

# Supporting Information

## Crucial role of the Co cations on the destabilization of the ferrimagnetic alignment in Co-ferrite nanoparticles with tunable structural defects

Carlos Moya,<sup>1,2</sup> Arantxa Fraile Rodríguez,<sup>1, +</sup> Mariona Escoda-Torroella,<sup>1</sup> Montserrat García del Muro,<sup>1</sup> Sridhar R. V. Avula,<sup>3</sup> Cinthia Piamonteze,<sup>3</sup> Xavier Batlle,<sup>1</sup> and Amílcar Labarta,<sup>1</sup>

<sup>1</sup>*Departament de Física de la Matèria Condensada, Institut de Nanociència i Nanotecnologia, Universitat de Barcelona (IN2UB), Martí i Franquès 1, Barcelona 08028, Spain.*

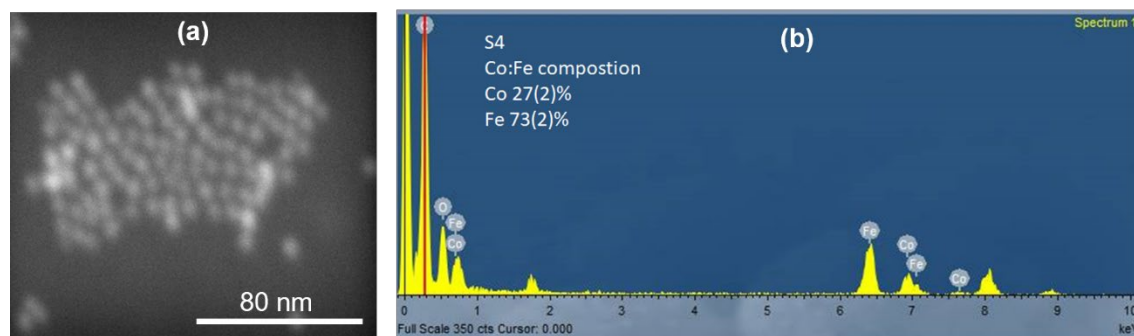
<sup>2</sup>*Université libre de Bruxelles (ULB), Engineering of Molecular Nanosystems, 50 Avenue F.D. Roosevelt, 1050 Bruxelles, Belgium.*

<sup>3</sup>*Swiss Light Source, Paul Scherrer Institut, CH 5232 Villigen PSI, Switzerland.*

<sup>+</sup>Corresponding author: [arantxa.fraile@ub.edu](mailto:arantxa.fraile@ub.edu)

Table of contents	Page
• Figure S1. HAADF images and EDX maps	S2
• Figure S2. Fits of the magnetization curves to Eq. (1)	S3
• Figure S3. XMCD spectra calculated using ligand field multiplet theory for Fe and Co cations in Oh and Td sites	S4
• Figure S4. Comparison of the XMCD hysteresis loops recorded in TEY and TFY modes for sample S4	S5

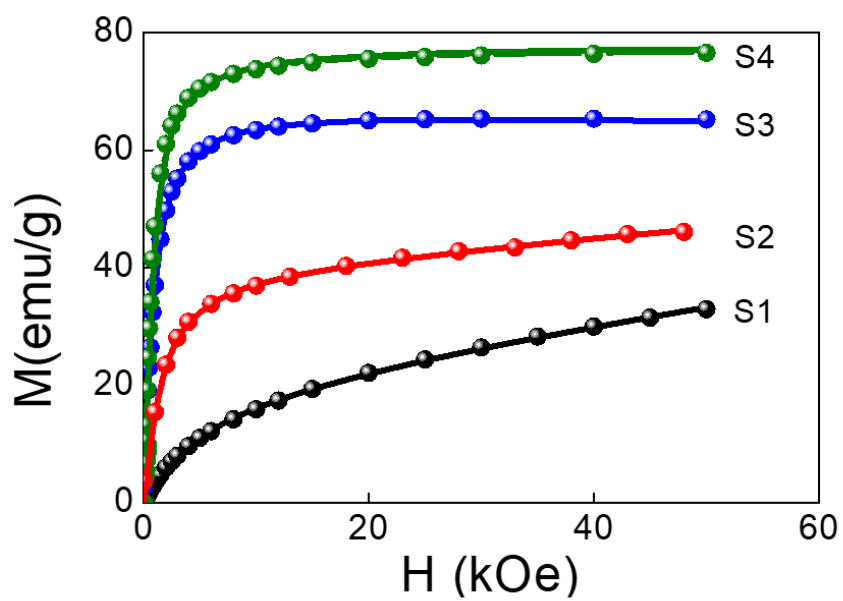
**Figure S1.** (a) High-angle annular dark-field (HAADF) image of several dozens of NP for sample S4. (b) Energy Dispersive X-ray (EDX) spectrum of the area of NP shown in image (a). Peaks correspond to C, Co, Fe and O elements. (c) Table of the comparison of Fe and Co percentages for samples S1 and S4. Errors are indicated in parenthesis.



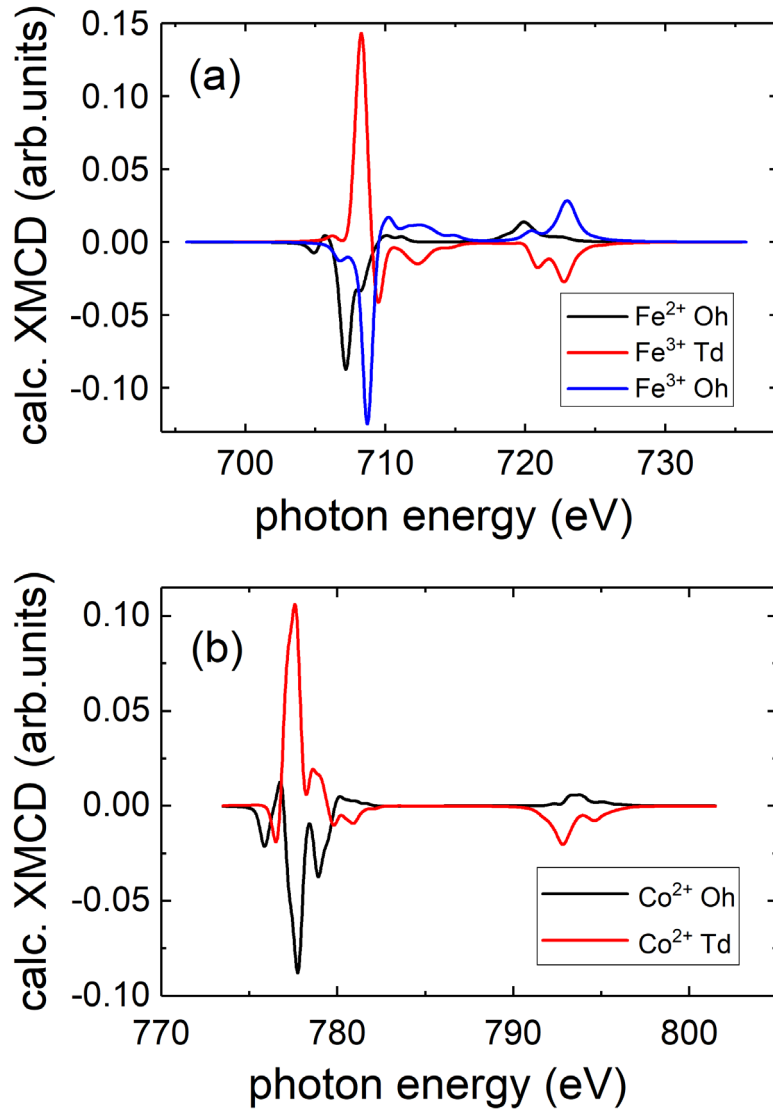
(c)

Element	S1 (%)	S4 (%)
Co	33 (4)	27 (2)
Fe	67 (7)	73 (2)

**Figure S2.** Langevin fits to Eq. (1) (solid lines) of the magnetization curves at 300 K for S1 (green spheres), S2 (blue spheres), S3 (red spheres) and S4 (black spheres) samples.



**Figure S3.** XMCD spectra calculated using ligand field multiplet theory (a) Spectra for  $\text{Fe}^{3+}$  (Oh),  $\text{Fe}^{2+}$  (Td),  $\text{Fe}^{2+}$  (Oh). The most relevant simulation parameters are: i) reduction of 70% (80%) for  $dd(pd)$  Slater integrals; ii) exchange = 10 meV and -10meV for Oh and Td sites, respectively; iii) broadening: gaussian = 0.25 eV, lorentzian = 0.25eV (0.5eV) for  $L_3$  ( $L_2$ ); iv)  $10Dq$  = 1.2eV and -0.6eV for Oh and Td sites, respectively. Temperature = 3K. (b) Spectra for  $\text{Co}^{2+}$  (Oh) and  $\text{Co}^{2+}$  (Td). The most relevant simulation parameters are i) reduction of 70%, 80% and 75% for  $Fdd$ ,  $Fpd$  and  $Gpd$  Slater integrals; ii) exchange = 12.6 meV and -12.6 meV for Oh and Td sites, respectively; iii) broadening: gaussian = 0.2eV, lorentzian = 0.1eV (0.3eV) for  $L_3$  ( $L_2$ ); iv)  $10Dq$  = 1.2 eV and -0.6 eV for Oh and Td sites, respectively. Temperature = 3K.



**Figure S4.** XMCD hysteresis loops in surface-sensitive TEY mode (black) and bulk-sensitive TFY mode (red) recorded with a Si photodiode at 2 K within  $\pm 69$  kOe (for clarity, only data within  $\pm 40$  kOe are shown) for the sample S4 for the cationic sites:  $\text{Fe}^{2+}$  (Oh),  $\text{Fe}^{3+}$  (Oh),  $\text{Fe}^{3+}$  (Td) and  $\text{Co}^{2+}$  (Oh). The XMCD loops were collected at the Fe and Co absorption peaks from Fig. 4 corresponding to the following energies:  $\text{Fe}^{2+}$  (Oh) = 706.9 eV,  $\text{Fe}^{3+}$  (Td) = 708.1 eV,  $\text{Fe}^{3+}$  (Oh) = 708.7 eV, and  $\text{Co}^{2+}$  (Oh) = 777.7 eV. Note that the hysteresis loop for the  $\text{Fe}^{3+}$  (Td) has been reversed along the magnetization axis for the sake of comparison with the Oh loops.

