Magnetic studies of ultrafine $CoFe_2O_4$ nanoparticles with different molecular surface coatings

Ewa Mosiniewicz-Szablewska[1], Leandro Carlos Figueiredo[2] Atailson Oliveira da Silva[3], Marcelo Henrique Sousa[4] and Paulo Cesár de Morais[2,4]

[1]Institute of Physics, Polish Academy of Sciences, Warsaw, Poland,
[2]Institute of Physics, University of Brasilia, Brazil,
[3]Green Nanotechnology Group, University of Brasilia, Brazil
[4]Genomic Sciences and Biotechnology, Catholic University Of Brasilia, Brazil

ABSTRACT

Surface functionalized ultrafine $CoFe_2O_4$ nanoparticles, with mean diameter ~5 nm, were investigated by means of DC magnetization and AC susceptibility over the temperature range of 4–400 K.

All nanoparticles present the same $CoFe_2O_4$ core, with different molecular surface coatings, increasing gradually the number of carbon atoms in the coating layer: glycine ($C_2H_5NO_2$), alanine ($C_3H_7NO_2$), aminobutanoic acid ($C_4H_9NO_2$), aminohexanoic acid ($C_6H_{13}NO_2$), and aminododecanoic acid ($C_{12}H_{25}NO_2$).

Samples were intentionally fabricated in order to modulate the core–core magnetic dipolar interaction, as the thickness of the coating layer increases with the number of carbon atoms in the coating molecule.

All investigated $CoFe_2O_4$ nanoparticles are in a magnetically blocked state at room temperature as evidenced by ZFC/FC measurements and the presence of hysteresis with ~700 Oe coercivity.

Low temperature magnetization scans show slightly constricted hysteresis loops with coercivity decreasing systematically with a decreasing number of carbon atoms in the coating molecule, possibly resulting from differences in magnetic dipole coupling between NPs.

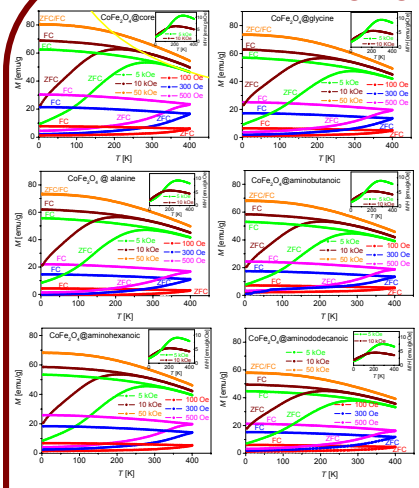
Large thermomagnetic irreversibility, slow monotonic increase in the FC magnetization and non-saturation of the magnetization give evidence for the cluster glass nature in the $CoFe_2O_4$ nanoparticles.

The out of phase part (χ'') of AC susceptibility for all samples shows a clear frequency dependent hump which was analyzed to distinguish superparamagnetic, cluster glass and spin glass behavior by using Neel–Arrhenius, Vogel–Fulcher, and power law fittings. These analyses rule out the superparamagnetic state and suggest the presence of significant intercluster dipolar interaction, giving rise to cluster glass cooperative freezing in the high-temperature region.

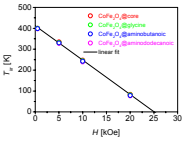
In the low-temperature range, however, the disordered spins on the nanoparticle's surface play an important role in the formation of the spin glass-like state, as evidenced by Arrott plots and temperature dependency of dM/dH in the initial magnetization curves.

In summary, the magnetic measurements showed that undercooling the system evolves from a superparamagnetic state of weakly interacting spin clusters, through the cluster glass state induced by strong dipolar interaction, to the spin glass state resulting from the frustration of the disordered surface spins.

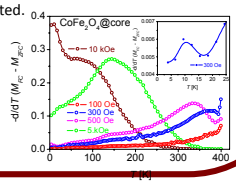
ZFC-FC magnetization



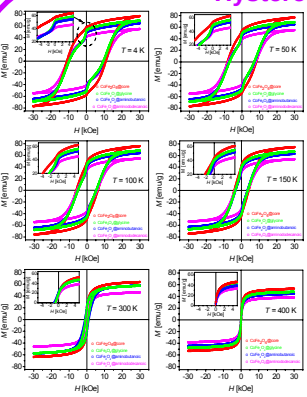
- ZFC and FC magnetization bifurcate and show a large magnetic irreversibility which is the signature of canonical spin glass, cluster glass, or superparamagnetic behavior.
- The ZFC magnetization shows a broad peak, which shifts to lower temperatures while increasing the applied field and a clear Curie-Weiss law behavior is not observed above the blocking temperature T_B. This finding indicates the existence of strong magnetic dipole-dipole interaction among the $CoFe_2O_4$ nanoparticles.
- The FC magnetization increases monotonically under cooling, running flat at lower temperatures, and resembling the cluster glass behavior.
- The irreversibility temperature T_{irr} follows de Almeida–Thouless model, $T_{irr} \sim -H^n$, but the exponent is $n = 1$, which is far above 2/3, the latter value predicted by the mean-field theory and earlier obtained for heavy doped cobaltites ($La_{0.5}Sr_{0.5}CoO_3$) in which the cluster glass state was indicated.



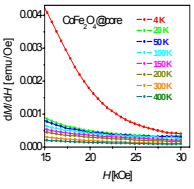
- The observed low-temperature peak in temperature derivative of the difference between the FC and ZFC magnetizations, $-d(MFC–MZFC)/dT$, may correspond to the picture of a frozen disordered magnetic state at low temperature (the cluster glass state).



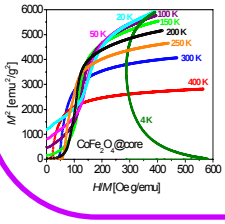
Hysteresis curves



- Hysteresis curves exhibit superparamagnetic nature only at 400 K.
- $M(H)$ curve does not saturate, especially at temperatures below 100 K, even at applied magnetic field as high as 30 kOe, again, indicating the onset of the cluster glass state at low temperature.
- Low temperature magnetization scans show slightly constricted hysteresis loops with coercivity decreasing systematically with decreasing number of carbon atoms in the coating molecule, possibly resulting from differences in magnetic dipole coupling between nanoparticles.

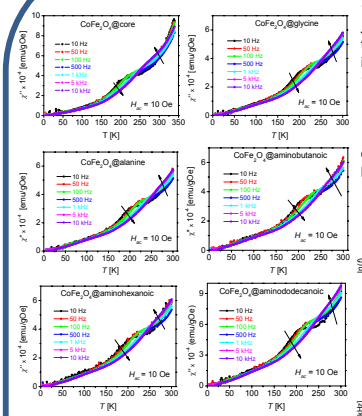


- Temperature dependence of dM/dH in the initial magnetization curves at high fields increases with decreasing temperature, and at 4 K displays a drastic increase, which indicates an increase in anisotropy due to the spin glass-like freezing.



- In Arrott plots, a notable change in the curvature is seen at temperatures below 200 K, which is associated with the onset of the cluster glass behavior.
- Moreover, S-shaped curves are observed with the inflection point shifted towards high values of H/M with decreasing temperature, which is one of the properties of cluster glass systems.
- Finally, there is a change in the sign of the slope of the $M^2(H/M)$ function, from a positive slope at $T \geq 20$ K to a negative one for $T = 4$ K, demonstrating that the magnetic interaction above 20 K exhibit long-range ferromagnetic order whereas those near 4 K are short-ranged due to increased role of surface effects at low temperature, responsible for forming the spin glass state.

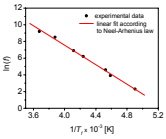
Ac magnetic susceptibility



- The AC susceptibility shows a frequency dependent hump in $\chi''(T)$ at temperature around 200 K, which shifts towards higher temperatures and reduces in magnetic strength with the increasing frequency.
- The Mydosh parameter (Φ), meaning frequency shift per decade:

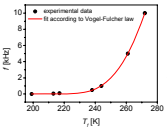
$$\Phi = \frac{\Delta T_f}{T_f \Delta \log_{10}(f)}$$

is 0.08 for all samples, which suggests that the frequency dispersion of $T_f(f)$ is due to cluster glass freezing and not superparamagnetic blocking.



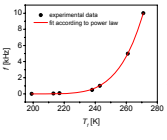
- Fitting of $\ln(f)$ vs $1/T_f$ with the Néel-Arrhenius law: $f = f_0 \exp\left(\frac{-E_a}{k_B T_f}\right)$

results in unrealistic high values of the attempt frequency ($f_0 = 2\times10^{13}$ Hz). It rules out the possibility of superparamagnetic nature of the $CoFe_2O_4$ nanoparticles and hints the presence of cooperative dynamics due to inter-cluster interactions in the cluster glass state.



- Fitting of $\ln(f)$ vs $1/T_f$ with the Vogel-Fulcher law: $f = f_0 \exp\left(\frac{-E_a}{k_B(T_f - T_0)}\right)$

results in the nonzero value of $T_0 = 184$ K, which signifies interaction among clusters, and value of $f_0 = 1.3\times10^6$ Hz, which reveals slow dynamics, as expected for cluster glass.



- Fitting of $\ln(f)$ vs $1/T_f$ with the power law: $f = f_0\left(\frac{T_f - T^*}{T^*}\right)^{zv'}$

results in the fitting parameters: $f_0 = 1.1\times10^6$ Hz, $zv' = 4.7$ K and $T^* = 197$ K, which lie in the range specified for the cluster glass system.

Values of T^* and f_0 obtained using the power law are comparable to T_0 and f_0 typical values for the Vogel-Fulcher law. Thus, both power law and Vogel-Fulcher law fits confirm the cluster glass freezing in the $CoFe_2O_4$ nanoparticles below 184 K.

Conclusions:

The static and dynamic magnetic behaviors uphold that:

1. At $T \geq 400$ K, $CoFe_2O_4$ nanoparticles are in the superparamagnetic state.
2. Below 400 K, the strong dipole interaction is responsible for the cluster glass behavior.
3. As the temperature is lowered, cluster regions grow and evolve towards a collective freezing, which may be responsible for the blocking of the clusters at T_B.
4. In the low-temperature range, i.e. below 20 K, the disordered spins on the nanoparticle's surface play an important role in the onset of the spin glass state, which results from the frustration of the disordered surface spins.

Reference:

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