Blocking of magnetic nano-clusters in Hf-Fe system

Damir Pajić [1] , Emil Babić [1] , Krešo Zadro [1] , Ramir Ristić [2]

[1] **Department of Physics, Faculty of Science, University of Zagreb, Croatia**

[2] **Department of Physics, University of Osijek, Croatia**

Investigated system: $Hf_{100-x}Fe_x$ [1,2]

- for x≥50 magnetic ordering
- for x≤35 paramagnetism
- 35<x<50 ???
  - below the threshold for long range magnetic ordering
  - not paramagnetic
  - above the percolation limit

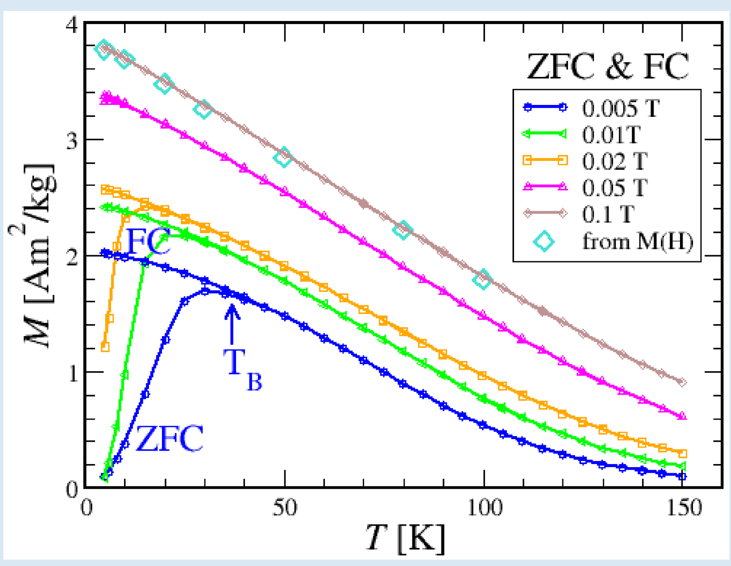
Here we have investigated in more detail the magnetic moment blocking phenomena for x = 35, 40, 43 amorphous alloys. For magnetization measurements we have used SQUID magnetometer.

Previous findings for $Hf_{57}Fe_{43}$ amorphous alloy [3]:

- finite magnetic clusters mainly of size 3.5-6nm inside non-magnetic host
- relatively large magnetic moment sitting on clusters
- anisotropy energy density K≈3·10^{4}J/m^3
- blocking of magnetic moments and slow relaxation of magnetization visible in splitting between zero-field cooled and field cooled M(T) curves, hysteresis loops and measured time relaxation of magnetization
- magnetic behaviour shows the similarities with anisotropic superparamagnetic particles
- nanometer sized magnetic clusters relax their magnetization thermally over the anisotropy energy barriers

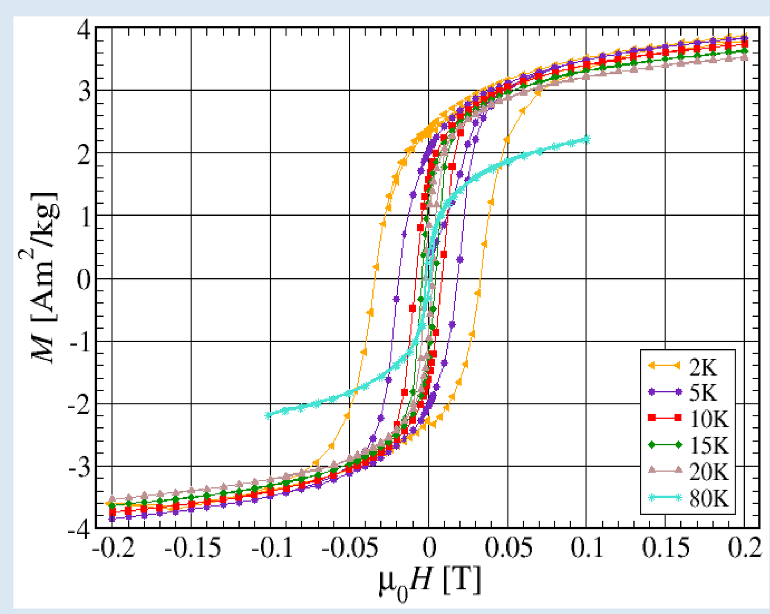
D.Pajić et.al., J.Phys.:Condens.Matter **19** (2007) 296207 and cond-mat:0608307

Introduction to blocking phenomena of superparamagnetic entities: example of $Hf_{57}Fe_{43}$



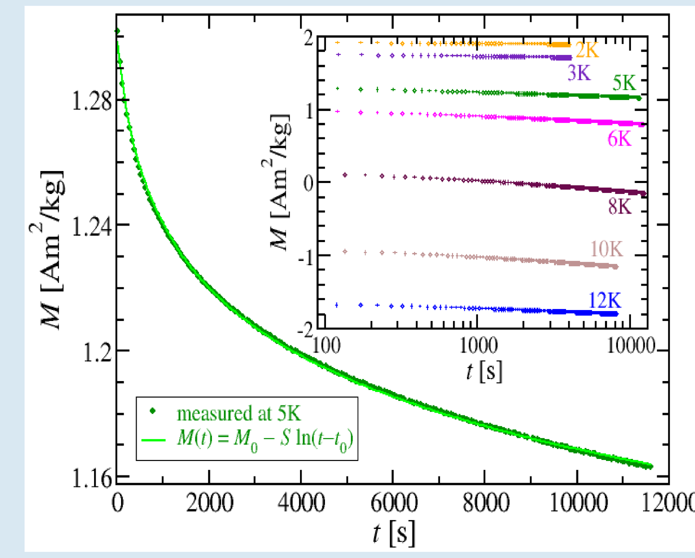
Dependence of magnetization M on temperature T in different applied magnetic fields after zero-field cooling (ZFC) and field cooling (FC).

Splitting between zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ curves below the so called blocking temperature T_B points to the blocking of magnetic moments caused by anisotropy barriers.
Applied magnetic field H lowers T_B , showing that the blocking barriers become lower.



Magnetic hysteresis loops measured at different temperatures.

Magnetic hysteresis below T_B originates from the blocking of magnetic moments. Increasing the temperature the loops become more and more narrow because lower field is needed to turn magnetic moment over the barriers if they have bigger thermal energy.

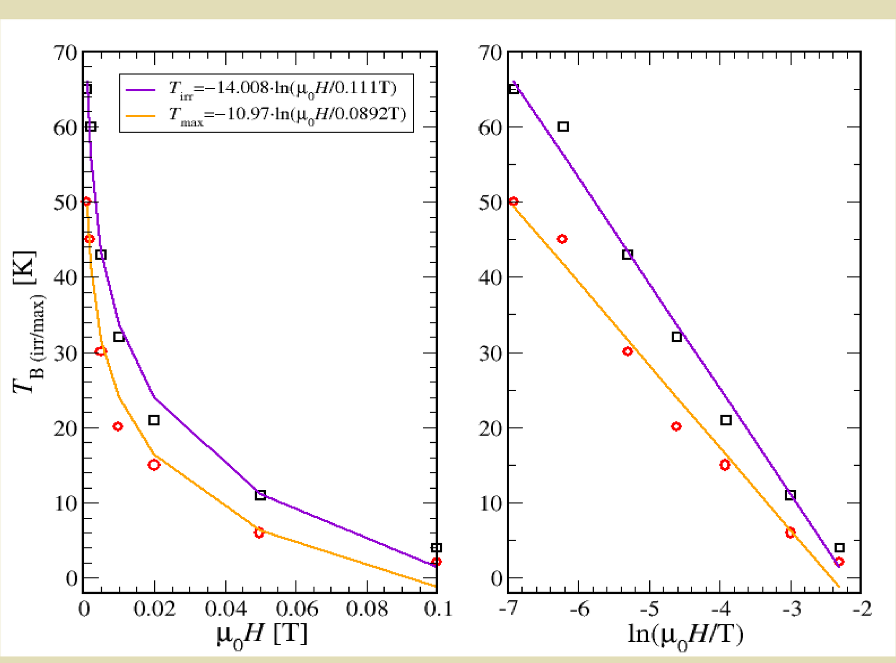


Relaxation of magnetization after cooling in magnetic field 0.01T and changing to -0.01T at different temperatures.

Below T_B relaxation is slow on the experimental time-scale. Logarithmic relaxation $M(t)=M_0-S\cdot\ln(t-t_0)$ comes out when the thermal relaxation of magnetic moments of clusters over barriers with broad distribution is observed.

Frequency τ^{-1} of magnetic moment transition over the anisotropy barrier of height U at temperature T according to thermal activation law is given by $\tau=\tau_0 e^{U/kT}$, where τ_0~10^{-10}s. Magnetization of ensemble of magnetic moments with equal barriers relaxes exponentially with relaxation time τ. At T_B, the relaxation time τ for magnetization of set of magnetic moments over highest barriers equals to the time of one measurement (~100s). From this follows the maximal barrier height U≈5·10^{-21}J in small applied field (0.001T). From hysteresis loops the anisotropy energy density K≈3·10^{4}J/m^3 is obtained. Thorough study of temperature dependent time-relaxation resulted with the distribution of magnetic moments over the barrier heights, that increases almost linearly from U≈5·10^{-22}J to U≈3.5·10^{-21}J and decreases abruptly at U≈6·10^{-21}J. Therefore, the magnetic clusters are uniformly distributed mainly with size 3.5-6nm with small amount of clusters up to 7.5nm, assuming their spherical shape.

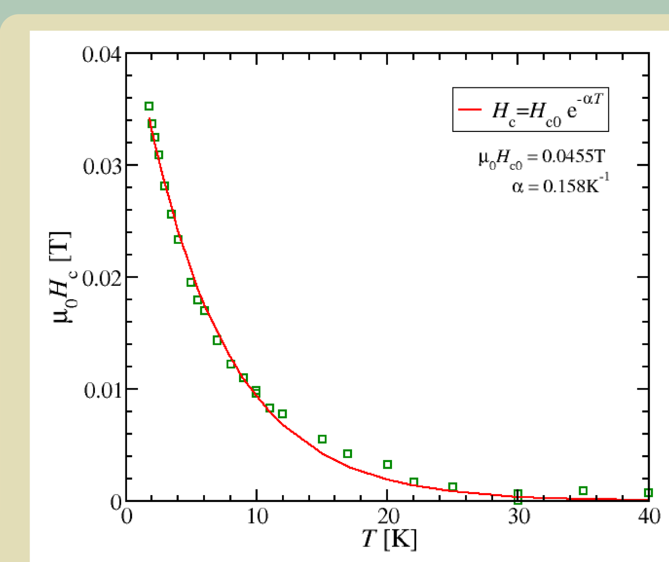
Field dependence of blocking temperature: $Hf_{57}Fe_{43}$



Dependence of blocking temperature T_B on applied magnetic field H for $Hf_{57}Fe_{43}$ alloy.

Blocking temperature of amorphous $Hf_{57}Fe_{43}$ depends on magnetic field logarithmically in whole range of measured fields and available temperatures. This T_B~ln(H) dependence could be understood as a consequence of distribution over barriers. As magnetic field sweeps up, the system comes to higher and higher barriers. This distribution was the origin of logarithmic relaxation in time, too.

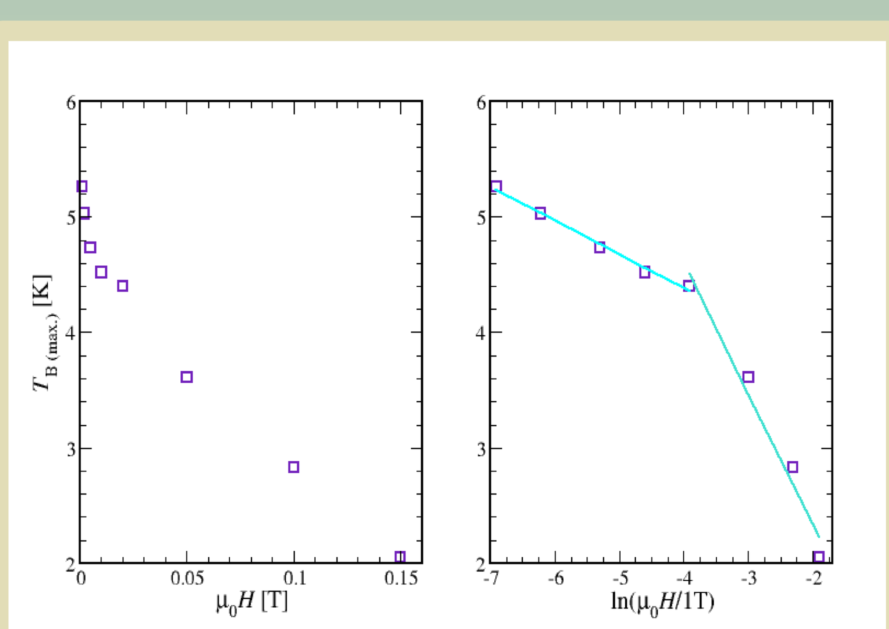
It was found previously for nanoparticles ΔT_B~H^2 for low field and ΔT_B~$H^{2/3}$ for moderate fields [4]. In magnetite nanoparticles it was found the change in ΔT_B~H^λ from λ=2 to λ=3/2 when increasing field above 0.05T. [5]
λ=2 is in accordance with Néel/Arrhenius model and λ=3/2 appears in spin-glass instability line. Exponent 2 was observed in Co-Ag granular alloy [6].
In our sample no potential law was successful in describing the $T_B(H)$.



Temperature dependences of coercive field H_c for $Hf_{57}Fe_{43}$ alloy.

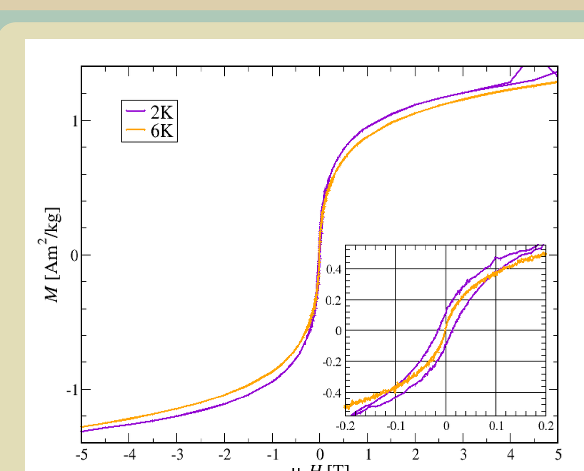
Coercivity and remanence behaviour with temperature is in accordance with properties of nanoparticulated magnetic materials where randomly oriented single domain particles/ clusters have broad size distribution.
M-H curves point to magnetic moments mainly between 600-3000μ_B.
Magnetic relaxation experiments confirmed it through magnetization weighted distribution of magnetic moments of the clusters over the barrier heights.

$Hf_{60}Fe_{40}$



Dependence of blocking temperature T_B on applied magnetic field H for $Hf_{60}Fe_{40}$ alloy.

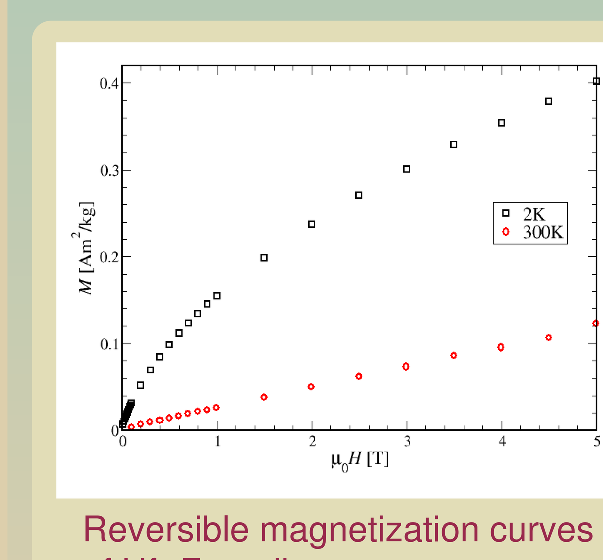
Blocking temperatures in $Hf_{60}Fe_{40}$ are significantly lower than in $Hf_{57}Fe_{43}$.
Magnetic hysteresis is observable only at lowest temperatures - below 5K.
Splitting between ZFC and FC curves is weaker than in $Hf_{57}Fe_{43}$, but is well observable.
All of this points to considerably lower barriers, i.e. smaller clusters and/or lower anisotropy density.
This is also in accordance with *M-H* from which follows that magnetic moments are mainly between 100-300μ_B.



Magnetic hysteresis loops of $Hf_{60}Fe_{40}$ alloy.

$Hf_{60}Fe_{40}$ shows logarithmic $T_B(H)$ in two parts. Possible explanation is the presence of peculiar distribution of cluster sizes and/or their anisotropy. The activation of superparamagnetic moments over anisotropy barriers is confirmed also by ac magnetic susceptibility measurements for both alloys $Hf_{60}Fe_{40}$ and $Hf_{57}Fe_{43}$.

$Hf_{65}Fe_{35}$



Reversible magnetization curves of $Hf_{65}Fe_{35}$ alloy.

In $Hf_{65}Fe_{35}$ there is no magnetic hysteresis measured at lowest temperature of 2K.
Only slight splitting between ZFC and FC curves in low field appears.
M-H curves point to magnetic moments up to order 10$^1\mu_B$.
Small superparamagnetic clusters with low anisotropy do not provide blocking phenomenology.

Conclusion:

- ✗ All of performed magnetic measurements on $Hf_{57}Fe_{43}$ point to the superparamagnetic behaviour of magnetic clusters inside the non-magnetic matrix. Splitting between the measured zero field cooled and field cooled magnetization curves below the so called blocking temperature, temperature dependent magnetic hysteresis loops, slow relaxation of magnetization and temperature dependence of coercive field, anisotropy field, remanent magnetization and magnetic viscosity all show that the magnetic clusters change the direction of their magnetic moment over the magnetic anisotropy barrier by thermal activation.
- ✗ The magnetic field dependence of blocking temperature for $Hf_{57}Fe_{43}$ is logarithmic in wide range of fields. This could be explained with the distribution of energy barrier heights. Logarithmic blocking temperature vs. applied field is consistent with the exponential temperature dependence of coercive field.
- ✗ For $Hf_{60}Fe_{40}$ behaviour is more complex with two ranges of different logarithmic dependences of the blocking temperature on applied field.
- ✗ For $Hf_{65}Fe_{35}$ the blocking temperature is below 2K, because of the lower magnetic anisotropy and decreased cluster sizes due to the lower iron concentration.
- ✗ $Hf_{57}Fe_{43}$ is interesting for low temperature investigation as a good candidate for quantum tunneling of magnetization of magnetic nano-clusters (no interaction, no exchange bias, but below ~0.1K) and for high temperature investigation of magnetization disorder development. Even smaller clusters in $Hf_{60}Fe_{40}$ are more promising for low temperature quantum phenomena investigation. $Hf_{65}Fe_{35}$ is interesting candidate for investigation of pathway from blocked superparamagnets to spin-glass systems that usually appear for lower concentration of magnetic atoms. Also, the small change in iron concentration transforms the system from ensemble of small noninteracting clusters to long range ordered magnetics, which is still an intriguing phenomenon.

References:

[1] R. Ristić, D. Pajić, K. Zadro, E. Babić, Ž. Marohnić,; Đ. Drobac, *Magnetic properties of the Hf-base metallic glasses*, J. Optoelectronics and Adv. Materials - Symposia **1** (2009) 348
[2] S.H. Liou, G. Xiao, J.N. Taylor, C. Chien, *Magnetic properties and hyperfine interactions of amorphous Hf-Fe alloys*, J. Appl. Phys. **57** (1985) 3535
[3] D.Pajić, K. Zadro, R. Ristić, I. Živković, Ž. Skoko, E. Babić, *Thermal relaxation of magnetic clusters in amorphous $Hf_{57}Fe_{43}$ alloy*, J.Phys.:Condens.Matter **19** (2007) 296207 (arXiv::cond-mat:0608307)
[4] H. Mamiya, I. Nakatani, *Dynamic study of iron-nitride fine particle system: field dependence of the blocking temperature*, J. Magn. Magn. Mater. **177-181** (1998) 966
[5] G.F. Goya, M.P. Morales, *Field Dependence of Blocking Temperature in Magnetite Nanoparticles*, J. Metastabl. Nanocrystall. Mater. 20-21 (2004) 673
[6] Y.D. Zhang, J.I. Budnick, W.A. Hines, C.L. Chien, J.Q. Xiao, *Effect of magnetic field on the superparamagnetic relaxation in granular Co-Ag samples*, Appl. Phys. Lett. **72** (1998) 2053

This work is financed by the Croatian Ministry of Science, Eduacation and Sports through the projects "Nanomagnets" and "Electromagnetic properties of nanostructured materials".