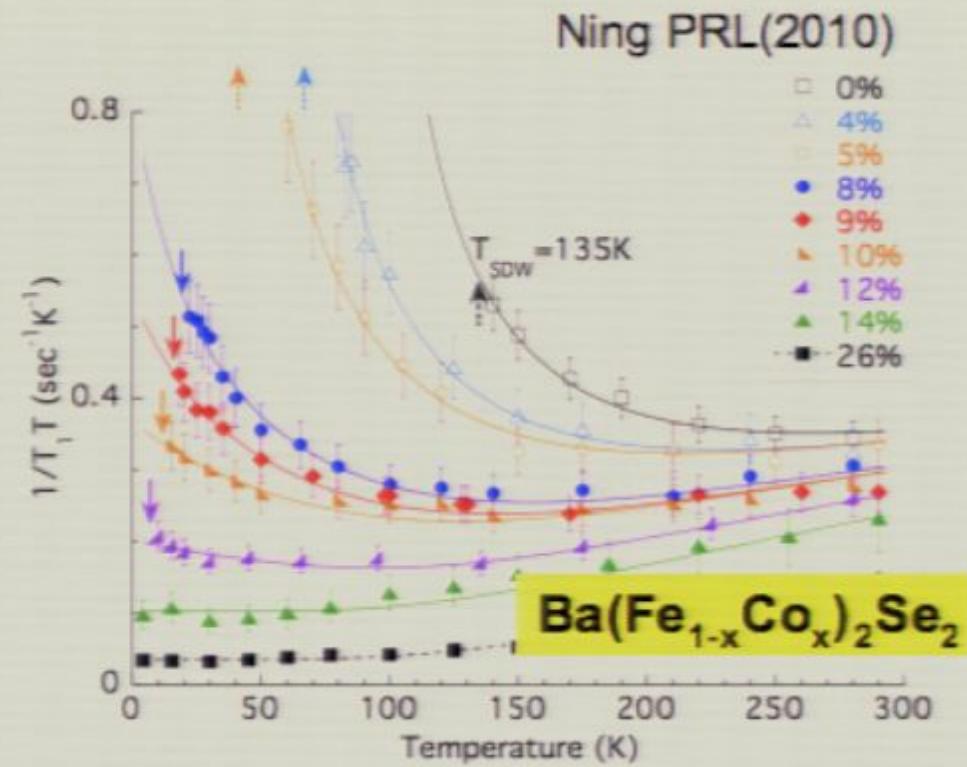
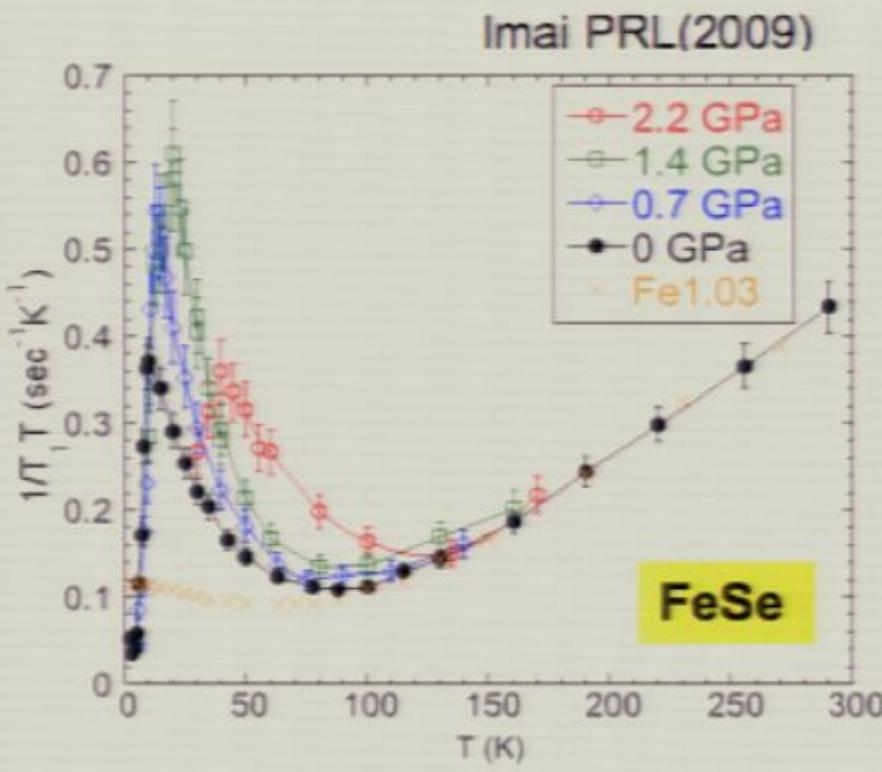
**FeSe**



- 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)

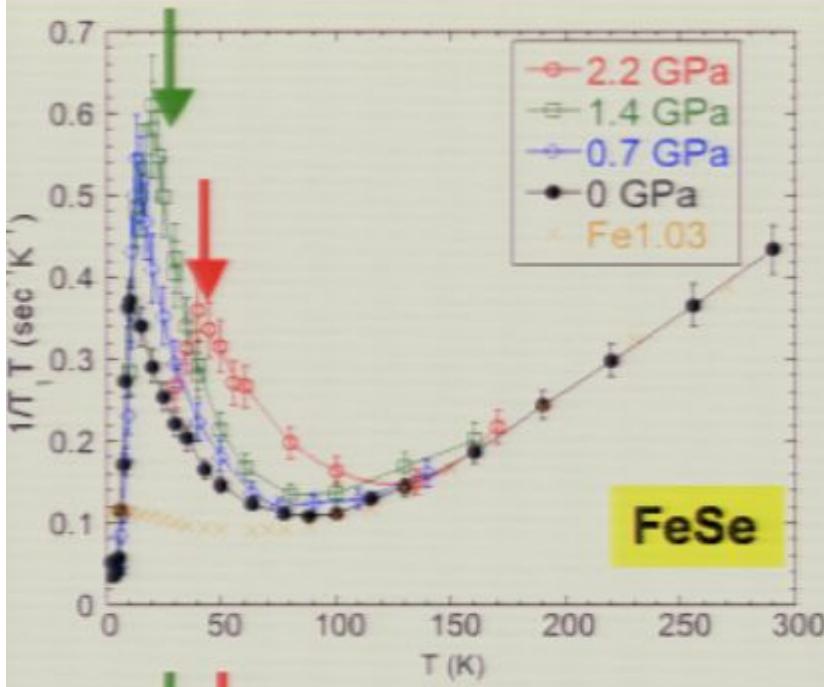


## Spin fluctuations $\chi''(q, f)$ as measured by $^{77}\text{Se}$ NMR $1/T_1 T$

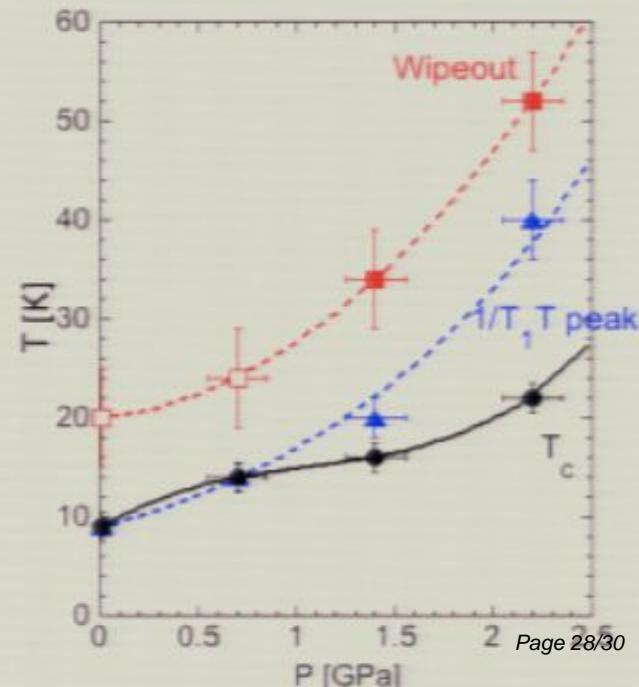
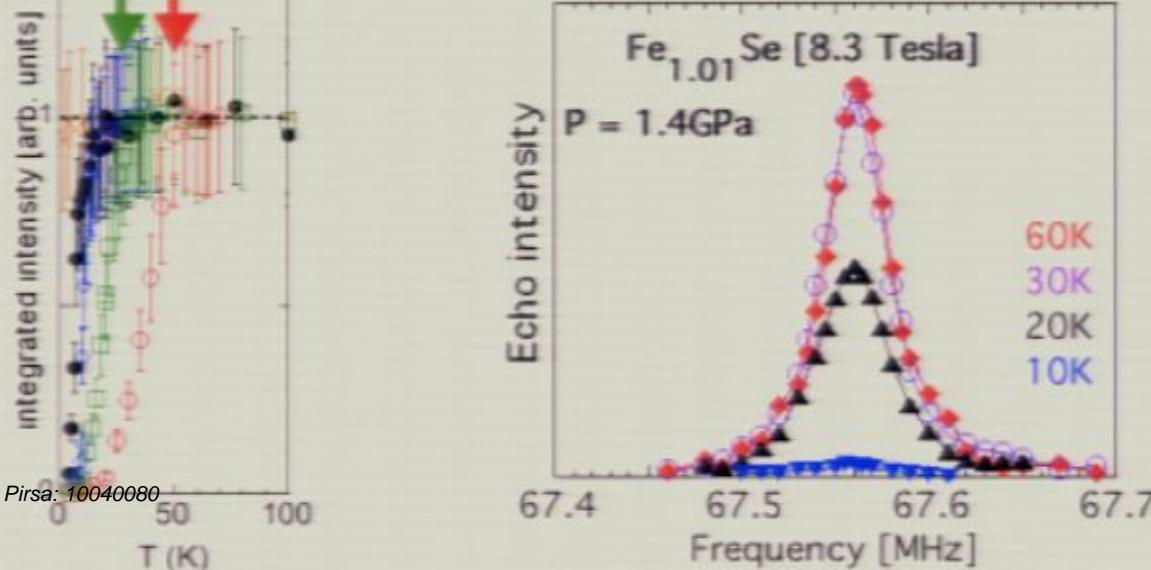


- 1)  $\text{Fe}_{1.01}\text{Se}$  ( $T_c=9\text{K}$ ): Qualitatively the same behavior as superconducting  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ .
- 2)  $\text{Fe}_{1.03}\text{Se}$  (Non-SC): No enhancement of AFSF at low T; qualitatively the same behavior as overdoped non-SC  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ .
- 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  $T_c$ .

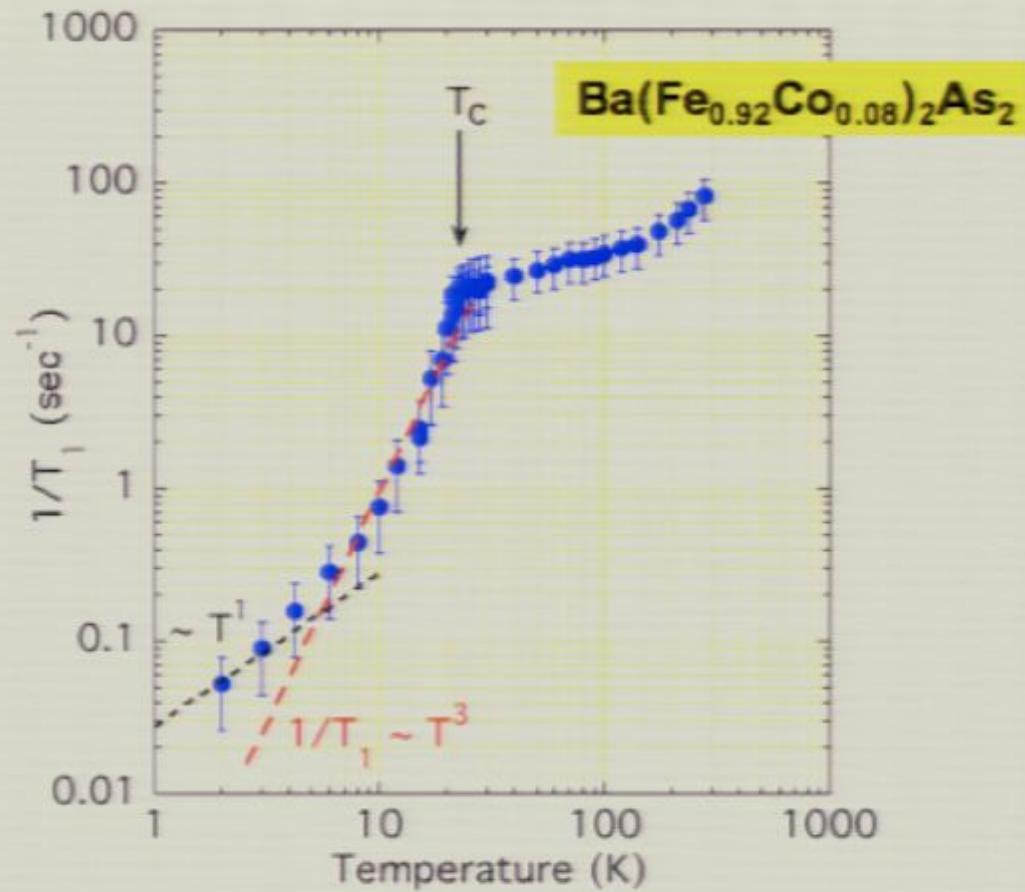
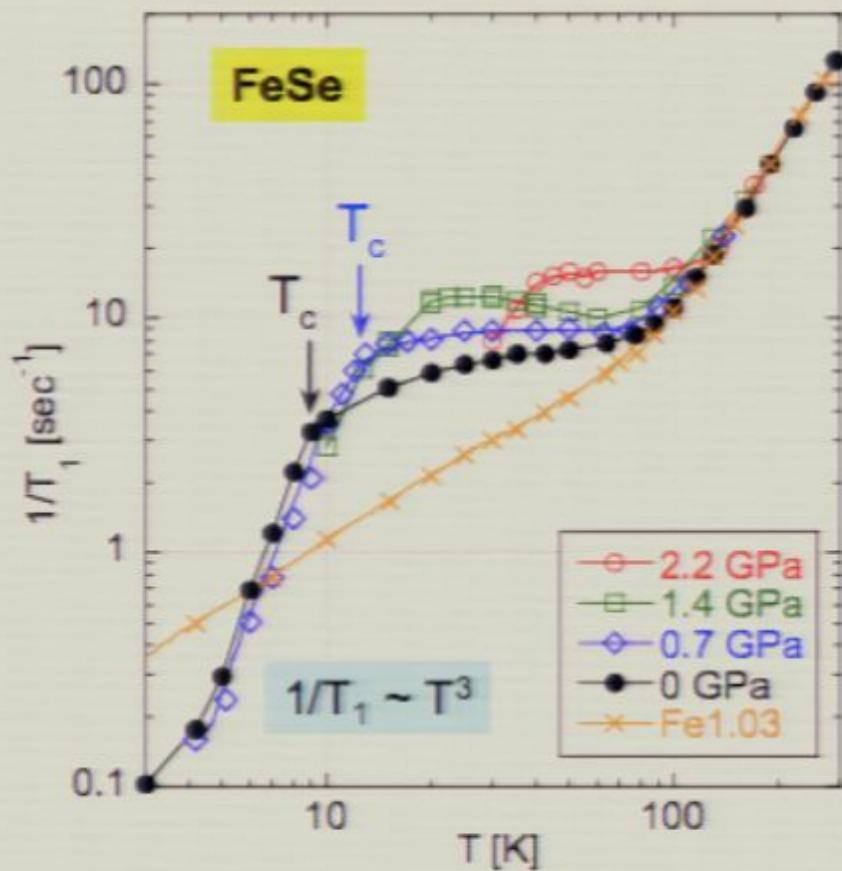
## Complications: NMR signal intensity wipeout; spin freezing and/or phase separation under pressure $P > 1$ GPa?



- 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)



# 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  $Ba(FeCo)_2As_2$  and FeSe.
3. Superconductivity optimized when AF spin fluctuations obey a Curie law  $\chi''_{AF} \sim 1/T$ , 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.