Electronic Supplementary Information

Origin of the Large Dispersion of Magnetic Properties in Nanostructured Oxides: Fe_xO/Fe_3O_4 Nanoparticles as a Case Study

Marta Estrader,*[ab] Alberto López-Ortega,[c] Igor V. Golosovsky,*[de] Sònia Estradé,[fg] Alejandro G. Roca,[h] German Salazar-Alvarez,[b] Lluís López-Conesa,[f] Dina Tobia,[i] Elin Winkler,[i] José D. Ardisson,[j] Waldemar A.A. Macedo,[j] Andreas Morphis,[k] Marianna Vasilakaki,[k] Kalliopi N. Trohidou,[k] Arsen Gukasov,[l] Isabelle Mirebeau,[l] O. L. Makarova,[m] Roberto D. Zysler,[i] Francesca Peiró,[f] Maria Dolors Baró,[n] Lennart Bergström,[b] and Josep Nogués[ho]

[a]Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 645, E-08028, Barcelona, Spain.
[b]Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, 10691 Stockholm, Sweden.
[c]INSTM and Dipartimento di Chimica "U. Schiff", Università degli Studi di Firenze, Via della Lastruccia 3, Sesto Fiorentino, I-50019 Firenze, Italy
[d]National Research Center "Kurchatov Institute", B.P. Konstantinov, St. Petersburg Nuclear Physics Institute, 188300, Gatchina, Russia.
[e]A.F. Ioffe Physico-Technical Institute RAS, 194021, St. Petersburg, Russia.
[f]LENS-MIND-IN2UB, Departament d'Electrònica, Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain.
[g]TEM-MAT, SCT, Universitat de Barcelona, Barcelona, Spain.
[h]ICN2 – Institut Catala de Nanociencia i Nanotecnologia, Campus UAB, E-08193 Bellaterra (Barcelona), Spain
[i]Centro Atómico Bariloche, CNEA-CONICET, 8400 S.C. de Bariloche, Río Negro, Argentina.
[j]Laboratório de Física Aplicada, Centro de Desenvolvimento da Tecnologia Nuclear, 31270-901Belo Horizonte, Minais Gerais,Brazil

[k]IAMPPMN, Department of Materials Science, NCSR "Demokritos", 153 10 Aghia Paraskevi, Attiki, Greece.
[l]Laboratoire Leon Brillouin, CEA/CNRS, F-91191 Gif-sur-Yvette Cedex, France
[m]National Research Center "Kurchatov Institute," 123182 Moscow, Russia
[n]Departament de Física, Universitat Autònoma de Barcelona, E-08193 Bellaterra (Barcelona), Spain.
[o]Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain.

[*]Corresponding authors: martaestrader@gmail.com, golosov@pnpi.spb.ru

Details of the simulation FMR spectra for CS_9 and CS_45 particles

In a first approximation, the FMR lines can be described as a system with uniaxial anisotropy. In this situation, the linewidth is related to the anisotropy constant as, $\Delta H_{pp} = 3H_A/2$, and thus to the effective anisotropy, K_{eff}, since $H_A = 2K_{eff}/M_S$.[1,2] The simulation of the room temperature FMR spectra shown in Fig. 5a,b was calculated for random oriented nanoparticles for CS_9 (with $K_{eff} = 0.7\times10^5$ erg/cm^3 and $H_r = 8.49$ kOe) and CS_45 (with $K_{eff} = 3.1\times10^5$ erg/cm^3 and $H_r = 8$ kOe), using the experimental M_S values, i.e. 47 emu/g and 64 emu/g for the smaller and larger core/shell nanoparticles, respectively.

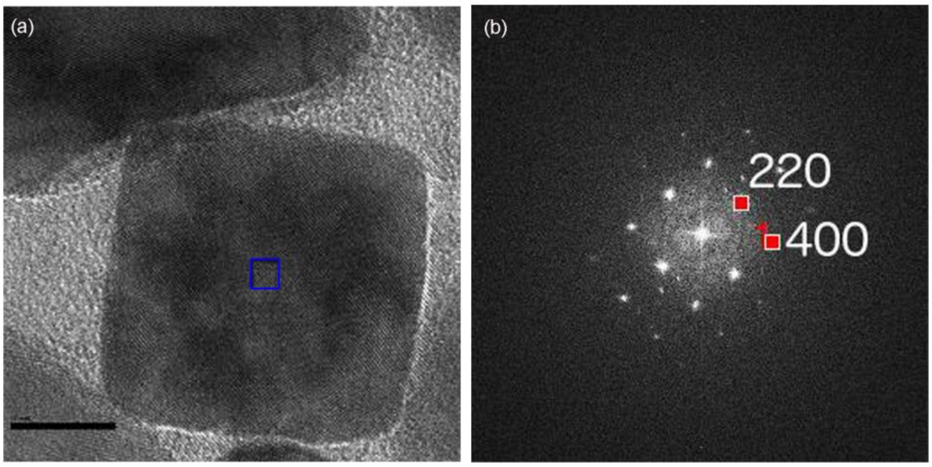

Fig. S1 (a) Bright-field TEM image of a CS_45 particle taken at the [001] zone axis (scale bar = 15 nm) and (b) its corresponding FFT, highlighting the $\mathbf{g}_{200(\text{wüstite})}/\mathbf{g}_{400(\text{spinel})}$ and $\mathbf{g}_{220(\text{spinel})}$ reflections. The box in (a) indicates the reference region used for the refining of the phase images.

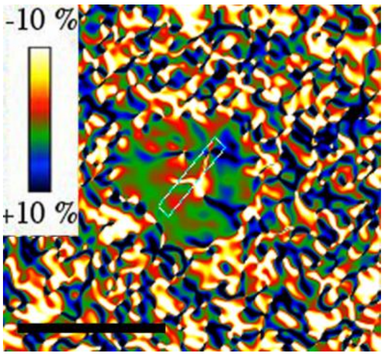

Fig. S2 Deformation maps obtained through the GPA of the $g_{220(spinel)}$ reflections for the CS_9 nanoparticles (scale bar = 10 nm).

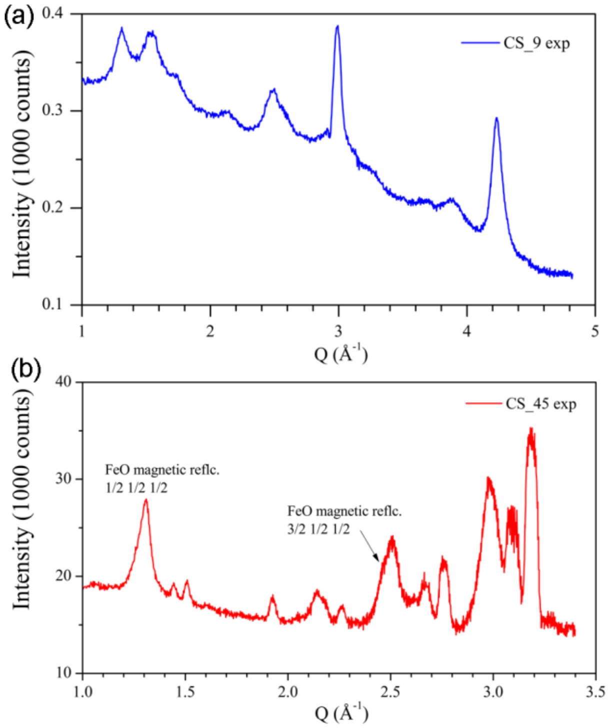

Fig. S3 Neutron diffraction patterns for (a) CS_9 particles at 10 K and (b) CS_45 particles at 15 K.

Table S1. Dimension and unit cell parameters obtained from the refinement of the X-ray patterns for CS_9 and CS_45 particles.

<table>
<tr><td>Sample</td><td>Fe_xO-core (nm)</td><td>Effective Fe_3O_4-shell thicknesss (nm)</td><td>Fe_xO unit cell parameter (nm)</td><td>Fe_3O_4 unit cell parameter (nm)</td></tr>
<tr><td>CS_9</td><td>10.1(5)</td><td>2.0(2)</td><td>0.42190(8)</td><td>0.8395(1)</td></tr>
<tr><td>CS_45</td><td>21(1)</td><td>8.0(3)</td><td>0.42986(1)</td><td>0.8391(2)</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td>CS_45</td><td colspan="2">core/shell particles
79 %</td><td>Fe_3O_4 nanoparticles (~ 7nm) impurities
19%</td><td>α-Fe impurities
< 2 %</td></tr>
<tr><td></td><td>Fe_xO-core
16 %</td><td>Fe_3O_4-shell
84 %</td><td></td><td></td></tr>
</table>

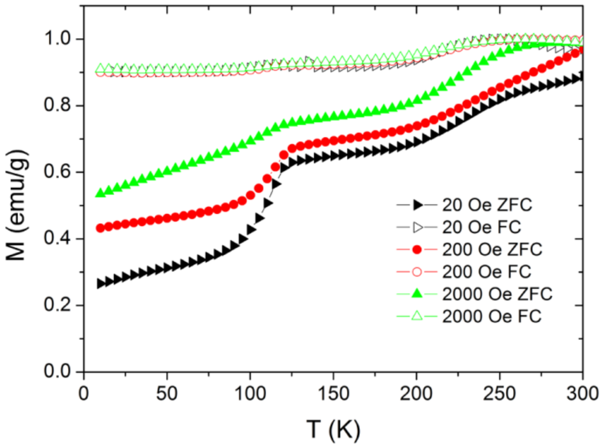

Fig. S4 Temperature dependence of the field cooled (FC) and zero field cooled (ZFC) magnetizations CS_45 particles at different applied fields.

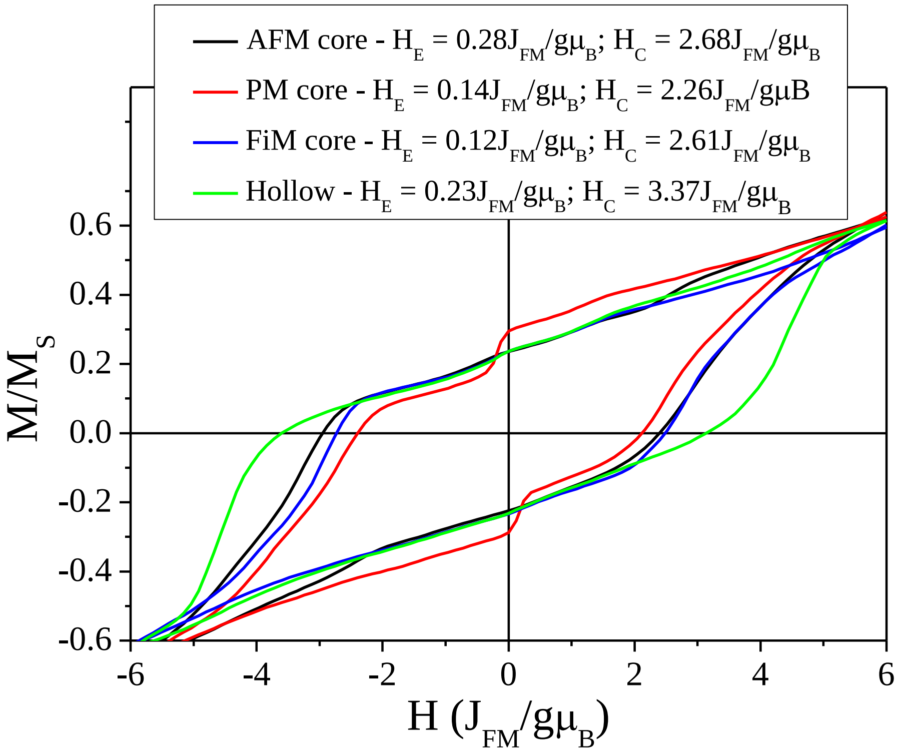

Fig. S5 Simulated hysteresis loops for diverse CS_9 core/shell nanoparticle configurations: AFM/FiM (black) and PM/FiM (red); and single phase systems: pure FiM (blue) and hollow-FiM (green).

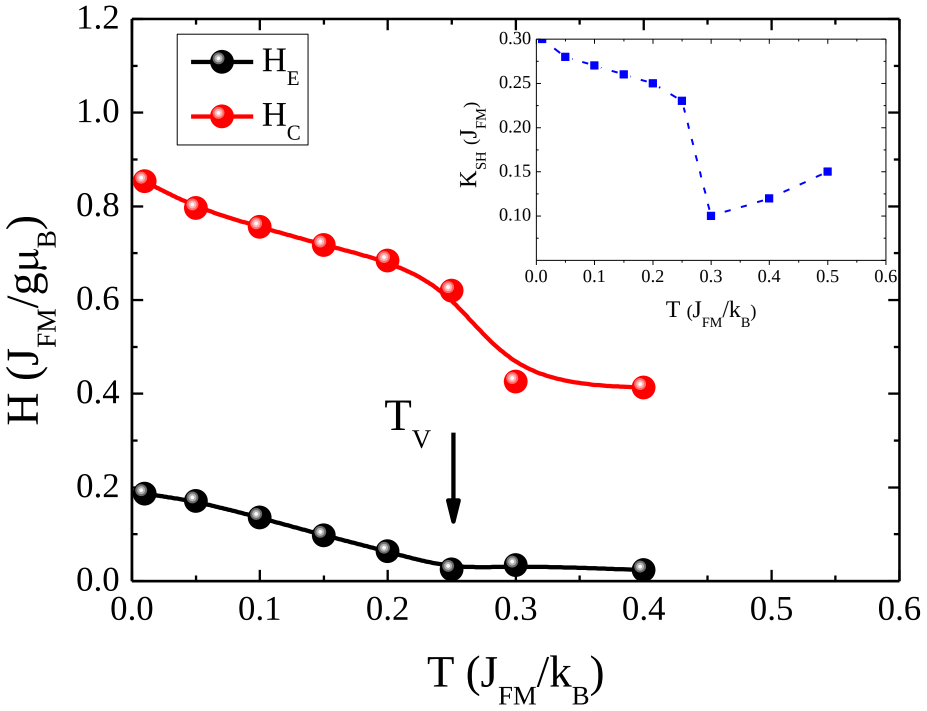

Fig. S6 Monte Carlo simulation of the temperature dependence of H_{C} and H_{E} for the CS_45 nanoparticles calculated using the temperature dependence of the Fe_3O_4-shell anisotropy shown in the inset.

Table S2. Mössbauer parameters for the sample CS_9 measured at 20 K and for the sample CS_45 measured at 300 K and 20 K: isomer shift δ (relative to α-Fe at room temperature), quadrupole splitting Δ, magnetic hyperfine field B_{HF} and spectral area of the different components. Note that an additional hyperfine field distribution (D) is also necessary to fit the room temperature spectrum. This distribution, with average δ = 0.55 mm/s and average B_{HF} = 32.9 T, can be attributed to interfaces and to a fraction of small Fe_3O_4 nanoparticles showing some magnetic relaxation at room temperature, in agreement with the X-ray results.

Spectrum	Component	δ (mm/s)	Δ (mm/s)	B_{HF} (T)	Area (%)
CS_9 @ 20 K	A	0.37	-0.01	50.5	33
	B1	0.56	-0.04	52.8	17
	B2	0.65	0.01	50.4	32
	B3	0.71	-0.02	35.2	13
	B4	1.62	1.71	35.2	5
CS_45 @ 300 K	A	0.28	0.00	48.3	19
	B	0.61	-0.09	45.2	36
	Fe_xO	1.00	0.34		20
	D	0.55	0	32.9	22
	α-Fe	0.00	0.00	33.0	3
CS_45 @ 20 K	A	0.40	-0.02	50.7	28
	B1	0.51	-0.11	52.7	16
	B2	0.93	-0.19	51.4	12
	B3	0.97	-0.37	46.3	14
	B4	1.04	2.15	33.6	3
	Fe_xO	1.14	0	31.8	24
	α-Fe	0.08	0.00	34.0	3

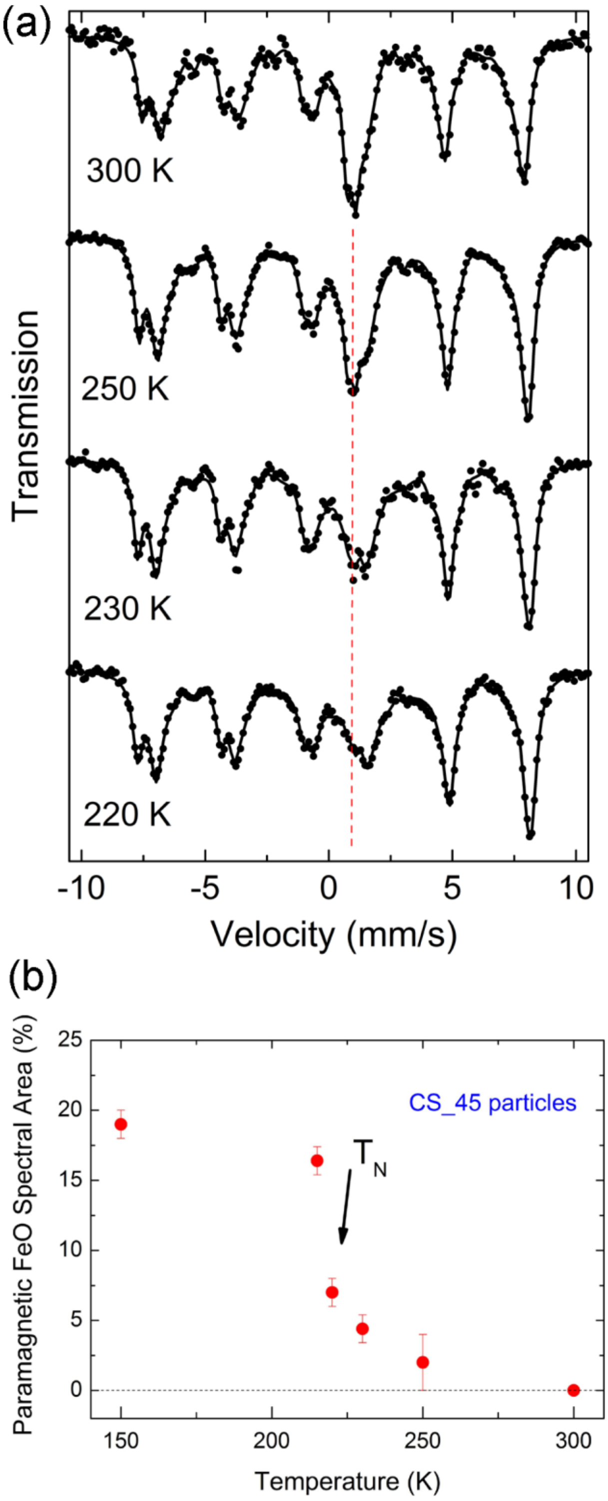

Fig. S7 (a) Mössbauer spectra for the CS_45 sample at different temperatures ranging from 300 K to 220 K. It is evident that the central paramagnetic peak of Fe_xO at 1.0 mm/s (red vertical line) is still noticeable at 230 K and almost disappears in the 220 K spectrum, indicating that the measurement is close to the ordering temperature T_N of the antiferromagnetic core. (b) Evolution of the paramagnetic Fe_xO spectral area with temperature, as determined by Mössbauer spectroscopy.

References

1. J. M. Vargas, E. Lima, R. D. Zysler, J. G. S. Duque, E. De Biasi and M. Knobel, *Eur. Phys. J. B*, 2008, **64**, 211–218.

2. E. De Biasi, C. A. Ramos and R. D. Zysler, *J. Magn. Magn. Mater.*, 2003, **262**, 235–241.