Advanced magnetic anisotropy determination of nanoparticles through susceptibility and remanence curves

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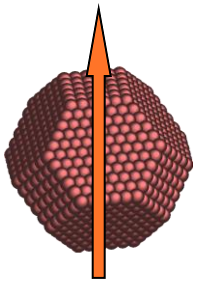
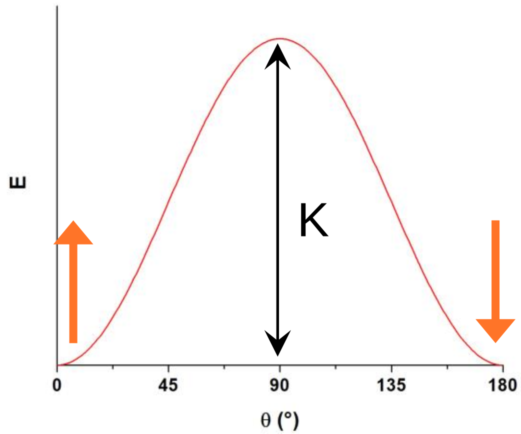
Introduction



Monodomain particle
(macrospin)



Crucial parameter of a nanomagnet:

Magnetic anisotropy energy (MAE)

➡ Switching energy barrier

• Controls the stability of nanomagnets

• Size dependence: $K = K_{eff} V$

➡ Small particles can be superparamagnetic, when $\tau_{measure} < \tau_{switch}$

Important for information storage applications (but also for other applications, for instance hyperthermia…)

Goal: characterization of a real nanoparticle sample

➡ Infer the **intrinsic magnetic properties of nanomagnets**

Introduction

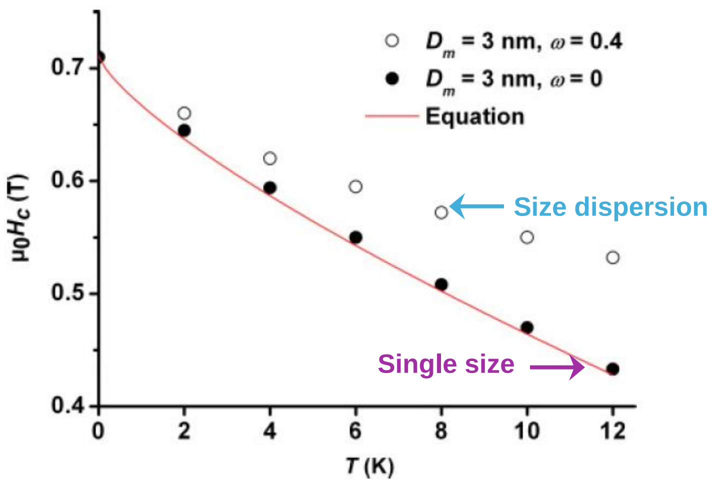
Description with simple models

Often with stringent assumptions: uniaxial macrospins, single anisotropy, single size, no interactions…

Are they valid? Can we use simple and reliable models in a realistic case?

Ex.: • Stoner-Wohlfarth model, at 0 K
• Sharrock formula for the coercive field, Hc(T)

$$H_c(T,V) = H_c(T=0K)[1-(25k_BT/|K_1|V)^{3/4}]$$



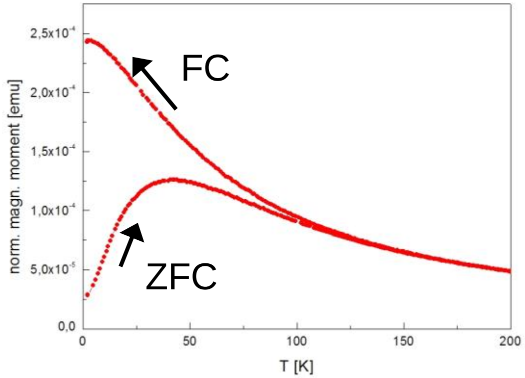
A. Tamion *et al.*, Phys. Rev. B **85**, 134430 (2012).

Widely used measurements:
Zero-field cooled/field cooled curves

ZFC/FC = low field susceptibility curves, as a function of temperature

blocked → superparamagnetic crossover

The anisotropy controls the entire curve.



Outline

- Isothermal remanent magnetization (IRM) curves
  - ⇒ Measurement and meaning of IRM, DcD and ΔM curves
- IRM curves simulation
  - ⇒ Combined Stoner-Wohlfarth and Néel switching time model
- ZFC/FC curves modeling
  - ⇒ Analytical formula, progressive crossover model
- Application to a Co nanoparticle sample
  - ⇒ Interest of combined IRM and ZFC/FC measurements
- Conclusion

Isothermal remanent magnetization (IRM)

Assembly of nanomagnets
(superparamagnetic at high T)

• First, the sample is demagnetized
(cooling to low T, with zero field)

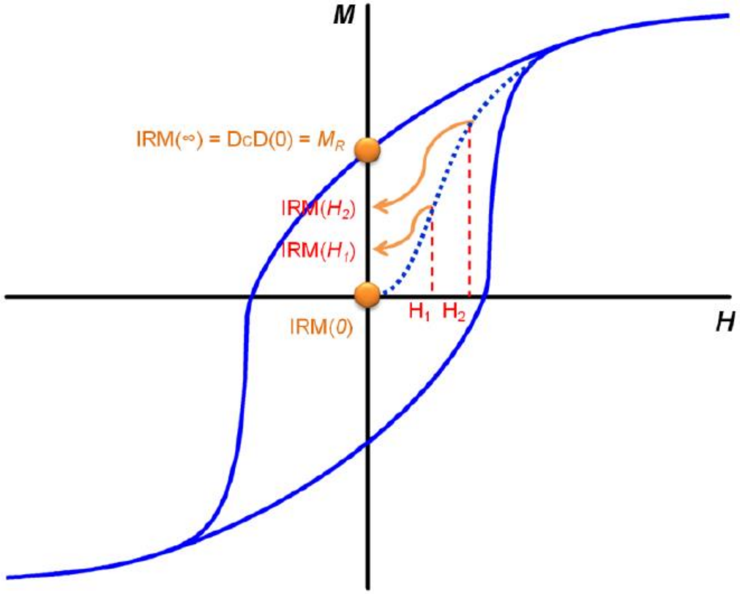
Measurement of the remanent magnetization
after having applied a given field

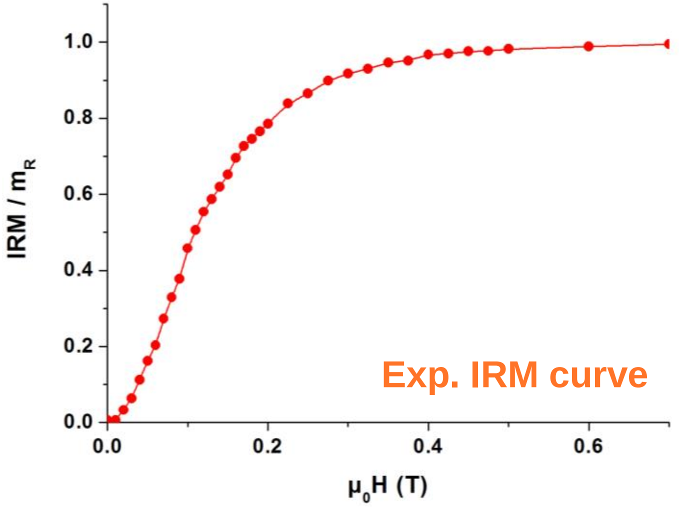
• The applied field is increased, step by step

IRM(H) curve ➡ **Signature of irreversible magnetization switching**

No spurious contribution:

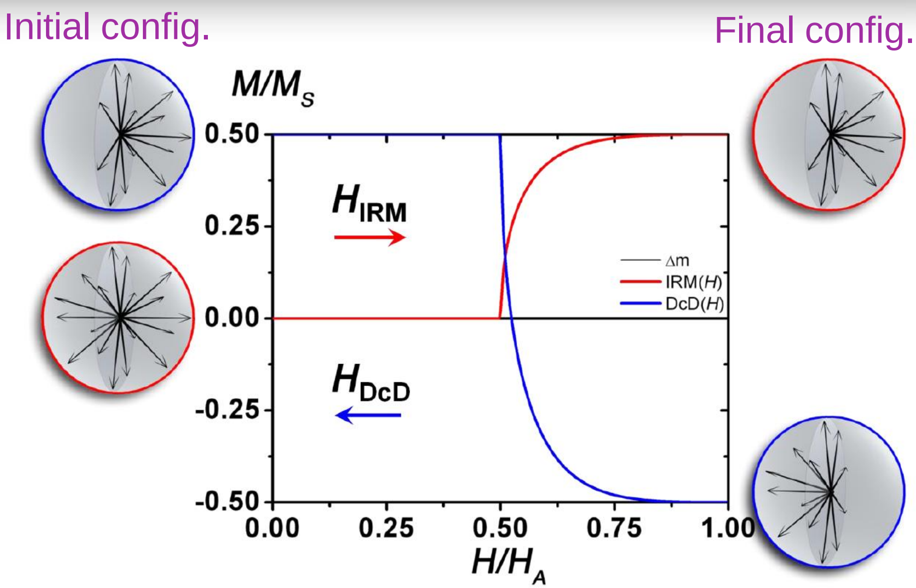
- Superparamagnetic particles
- Diamagnetic substrate, paramagnetic impurities





Measurements very easy to implement!

IRM, DcD and Δm curves



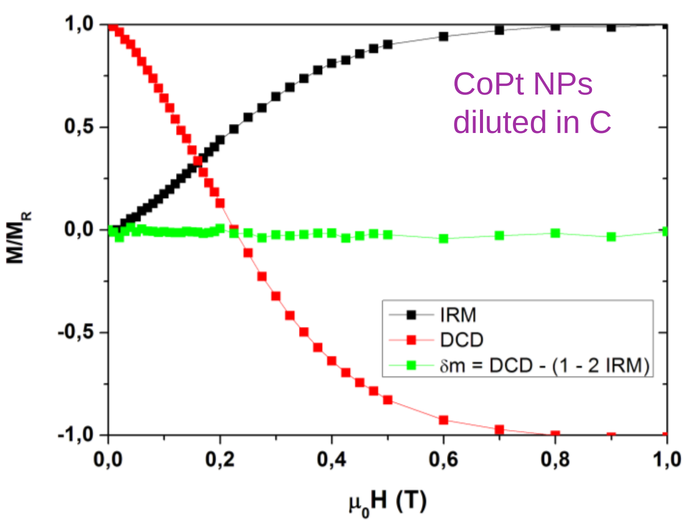
Direct current demagnetization (DcD)

➡ Measurement at remanence, but after having saturated the sample.

Different initial state:
- IRM: demagnetized
- DcD: saturated in the opposite direction, then M_R

If there is **no interaction** (each particle switches independently)

➡ Factor 2 in the number of switching particles: m_R – DcD = 2 IRM



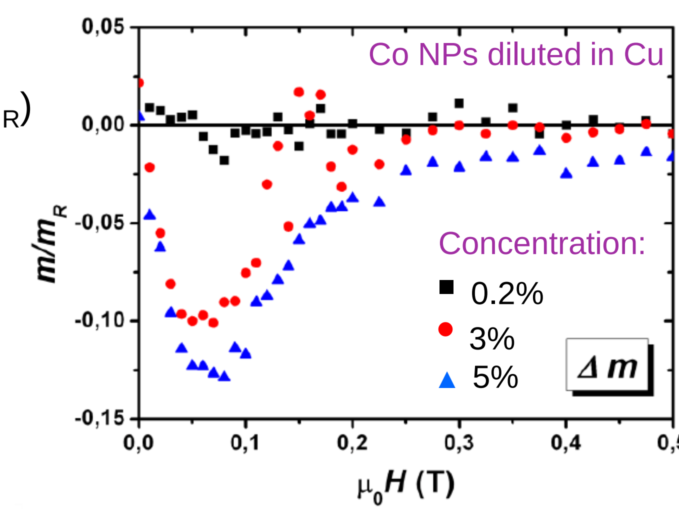
Δm parameter:

$\Delta m = DcD/m_R - (1 - 2\ IRM/m_R)$

No interaction

➡ **Δm = 0 verified**

Very sensitive to interactions!



IRM analytical formulation

Assembly of non-interacting macrospins

- Evolution of the energy barrier with the applied field:

$$\Delta E(H) = K_{\mathrm{eff}} V [1 - H/H^0_{\mathrm{sw}}(\theta)]^{3/2}$$ good approximation (random orientation)

- **Néel** switching time: $\tau = \tau_0 e^{\Delta E/(k_B T)}$

→ Switching if $\tau < \tau_m$ (measure): $\Delta E \leq \ln(\tau_m/\tau_0)\, k_B T \simeq 25\, k_B T$

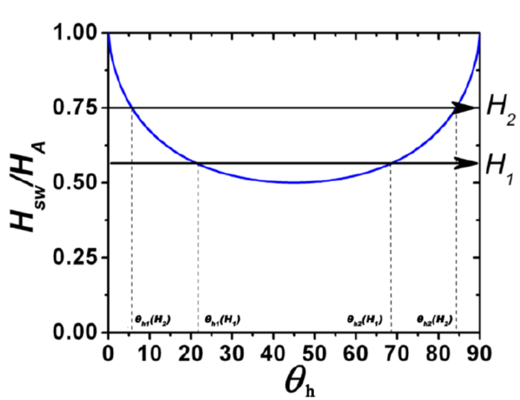
- Decrease of the switching field with T:

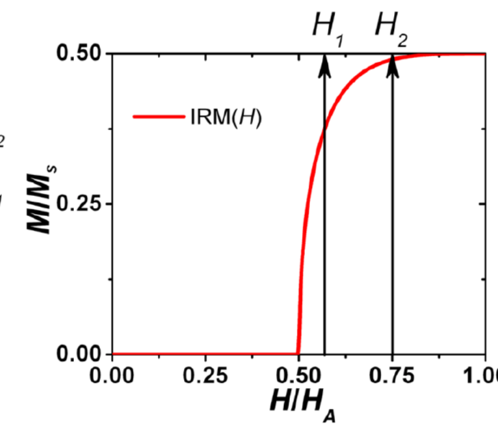
$$H_{\mathrm{sw}}(\theta, T) = c\, H^0_{\mathrm{sw}}(\theta) \text{ with } c = 1 - [25 k_B T/(K_{\mathrm{eff}} V)]^{2/3}$$

- Switching field for a uniaxial particle (**Stoner-Wohlfarth** model):

$$H^0_{\mathrm{sw}}(\theta) = H_A(\cos^{2/3}\theta + \sin^{2/3}\theta)^{-3/2}$$

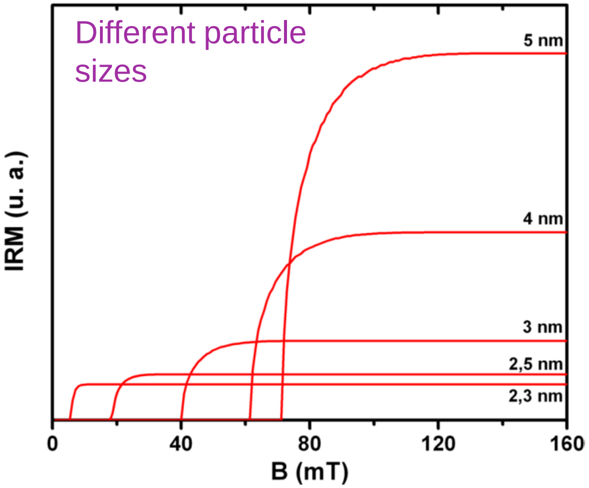
For a given H, determination of the orientations that will switch





Analytical formula: $\mathrm{IRM}(H,T) = m_R \dfrac{1-x^3}{1+x^3}$ with $x = \dfrac{1+2h^2 - \sqrt{12h^2-3}}{2(1-h^2)}$ and $h = H/(cH_A)$

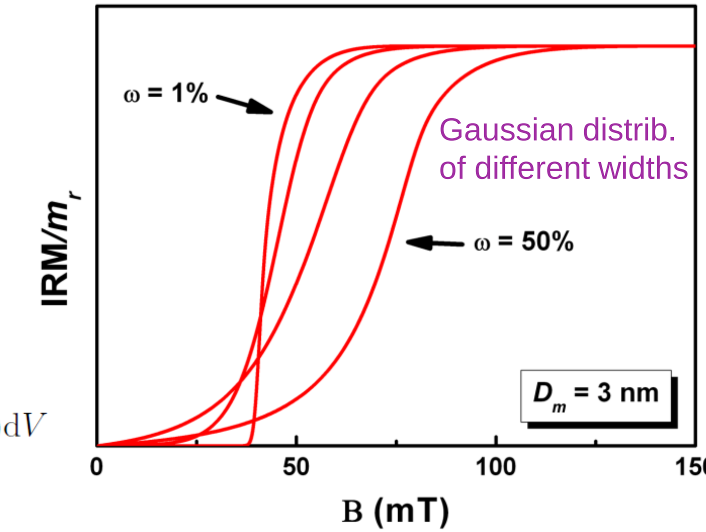
IRM curves simulation



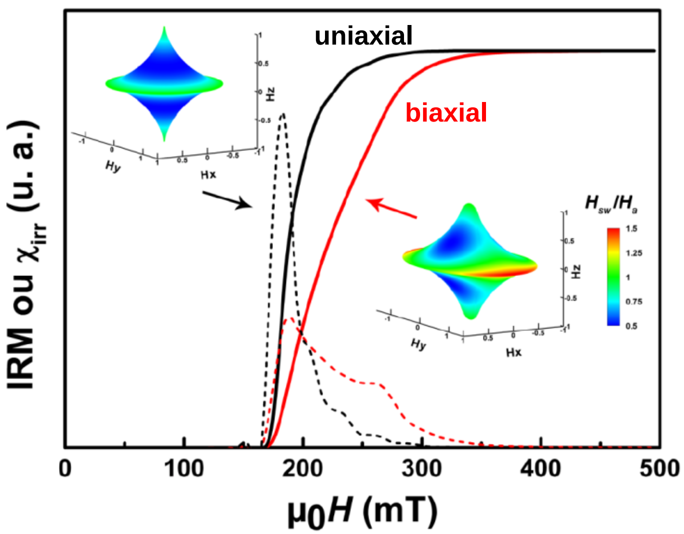
- Easy computation of IRM curves

Extension to the case of a size distribution

$$\mathrm{IRM}(H,T) = \frac{M_S}{2}\int_{V_{\min}}^{\infty} \frac{1-x^3}{1+x^3} V\rho(V)\mathrm{d}V$$



Smoothing due to size distribution ⟹ Satisfying approx. (ΔE, abrupt switching…)



IRM simulation taking into account the influence of

- ✓ Temperature
- ✓ Size distribution
- ✓ K_{eff} distribution
- ✓ Biaxial anisotropy K_2

Numerical approach:

$$\mathrm{IRM} = 2\iint_{\theta,\varphi}\int_{V_{\min}}^{V_{sw}^{\theta,\varphi}} M_S V\cos\theta\,\rho(V)\mathrm{d}V\,\rho(\theta,\varphi)\mathrm{d}\theta\mathrm{d}\varphi$$

A fit of experimental IRM curves is possible!

A. Hillion *et al*., Phys. Rev. B, in press (2013).

IRM vs. ZFC/FC measurements

Isothermal Remanent Magnetization (IRM)

IRM(H): the applied field is varied

→ Macrospin switching due to the applied field

Crucial parameter: switching field H_{sw}

Controlled by the **anisotropy field**

$H_A = 2\,K_{eff} / (\mu_0\,M_S)$

Moderate influence of the size distribution

Sensitive to a biaxial contribution

Zero-Field Cooled/Field Cooled suscept. (ZFC/FC)

ZFC(T): the temperature is varied

→ Thermal switching (relaxation to equilibrium)

Crucial parameter: blocking temperature T_B

Controlled by the **anisotropy energy**

$K = K_{eff}\,V$

High influence of the size distribution

Only sensitive to the uniaxial term (minimum energy barrier)

Different physical processes → **IRM and ZFC/FC curves are complementary!**

Institut Lumière Matière

ZFC/FC modeling

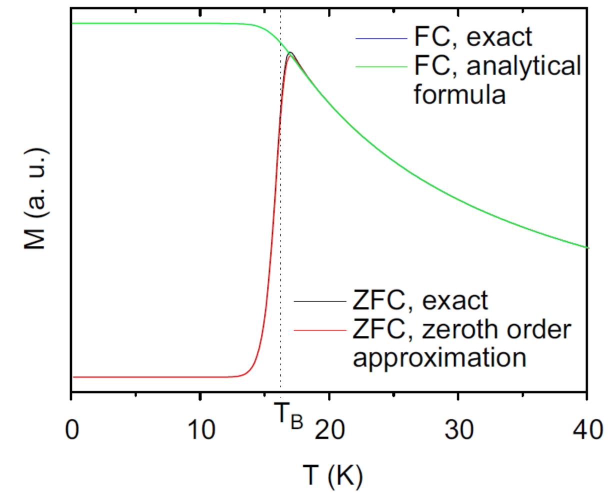
F. Tournus, E. Bonet, J. Magn. Magn. Mater. **323**, 1109 (2011).

Assembly of randomly oriented uniaxial identical macrospins

Dynamical linear susceptilibilty: $\tilde{\chi}(\omega) = \dfrac{\chi_{eq} + i\omega\tau\chi_b}{1 + i\omega\tau}$ with $\tau = 1/\nu \simeq \tau_0 \exp\left(\dfrac{\mathrm{K}}{k_\mathrm{B}\mathrm{T}}\right)$ Néel relaxation

➡ Differential equation for the ZFC/FC protocol:

$$\frac{1}{\nu}\frac{\mathrm{d}M}{\mathrm{d}t} + M = \frac{\mu_0 \mu^2 H}{3 k_B T}$$



Solution for a temperature sweep:

Remarkably simple approximate expression (very close to the exact one)

$$M^0_{ZFC}(T) = M_b e^{-\nu\delta t} + M_{eq}(1 - e^{-\nu\delta t})$$

with $\delta t(T)$ effective waiting time

➡ **Progressive crossover** from blocked to superparamagnetic (equilibrium) regime

• Improved description compared to the *abrupt transition model* where the macrospins are either fully blocked or superparamagnetic, with a transition at $T_B = \dfrac{K}{k_B \ln(\nu_0 \tau_{\mathrm{meas}})}$

• Extension of the blocking temperature concept, taking into account the temperature sweeping rate: *crossover temperature* $\mathrm{T_X}$ (depends on several parameters).

ZFC/FC simulation and fit

F. Tournus, A. Tamion, J. Magn. Magn. Mater. **323**, 1118 (2011).

Analytical expression for the FC and ZFC curve, with well defined approximations

➡ Easy simulation for the case of a MAE distribution (particle size distribution)

✓ Smoothing due to the distribution: progressive and abrupt model are comparable

Usual expression:

$$M_{ZFC} = \frac{\mu_0 H M_S{}^2}{3\, k_B T} \int_0^{V_{lim}} V^2 \rho(V) dV + \frac{\mu_0 H M_S{}^2}{3\, K_{eff}} \int_{V_{lim}}^{\infty} V \rho(V) dV$$

Superparamagnetic contribution

Blocked contribution

Transition at a given volume: ~~$V_{lim} = 25\, k_B T / K_{eff}$~~

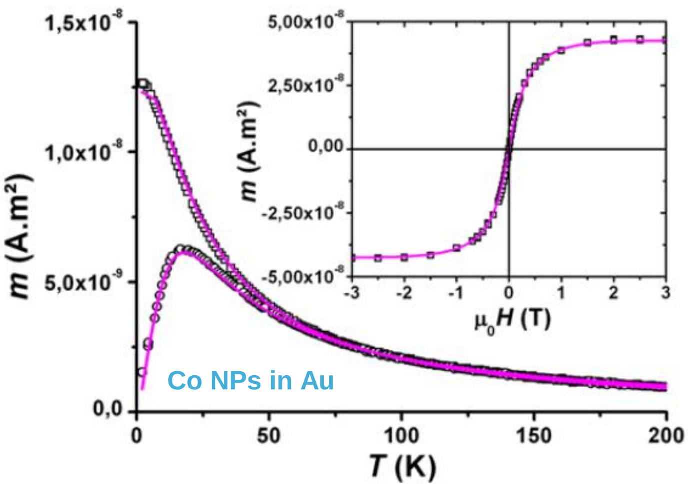
➡ "Improved abrupt transition model": V_{lim} such as $T_X(V_{lim}) = T$ (implicit equation)

Efficient and reliable simulation of the entire curves

➡ Simultaneous fit of ZFC/FC curves and a room temperature m(H)

Better accuracy with the "Triple fit" procedure

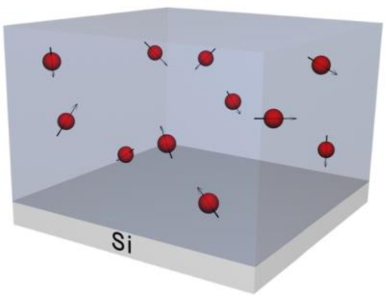
A. Tamion *et al.*, Appl. Phys. Lett. **95**, 062503 (2009).



The use of T_{max} only (ZFC peak) is hazardous…

Application to Co nanoparticles

Experimental study



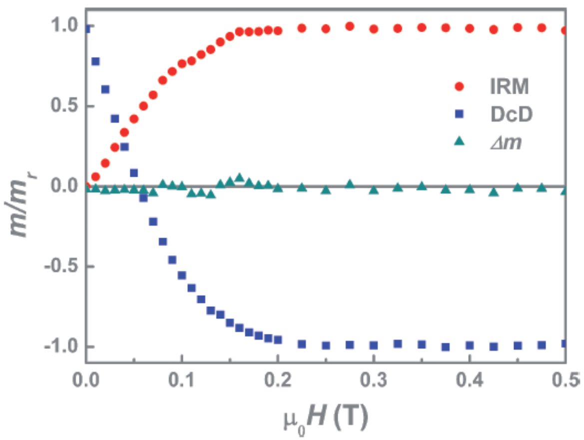
Co nanoparticles around 2.5 nm diameter

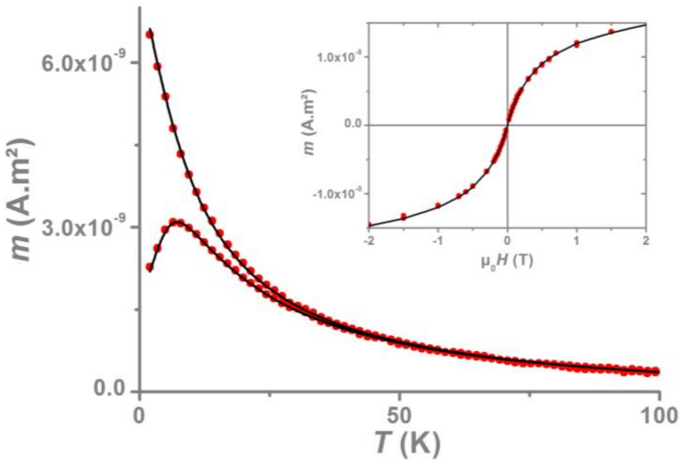
• Prepared by low energy cluster beam deposition (laser vaporization and UHV deposition)

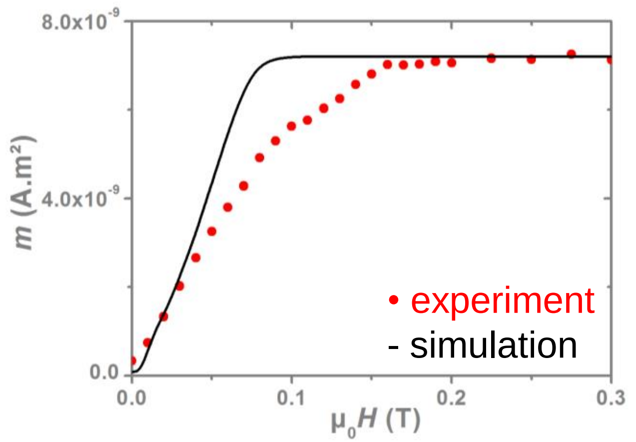
• Embedded in an amorphous carbon matrix

No interaction detected (Δm = 0)

Triple fit: ZFC/FC + m(H) at 300 K → f(D) and K_{eff}







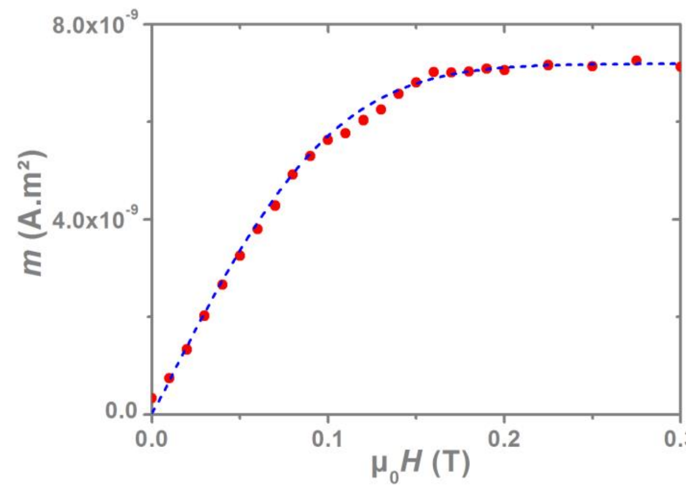
These parameters are then used to simulate the IRM curve

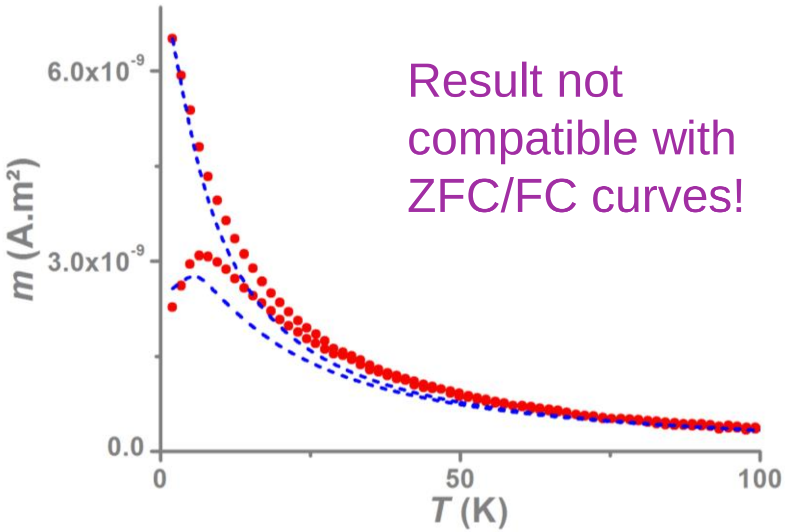
→ **Complete disagreement with the experimental IRM!**

Application to Co nanoparticles

Use of a K_{eff} distribution to fit the IRM

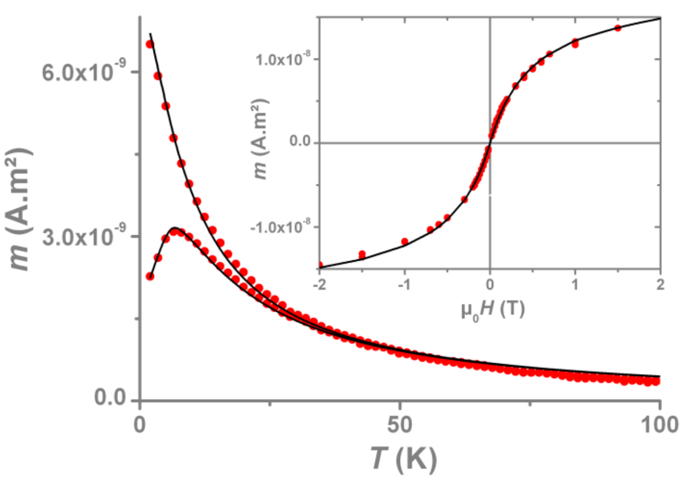
➡ Can reflect the variety of particle shapes

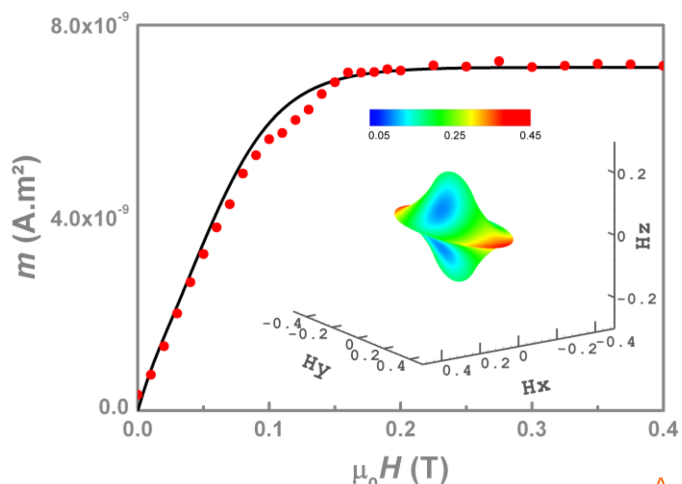




Result not compatible with ZFC/FC curves!

✓ Consistent solution if a biaxial anisotropy is used, in addition to a K_{eff} dispersion





A. Hillion *et al.*, Phys. Rev. B, in press (2013).

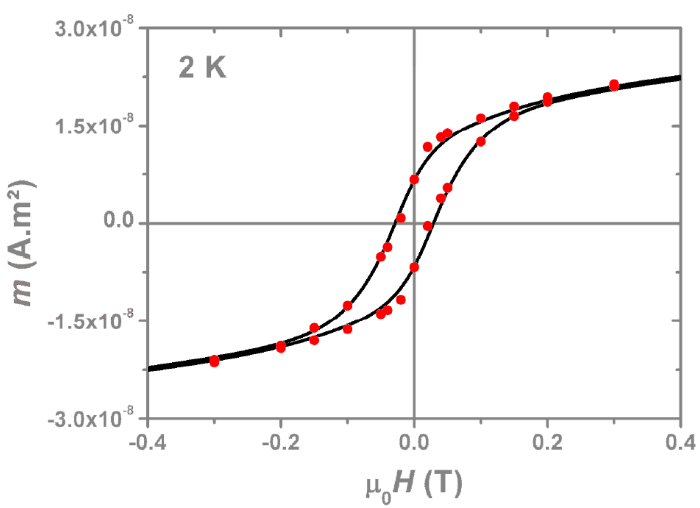
Advanced anisotropy determination

A. Hillion *et al.*, Phys. Rev. B, in press (2013).

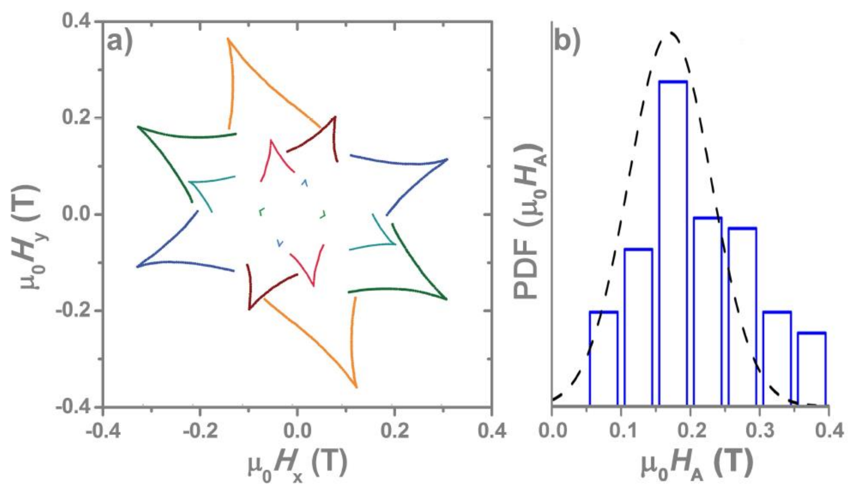
The K_2 term has no influence on the ZFC/FC curves, while it broadens the switching field distribution for the IRM

Combined fit: exploit the fact that IRM measurements and ZFC/FC are complementary (different types of switching processes)

➡ Advanced characterization of the magnetic anisotropy of Co nanoparticles, from <u>simple measurements on an assembly</u>



Results validation



✓ Simulation of the low temperature hysteresis loop

✓ Anisotropy field dispersion, from µ-SQUID measurements on <u>individual particles</u>

Conclusion

- Conventional measurements on nanoparticle assemblies

  ⇒ Accurate information on their intrinsic magnetic properties

- Combined fit of IRM and ZFC/FC curves, in addition to room temperature m(H)

  ⇒ Size distribution and magnetic anisotropy

- Efficient and accurate modeling

  ⇒ Validation of the underlying models and improved analysis of experimental data

- Original results on Co nanoparticle

  ⇒ Anisotropy constant distribution and importance of the biaxial term

- IRM/DcD are simple measurements, easier to interpret than hysteresis loops

  ⇒ No reason not to do it!

References

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Advanced magnetic anisotropy determination through isothermal remanent magnetization of nanoparticles

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Efficient hysteresis loop simulations of nanoparticle assemblies beyond the uniaxial anisotropy