# Spin glass behaviour in interacting magnetic nanoparticles

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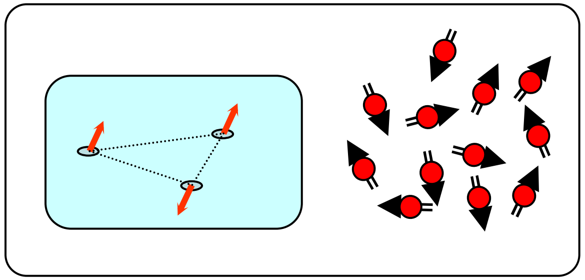
Tokyo University, May 2008

# Spin glass, superspin glass: introduction

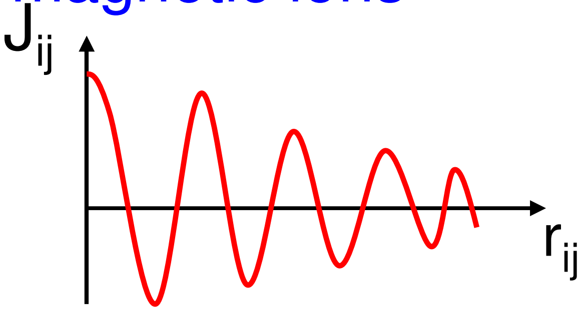
# What is a spin glass ?

**Theory :** random bonds $\mathcal{H} = -\sum J_{ij} S_i.S_j$ $\{J_{ij}\}$ gaussian, or ±*J*



**a disordered *and* frustrated** magnetic system

***"Real"* spin glasses :** random dilution of magnetic ions



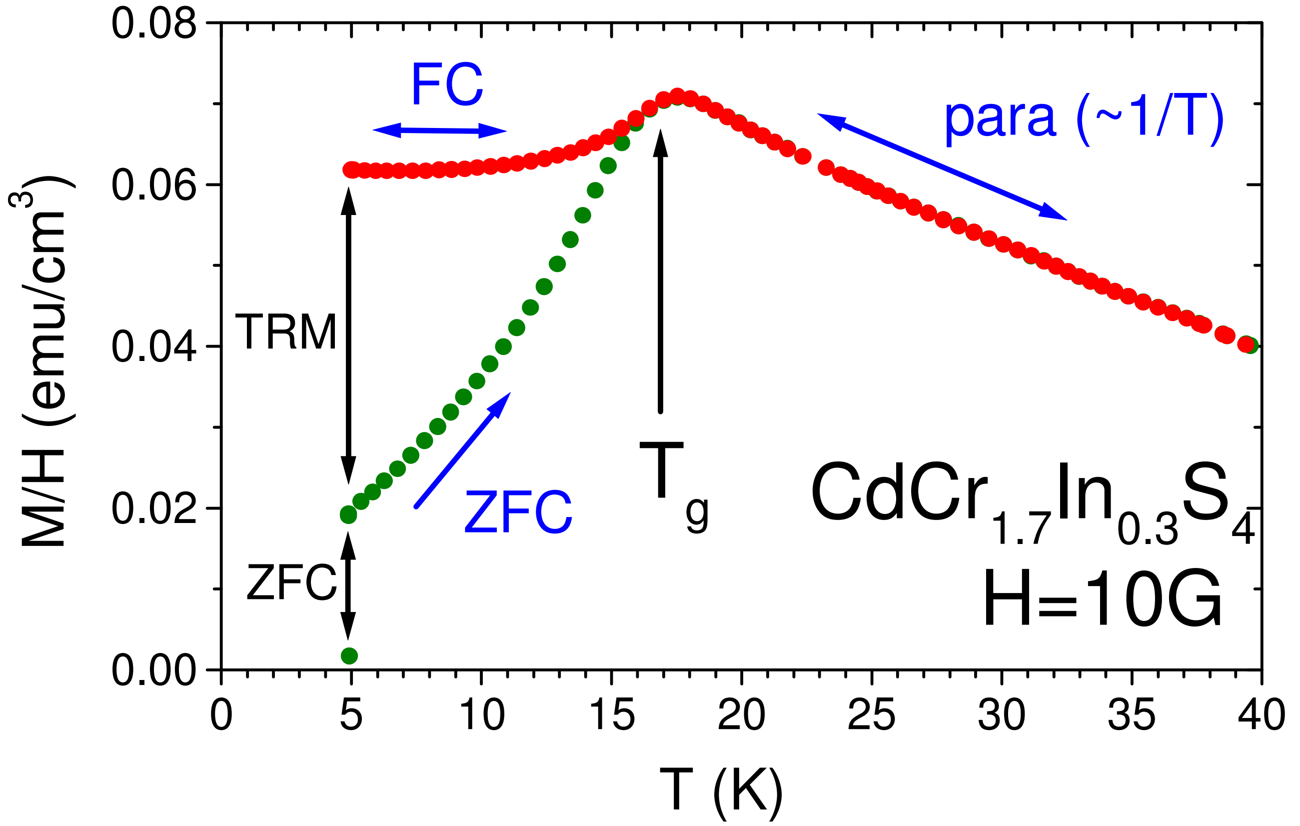
example: metallic alloys, Cu:Mn 3%

*RKKY interactions*

same generic behaviour in all samples
(Tc≠0 in 3d, slow dynamics, aging...)

→ « *model* » *disordered systems*

# SPIN GLASS: HISTORY-DEPENDENT BEHAVIOUR



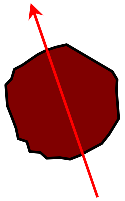
**FC** ≡ **F**ield-**C**ooled magnetization

**ZFC** ≡ **Z**ero-**F**ield **C**ooled magnetization

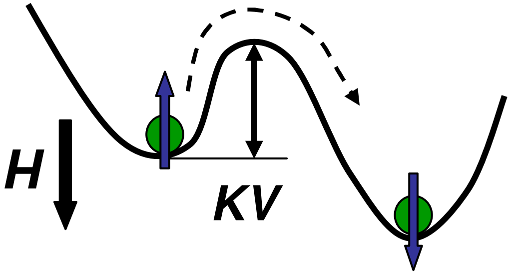
**TRM** ≡ **T**hermo-**R**emanent **M**agnetization

# Super-spins, superspin glass

- Small enough ferromagnetic nanoparticle→ single domain
- T<<$T_c$ : response of single nanoparticle ~ response of single spin
  → a ‘superspin’



- Anisotropy barrier ~K.V
  T<<KV → blocking of magnetization



- Varying concentration of nanoparticles in a liquid dispersion changes dipole-dipole interparticle interaction

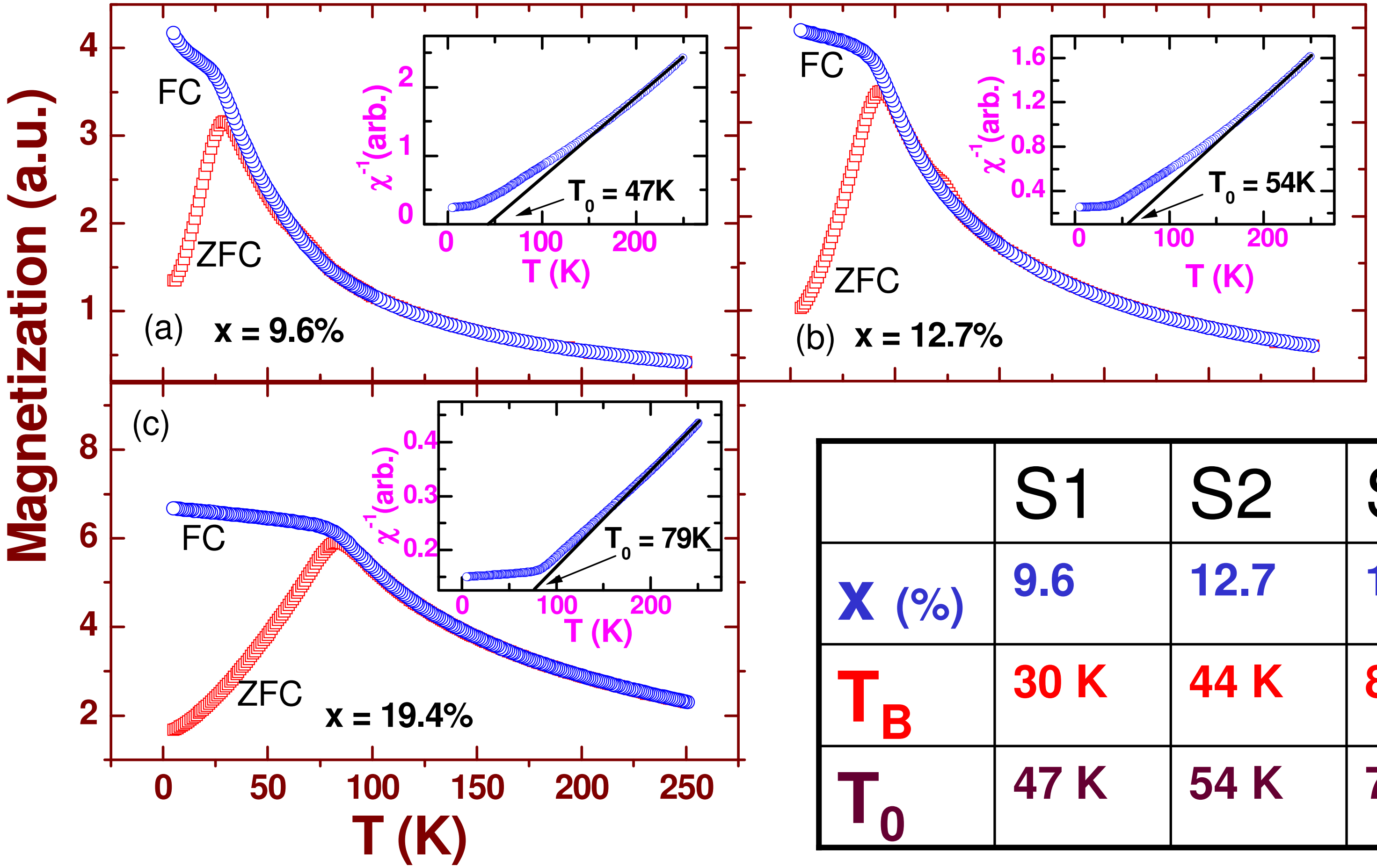
Dilute nanoparticle system
↓
Non-interacting superspins
Superparamagnet

Concentrated nanoparticle system
↓
Interacting superspins
Superspin glass ?

# Co nanoparticles in Ag matrix

## ($Co_xAg_{1-x}$ , metal matrix → RKKY interactions)

X.X. Zhang group, Phys. Rev. B75, 014415 (2007)

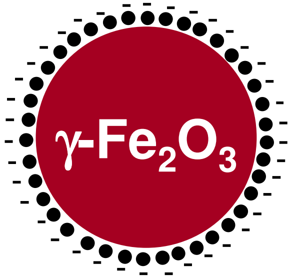


| | S1 | S2 | S3 |
|---|---|---|---|
| $x$ (%) | 9.6 | 12.7 | 19.4 |
| $T_B$ | 30 K | 44 K | 84 K |
| $T_0$ | 47 K | 54 K | 79 K |

With increasing x : increase of $T_B$ and $T_0$, flattening of FC curve

# $\gamma$-$Fe_2O_3$ nanoparticles

- $\gamma$-$Fe_2O_3$ (maghemite, $T_c$=970K ferrimagnet) nanoparticles dispersed in $H_2O$ (→ dipole-dipole interactions only)
- Citrate molecules adsorbed onto particle surface to prevent aggregation



- Mean diameter ~ 8.5 nm
  ~ log-normal distribution of particle size ($\sigma \approx 0.25$)
- Volume fractions ($\Phi$) ranging from 0.01 % → 35 %
  *dipole-dipole interaction energies varying*
  *from << 1 K to ~ 45K*

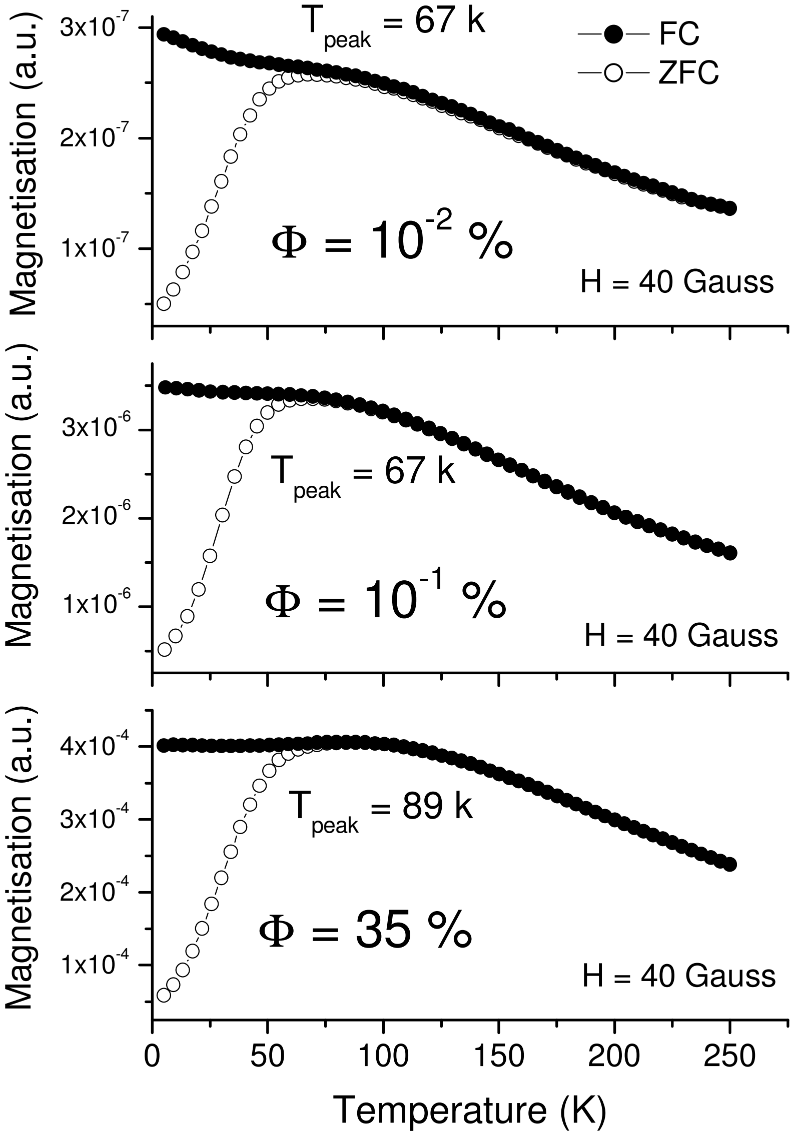
F. Gazeau et al, J. Magn Magn. Mat. **186,** 175 (1998)

# Effect of the nanoparticle interactions

## (dipole-dipole interactions)

- The ZFC-peak temperature increases with increasing concentration Φ

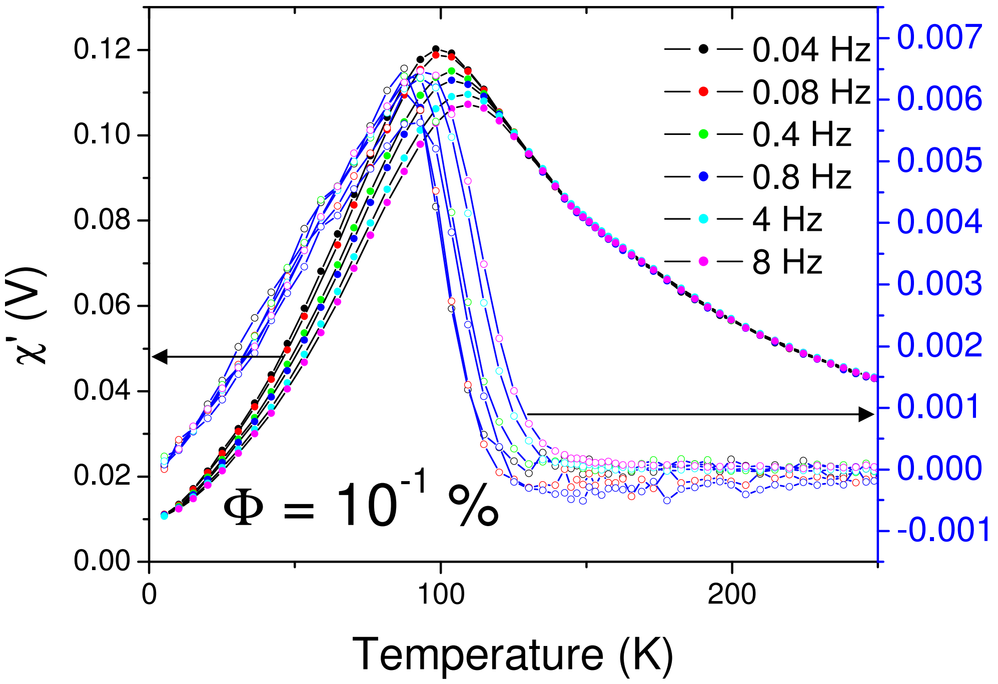
- The FC magnetization *flattens* with increasing concentration (spin glass-like behaviour)

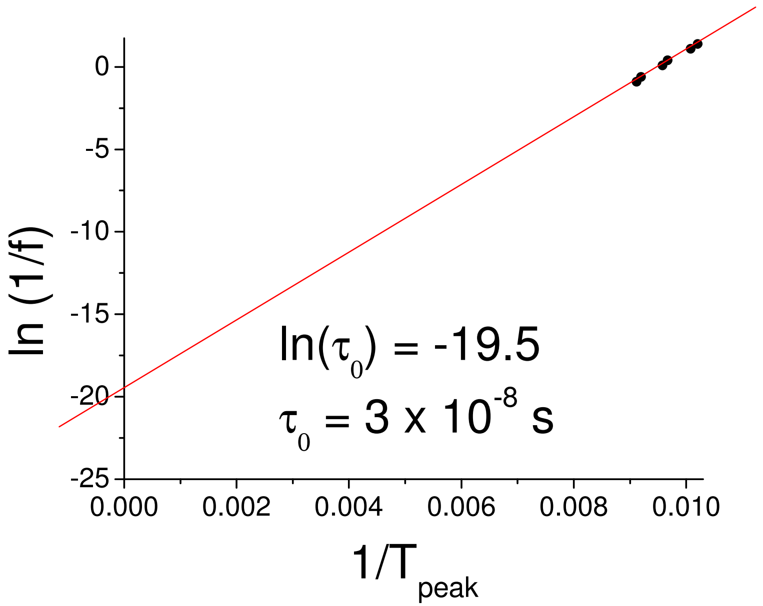


Parker et al, *J. Appl. Phys.* **97**, 10A502 (2005)

# Superspin glass transition: critical behaviour (from *ac*)

# Dilute nanoparticles ($\Phi = 10^{-1}$ %) : frequency dependence of the AC susceptibility peak





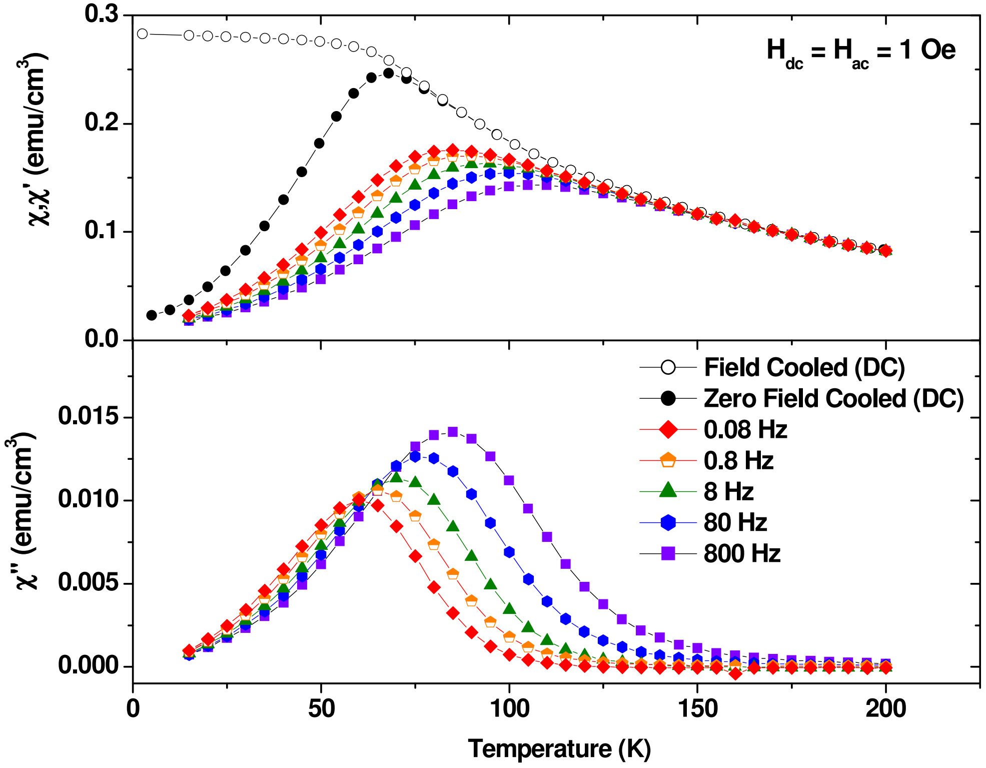
Shift in χ' peak with frequency, as expected for *both* superparamagnets and spin glasses

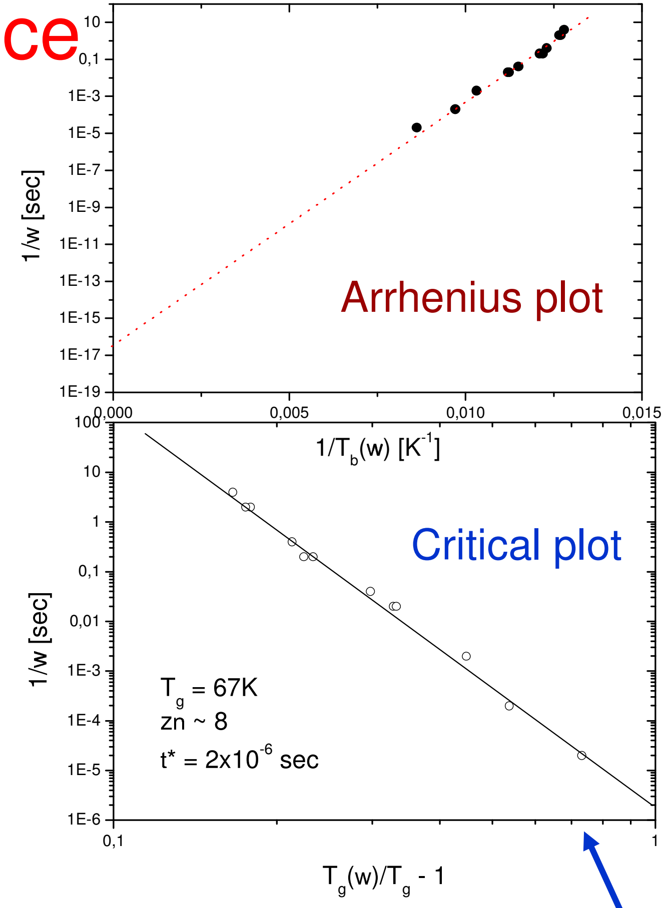
Quantitatively: good fit to Arrhenius Law $1/f = \tau = \tau_0 \exp\left(E_a/k_B T_{peak}\right)$

with $\tau_0 \approx 10^{-8}$ s

→ consistent with superparamagnetic freezing of independent particles

# Concentrated nanoparticles (Φ = 15 %): *critical* frequency dependence





- Shift in χ' peak with frequency (expected for both SPM and SG)
- Quantitatively: Arrhenius Law: $1/\omega = \tau = \tau_0 \exp(E_a/k_B T_{peak})$ yields

$\tau_o \approx 10^{-17\sim18}$ s → *unphysically small*

signature of cooperative behaviour (interactions)

Fits well to critical slowing down:

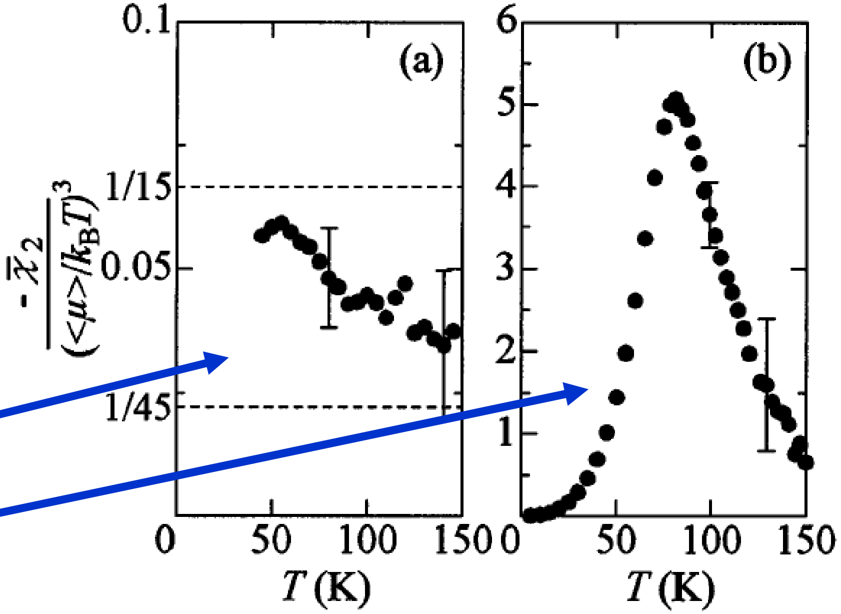
$$1/\omega = \tau = \tau_0 \xi^z = \tau_0 \left( \frac{T_{peak}(\omega) - T_g}{T_g} \right)^{-z\nu}$$

# Cooperative behaviour also seen in dc non-linear susceptibility (like in spin glasses)

Example:

$Fe_3N$ 6nm nanoparticles

Mamiya et al, PRL 80, 177 (1998)



Diluted sample

Dense sample

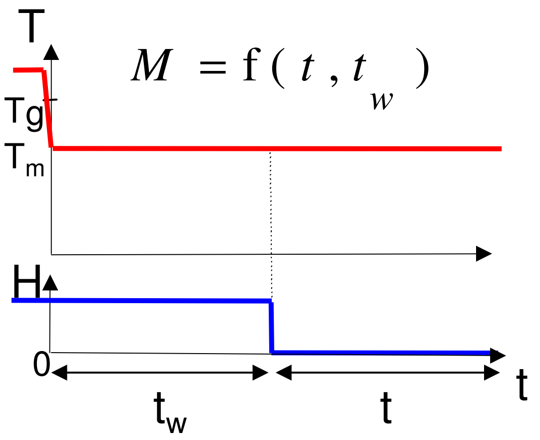
FIG. 4. Temperature dependence of the nonlinear susceptibility $\overline{\chi}_2$ divided by $(\langle\mu\rangle/k_B T)^3$ (a) for diluted sample d6 and (b) for dense sample d1.

see also numerous results by P. Jönsson and Uppsala group

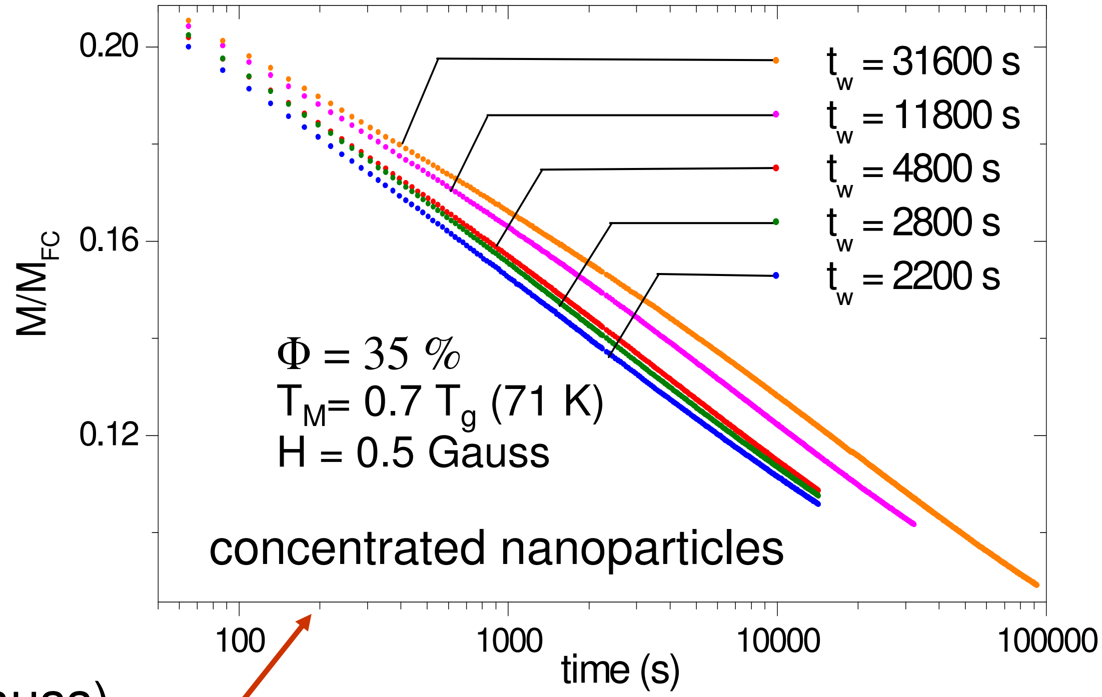
# Aging effects
# in the superspin glass

# Relaxation of the **T**hermo-**R**emanent **M**agnetization

TRM protocol



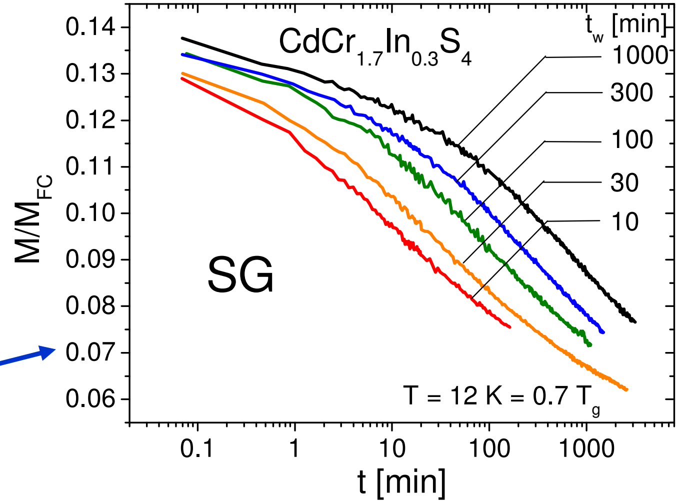
$t_w$ = waiting time
t = measuring time



small excitation field (0.5 Gauss)

Slow relaxation of the magnetization + $t_w$-dependence (as in an atomic spin glass)

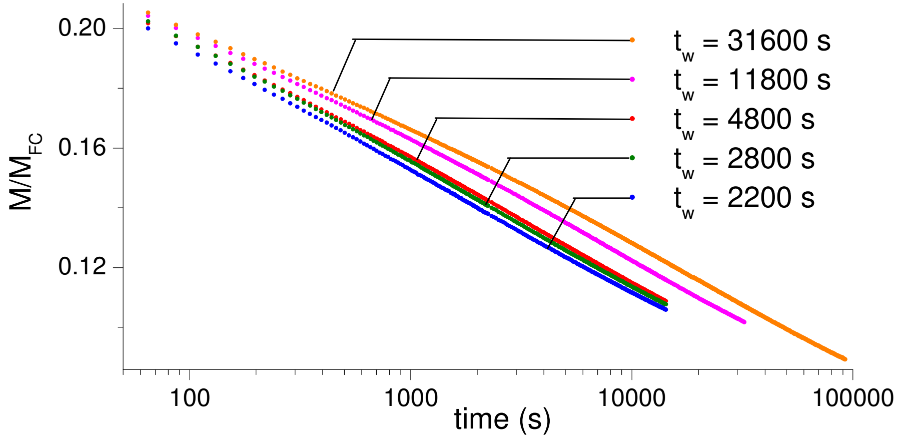
*But separation of relaxation curves much less than for atomic spin glasses*

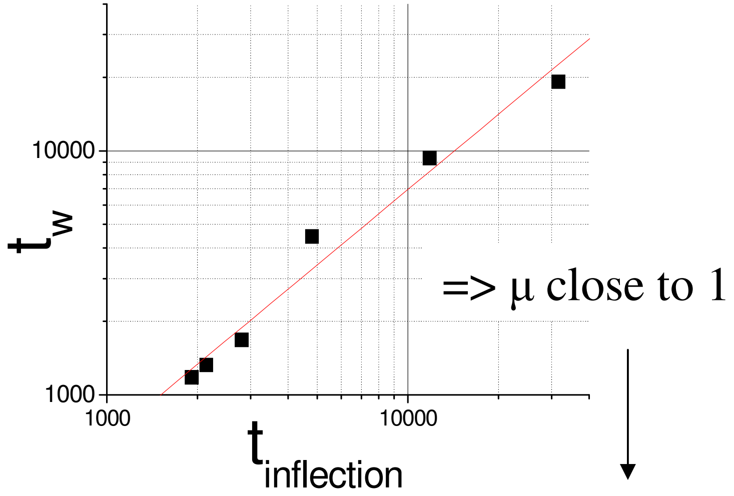


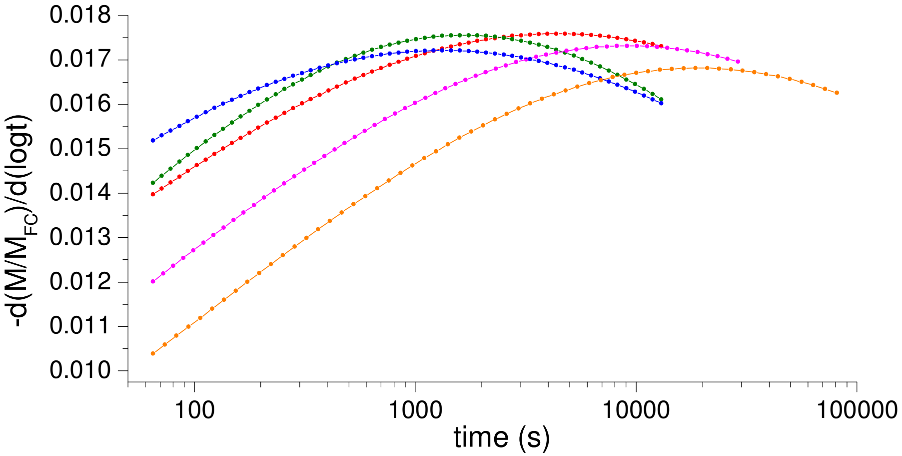
# Scaling of the relaxation curves

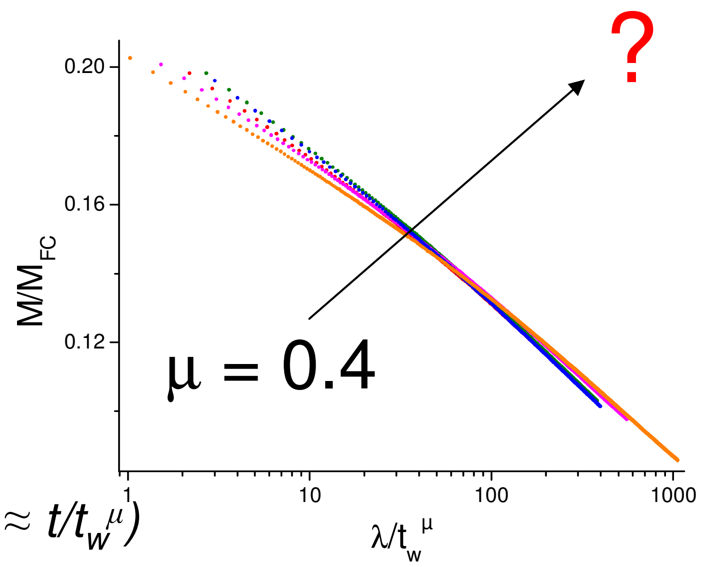
log $t_{inflection} \approx$ log $t_w$ (as in atomic spin glasses)

→ Expect rough scaling of relaxation curves as a function of $t/t_w^{\mu}$ with $\mu$ close to 1* … *but this is not the case*





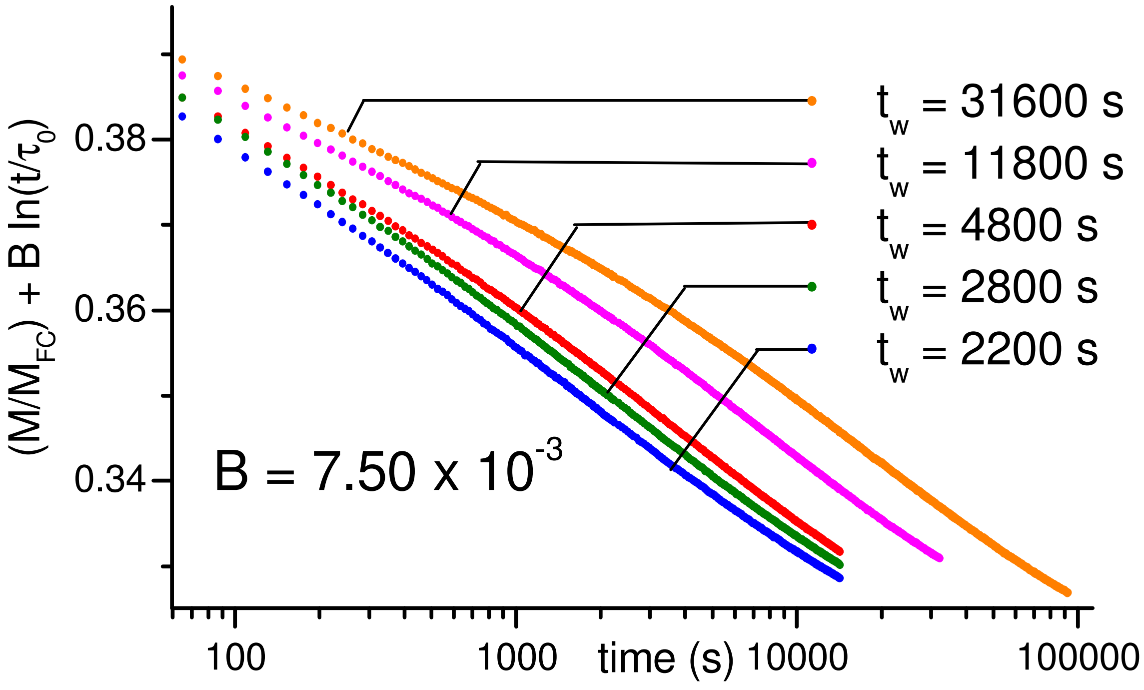




*(or more precisely $\lambda/t_w^{\mu} = t_w^{1-\mu}\,[(1+t/t_w)^{1-\mu} - 1]/[1-\mu] \approx t/t_w^{\mu}$)*

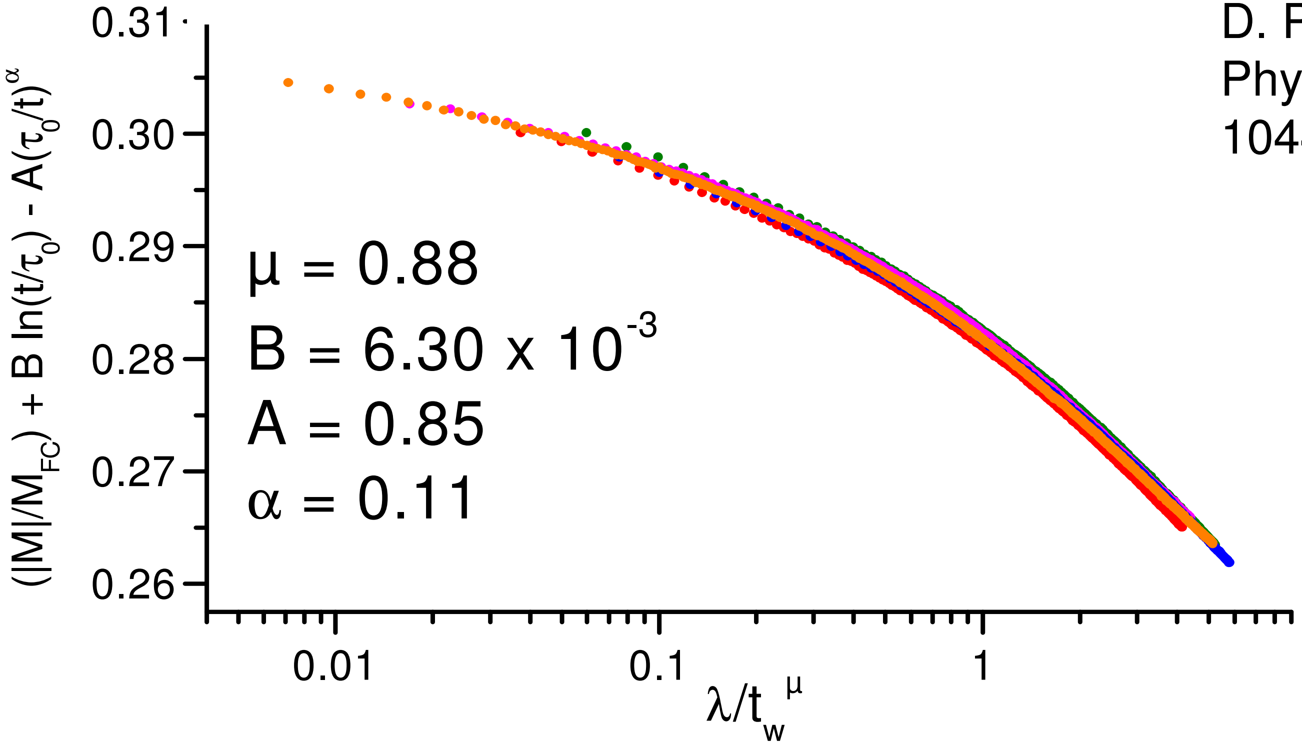
# Accounting for relaxation of independant particles

- Distribution of particle size → distribution of anisotropy energies $E_a = KV$
- Small particles have $E_a$ << dipole-dipole interaction <J>
- But larger particles with $E_a \geq$ <J> may relax independently of interparticle interactions
- → correct $M/M_{FC}$ by subtracting $-B \ln(t/\tau_0)$ term to account for superparamagnetic-like relaxation of larger particles



# Spin glass-like scaling of the corrected TRM curves

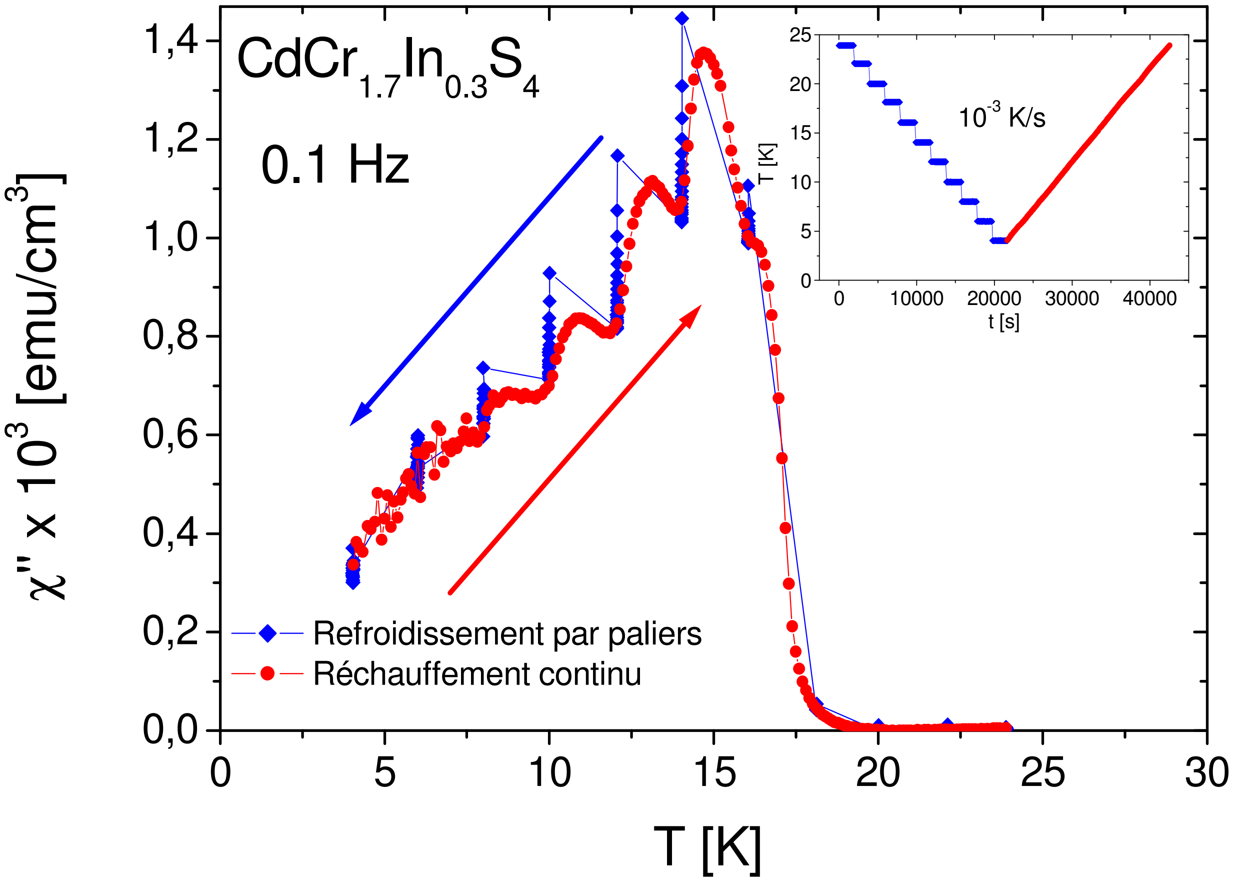
- Scaling of the relaxation curves can be achieved after subtracting –B ln($t/\tau_0$) term
- Scaling parameters are comparable to those found for atomic spin glasses



D. Parker et al,
Phys. Rev. B 77,
104428 (2008)

# Memory effects
# in the superspin glass

# Rejuvenation and memory effects in a spin glass



T↓ : rejuvenation

T↑ : memory

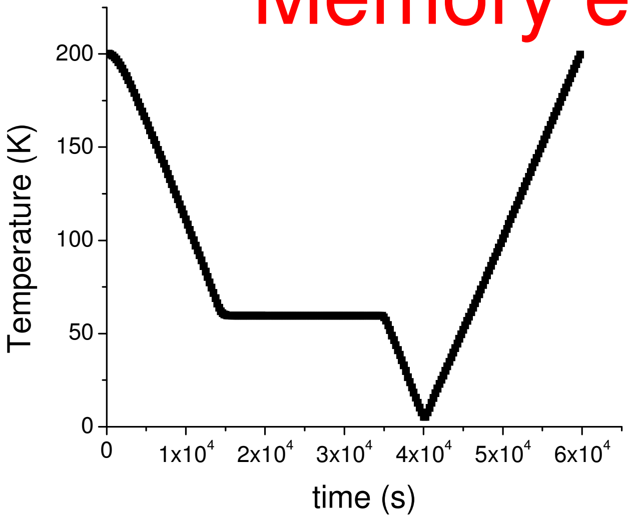
« memory dips » experiments:

Uppsala / Saclay *PRL* **81**, 3243 (1998)

S. Miyashita and EV, Eur. Phys. J. B **22**, 203 (2001)

*See more details and references in cond-mat/0603583*

# Memory effects in a superspin glass

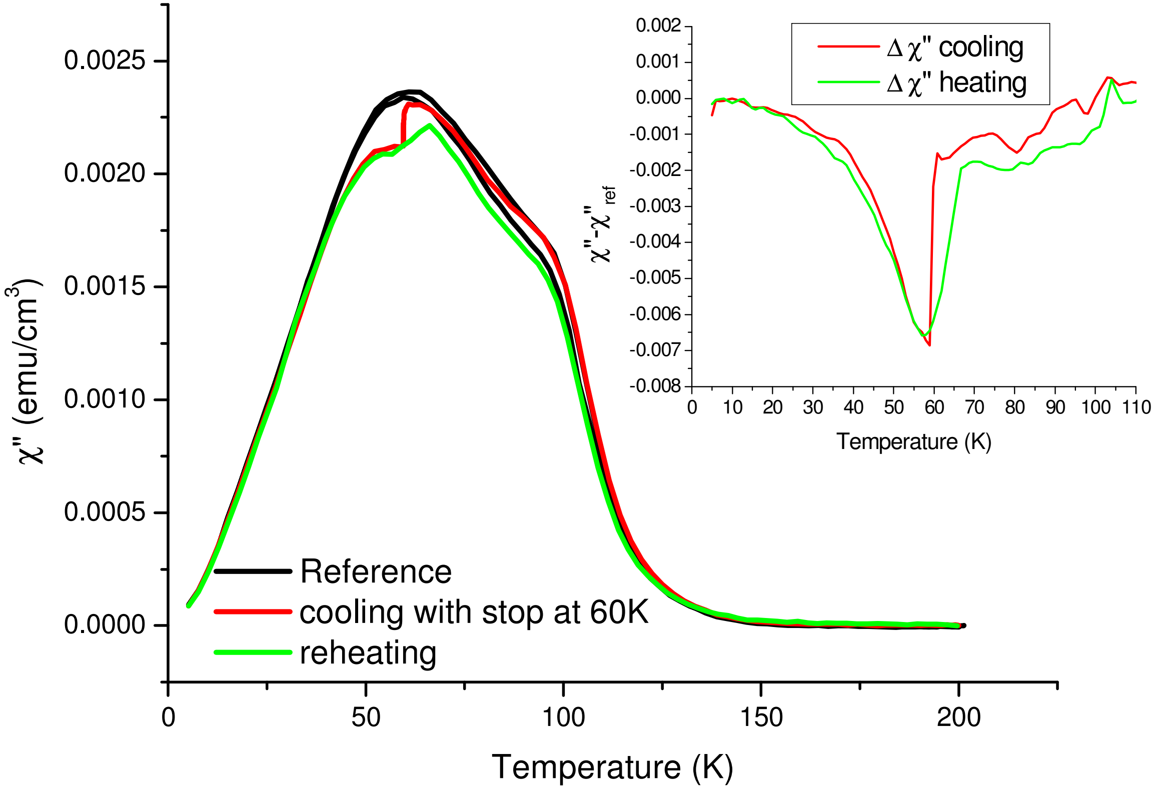


$\gamma$-$Fe_2O_3$ nanoparticles in water

d=8.5nm

$\Phi$=35%

- no visible rejuvenation
- but clear memory effect



V. Dupuis et al, AIP Conf. Proc. 832, 295 (2006)

PHYSICAL REVIEW B **71**, 104404 (2005)

## Absence of strong rejuvenation in a superspin glass

P. E. Jönsson,[1] H. Yoshino,[2] H. Mamiya,[3] and H. Takayama[1]

Concentrated $Fe_3N$ nanoparticle system

Clear T-specific memory effect, although not so well-marked as in atomic SG's

SSG $\tau_0 \approx 10^{-9}$ s (or longer)
SG $\tau_0 \approx 10^{-12}$ s
*longer $\tau_0 \rightarrow$ shorter accessible time scale $t_{exp}/\tau_0$*

(see next section)

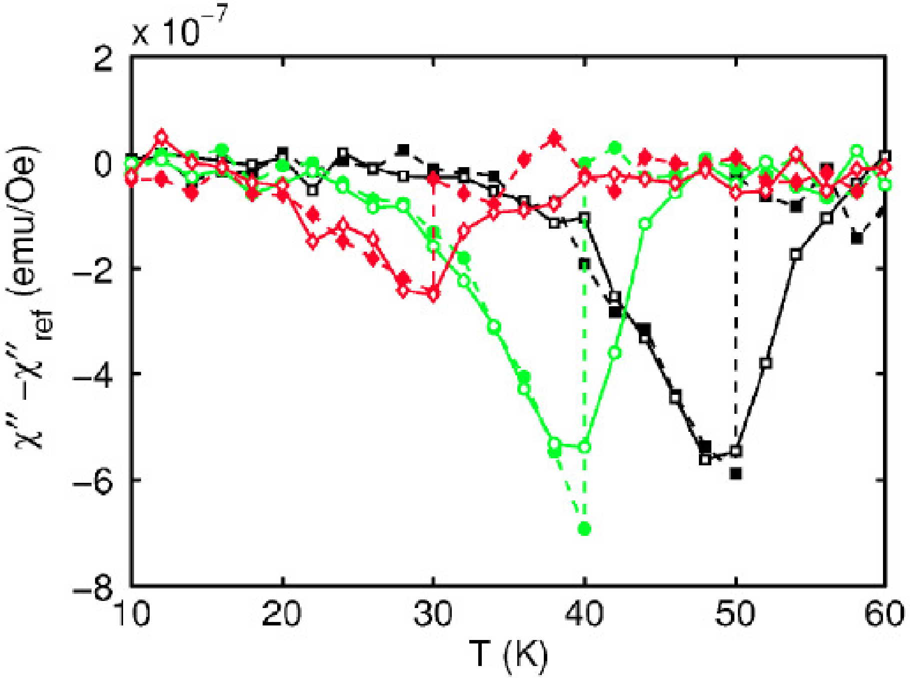


FIG. 7. (Color online) $\Delta\chi''$ vs temperature measured on cooling (filled symbols connected by dashed lines) and reheating (open symbols connected by solid lines). A temporary stop is made on cooling at $T_s$=50, 40, or 30 K for $t_s$=9000 s. $\omega/2\pi$=510 mHz.

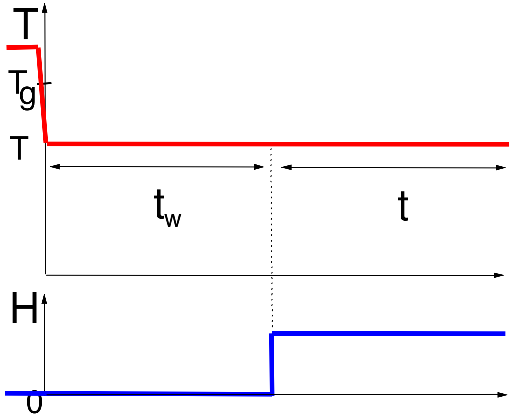
# Aging seen as *slow growth of a “glassy order”*

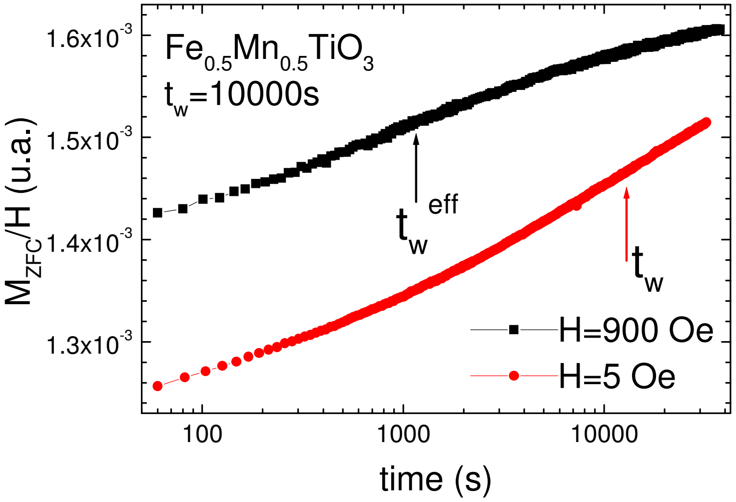
# Growing number of correlated spins from field effect experiments

Field amplitude influence on the *dc*-magnetization relaxation (TRM or ZFC)

Relaxation becomes faster with H (inflection point $t_W \rightarrow t_W^{eff}$ )

Atomic SG example





Inflection at ~ $t_W$ = maximum relaxation rate : typical energy barrier $\Delta$

$$t_w = \exp(\Delta / k_B T) \rightarrow \Delta = k_B T \ln(t_w) \qquad \Delta - E_Z(H) = k_B T \ln(t_w^{eff}(H))$$

$$E_Z = k_B T \ln\left(t_w / t_w^{eff}\right)$$

Zeeman Energy : $H \leftrightarrow N_s(t_W)$ coupling after $t_w$

Y.G. Joh et al, PRL 82, 438 (1999), R.Orbach’s group in UCR + Saclay

F. Bert et al, Phys. Rev. Lett. 92, 167203 (2004)

What is the dependence of $E_Z = k_B T \ln(t_w / t_w^{eff})$ on $N_S(t_w)$?

Hyp. 1: $M(N_s) \propto \sqrt{N_s}$ *(Ising spins)*

then $E_Z(H,t_w) = \sqrt{N_s}\, m\, H$ *(m = moment of 1 spin)*

Hyp. 2: $M(N_s) \propto N_s$ *(Heisenberg-like spins)*

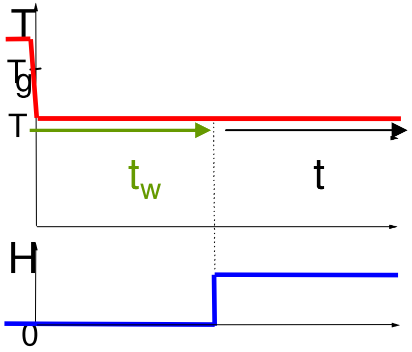
then $E_Z(H,t_w) = N_s\, \chi\, H^2$ *($\chi$ = susceptibility of 1 spin)*

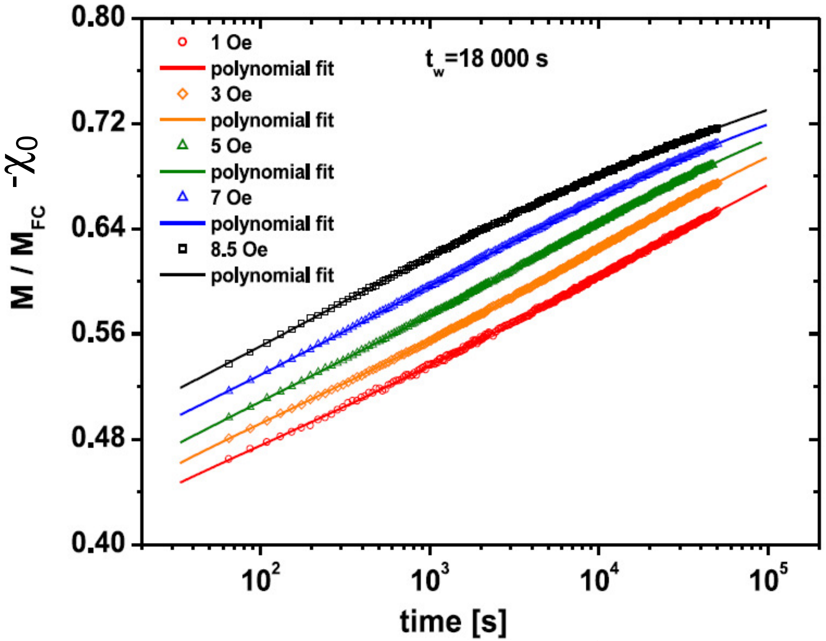
*Measure at various H & $t_w$ to construct $t_w^{eff}(H, t_w) \rightarrow E_Z(H,t_w)$*

→ number of correlated spins $N_s(t_w)$ *and* $L = N_s^{1/3}$

*Increase of $N_s(t_w)$ with $t_w$ → slow growth of a “spin glass order”*

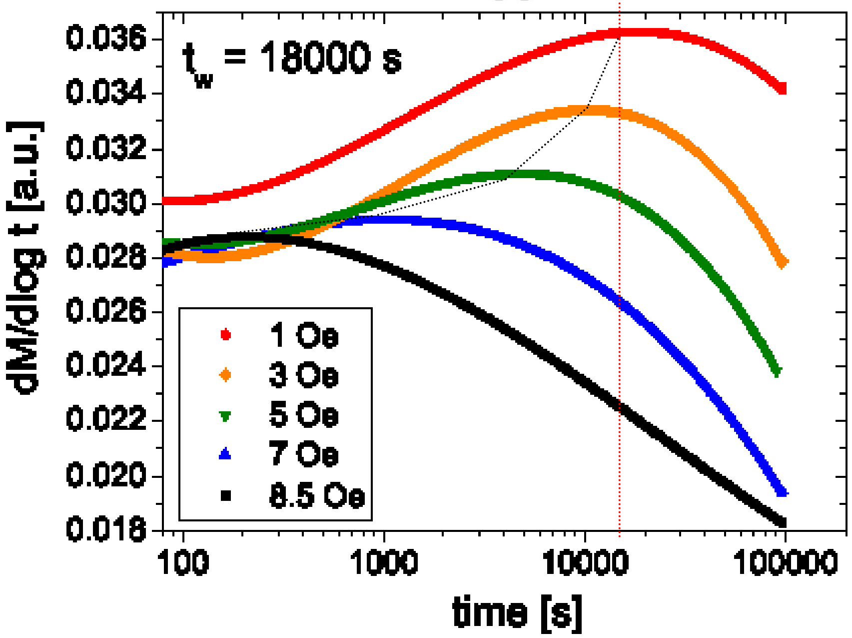
# Relaxation of the superspin glass: field effect



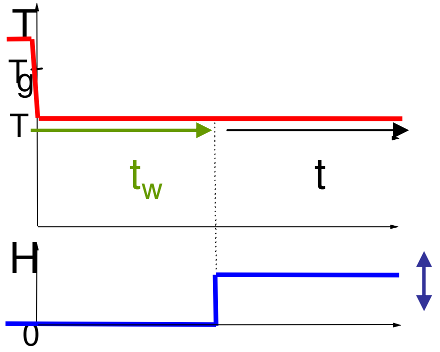


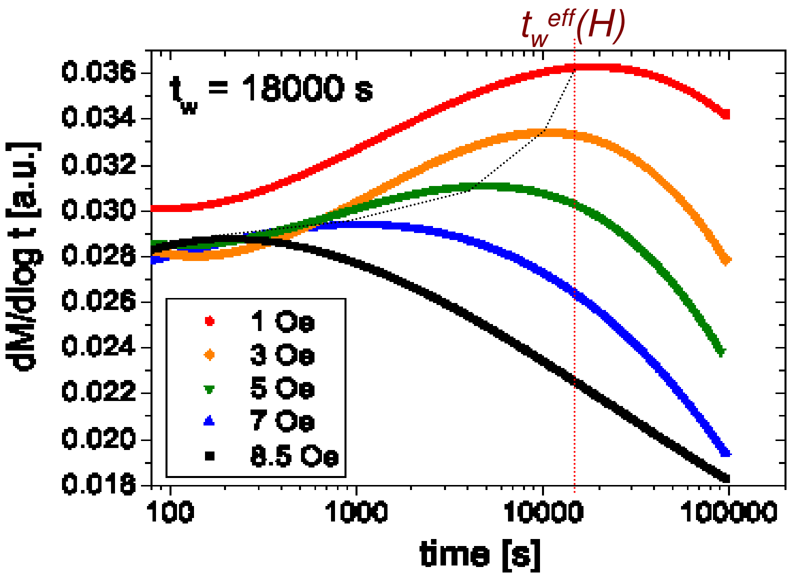
- Vary *H* amplitude and $t_w$
- Find $t_w^{eff}(H)$

$$\longrightarrow \quad E_Z = k_B T \ln\left(\frac{t_w}{t_w^{eff}}\right)$$



# Relaxation of the superspin glass: field effect

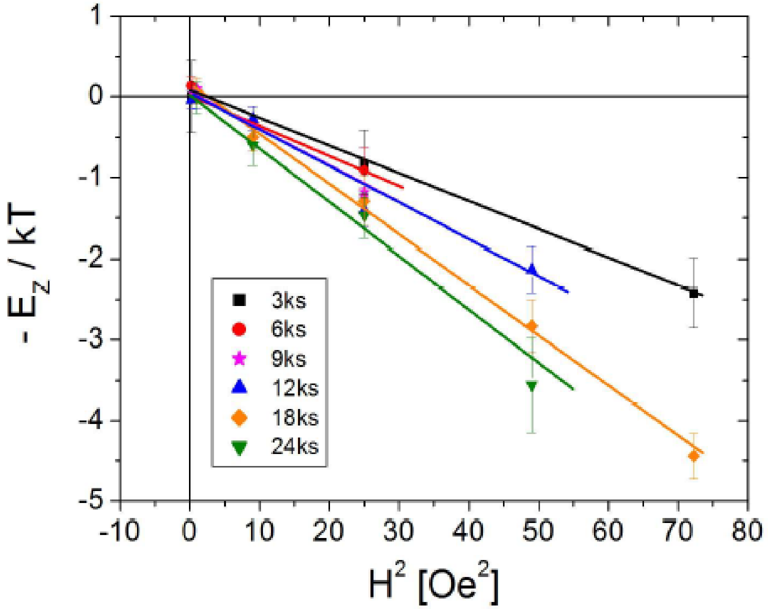




- Vary $H$ amplitude and $t_w$
- Find $t_W^{eff}(H)$

$$E_Z = k_B T \ln\left(\frac{t_w}{t_w^{eff}}\right)$$

*result:* $E_Z \propto N_s H^2$ *(Heisenberg-like)*



# Aging ≡ growing number of correlated (super)spins

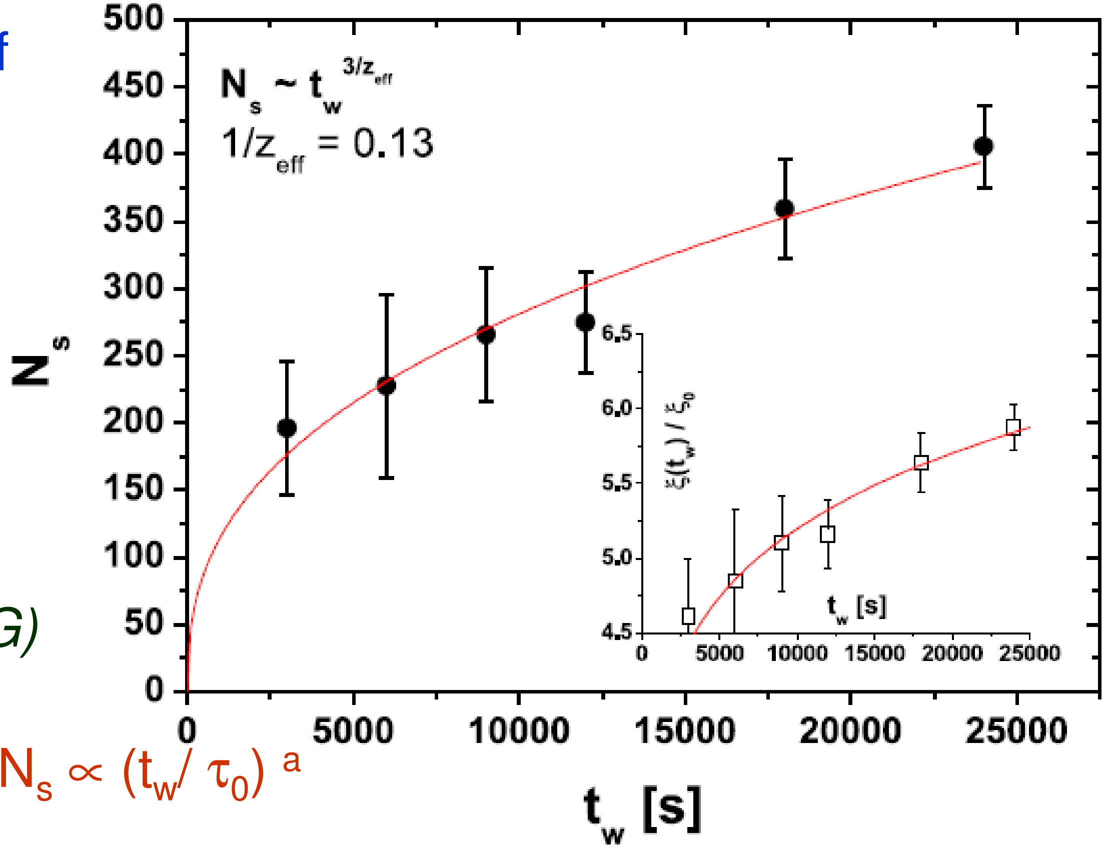
$N_s$ is growing ~ as a power law of $t_w$ (red curve = fit)

$N_s \sim t_w^{3/z\_eff}$ with $z_{eff} \sim 7.7$

*Similar power law as in Heisenberg-like spin glasses, but $N_s$ smaller here:*

*$N_s \sim 200 - 400$ ($\sim 10^4 - 10^6$ in SG)*

*$L \sim N_s^{1/3} \sim 4.5 - 6$   ($\sim 10-100$ in SG)*



$N_s$ grows with $t_w$ in units of $\tau_0$ : $N_s \propto (t_w/\tau_0)^a$

$\tau_0$ in atomic SG ~ $10^{-12}$ sec

but $\tau_0$ superspin is at least $10^{-8}$-$10^{-9}$s, or even ~ $exp(E_d/k_BT)$, as large as $\mu s$ → shorter time regime explored in SSG than in SG in units of $\tau_0$

→ $N_s$ smaller *(possible explanation of weaker rejuv. and memory effects…)*

*E. Wandersman PhD thesis, paper in progress*

# Conclusions

- Concentrated magnetic nanoparticles : many similarities with atomic spin glasses (super-spin glass, SSG)
- Frequency dependence of *ac* susceptibility → critical slowing down at the SSG transition
- Aging effects, spin glass-like scaling of the relaxation curves *after subtraction of additional superparamagnetic relaxation*
- SG-type memory effects can also be observed, although not so well-marked
- Time-growth of the number of correlated spins can be estimated from field-effect experiments (growing « spin glass order »). Similar power law in SSG as in SG. *SSG → shorter time regime than explored in SG (preliminary results in continuity with SG).*