

Supporting Information for:
Apparent auxetic to non-auxetic crossover driven
by Co^{2+} redistribution in CoFe_2O_4 thin films.

Elias Ferreiro-Vila,[†] Lucia Iglesias,[†] Irene Lucas del Pozo,[‡] Noa
Varela-Dominguez,[†] Cong Tinh Bui,[†] Beatriz Rivas-Murias,[†] J. M.
Vila-Fungueiriño,[¶] Pilar Jimenez-Cavero,[‡] Cesar Magen,[§] Luis Morellon,^{||} Victor
Pardo,^{⊥, #} and Francisco Rivadulla^{*, †}

[†]*Centro de Investigación en Química Biológica e Materiais Moleculares (CIQUS),
Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.*

[‡]*Instituto de Nanociencia de Aragón (INA), Departamento Física de la Materia, Pedro
Cerbuna 12, Condensada Universidad de Zaragoza, 50018 Zaragoza, Spain.*

[¶]*Institut d'Électronique et des Systèmes (IES), UMR 5214, CNRS – Université de
Montpellier, 860 rue Saint Priest, 34095 Montpellier, France.*

[§]*Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-CSIC,
and Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009
Zaragoza, Spain.*

^{||}*Instituto de Nanociencia de Aragón, INA, Departamento Física de la Materia
Condensada, Pedro Cerbuna 12, Universidad de Zaragoza, 50018 Zaragoza, Spain.*

[⊥]*Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago de
Compostela, 15782 Santiago de Compostela, Spain.*

[#]*Instituto de Investigaciones Tecnológicas, Universidade de Santiago de Compostela,
E-15782, Santiago de Compostela, Spain.*

E-mail: f.rivadulla@usc.es

Thin films of CoFe_2O_4 (15-18 nm thick) were deposited at different temperatures by Pulsed Laser Deposition (PLD, Nd:YAG $\lambda = 266$ nm, fluence ≈ 1.5 J/cm², 5 Hz) on MgAl_2O_4 (MAO, cubic, $a \approx 8.09$ Å), at an oxygen pressure of 1.2 mTorr. Another set of samples of the same composition were deposited at different temperatures on MAO by Polymer Assisted Deposition (PAD). Individual solutions of Co and Fe were prepared by dissolving the corresponding nitrates in water with ethylenediaminetetraacetic acid (EDTA, 1:1 molar ratio) and polyethylenimine (PEI) (1:1 mass ratio to EDTA). The total cationic concentration was adjusted to ≈ 200 mM, to obtain films in the ≈ 15 -17 nm thick range.

Ab initio electronic structure calculations were performed based on the density functional theory (DFT)^[1] using the full-potential, all-electron code WIEN2k.^[2] The exchange-correlation potential used was the generalized gradient approximation in the Perdew-Burke-Ernzerhof scheme.^[3] The muffin-tin radii utilized were 1.86 a.u. for Co, 1.99 a.u. for Fe and 1.60 a.u. for O. The RK_{max} parameter used was 7.0.

X-ray diffraction analysis was performed in a high-resolution Bruker D8 Advance diffractometer.

The high resolution reciprocal space maps (RSM) around the (115) Bragg reflection are shown in Figure S1 and Figure S2, for the films deposited by PLD and PAD, respectively. Each RSM corresponds to a sample deposited at a given temperature, as indicated in the plots.

As the deposition temperature increases, a widening of the diffraction peak along Q_x is observed. This effect can be appreciated better in the films deposited by PLD. Because of the much narrower peaks in this case, we can distinguish clearly an increasingly important contribution from a region with smaller Q_x , *i.e.* with larger in-plane lattice parameter, as temperature increases. This is in very good agreement with the observations by microstruc-

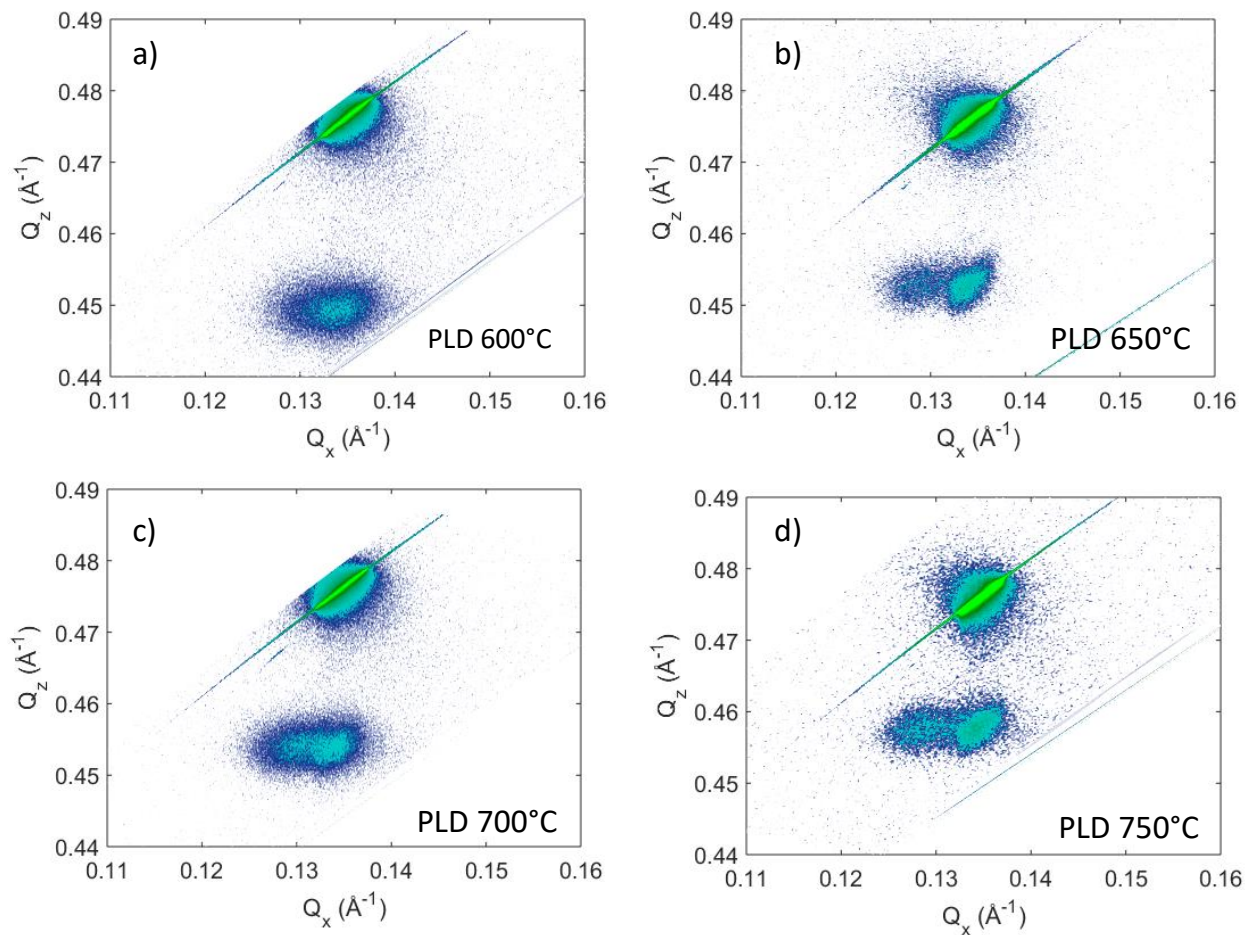


Figure S1: Reciprocal space maps around the (115) Bragg reflection of CoFe_2O_4 deposited by PLD at different temperatures. A partial relaxation of the structure is evident at the higher temperatures, with the appearance of a region with larger in-plane lattice parameter (smaller Q_x).

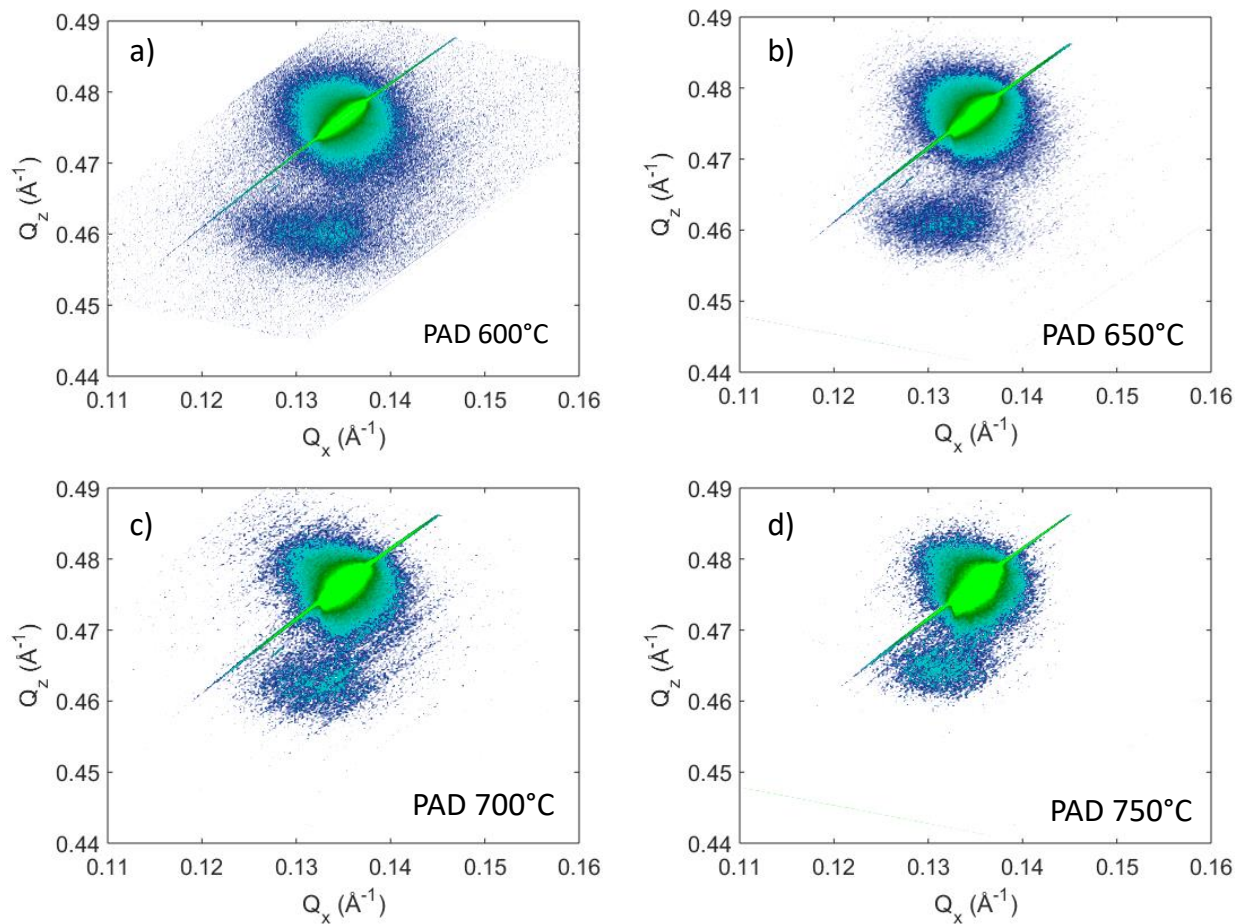


Figure S2: Reciprocal space maps around the (115) Bragg reflection of CoFe_2O_4 deposited by PAD at different temperatures.

tural STEM-GPA analysis discussed in the paper.

Field dependent magnetization was recorded at different temperatures, from 10 K to 300 K, in a SQUID MPMS from Quantum Design. The magnetic field was applied parallel to the surface of the films. As shown in Figure S3, there is a growing contribution from a magnetic-soft phase as the deposition temperature increases. This effect is observed irrespective of the method of synthesis. However, consistent with a larger in-plane lattice parameter, the films prepared by PAD show a contribution from the magnetically soft phase starting at lower deposition temperatures than those grown by PLD. For the films synthesized by PLD, the two-phase contribution is only observed in the magnetization at the higher temperatures probed in this work (750°C).

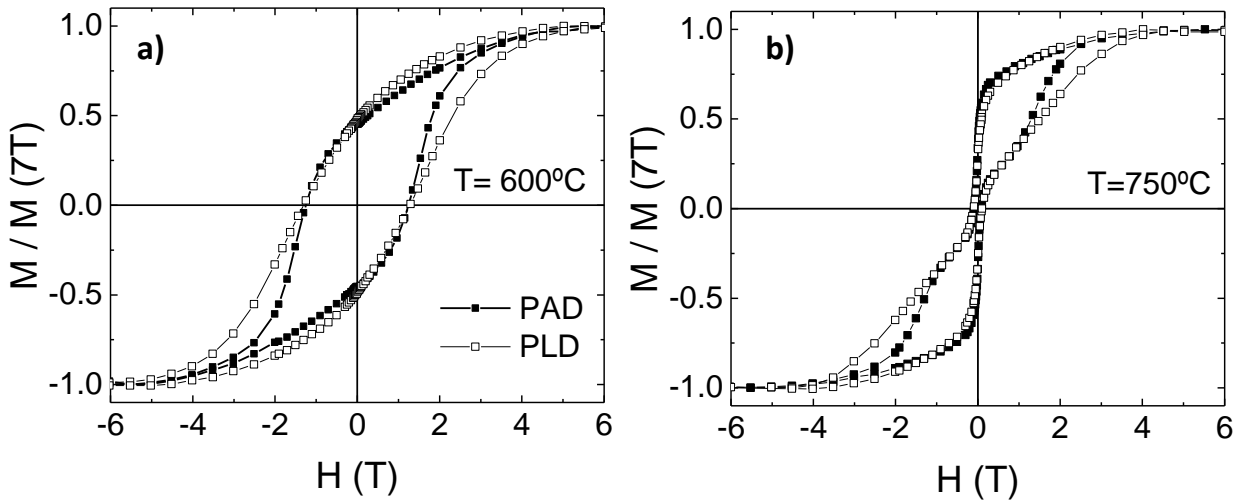


Figure S3: Magnetization vs. magnetic field hysteresis loops obtained at 10 K, for two sets of samples deposited at 600°C (a) and 750°C (b). Open and closed symbols correspond to films prepared by PLD and PAD, respectively.

The X-ray reflectivity and AFM topography images of the surface of two films deposited by PAD and PLD is shown in Figure S4.

The roughness of the PLD films is very low, smaller than 0.5 nm, at any temperature. On the other hand, the roughness of the films deposited by PAD is much larger at low temperatures (between 1.5 and 1.2 nm).

Local microstructure characterization was carried out by scanning transmission electron

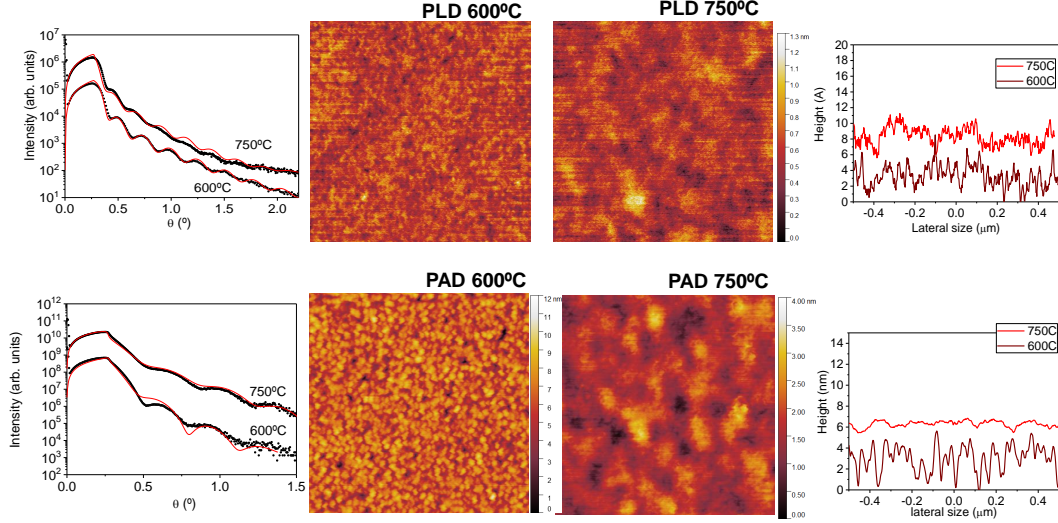


Figure S4: X-ray reflectivity of the samples synthesized by PLD (top) and PAD (bottom) at different temperatures. The red lines are the fittings of the experimental data. The surface roughness derived from these fittings is $\approx 0.25\text{-}0.3$ nm for the PLD films, and $\approx 1.2\text{-}1.5$ nm for the PAD films. The AFM topography images ($1 \times 1 \mu\text{m}^2$) of the films deposited by PLD and PAD is also shown, as well as the line topography.

microscopy (STEM) in an FEI Titan 60- 300 operated at 300 kV and equipped with a high brightness Schottky field emission gun, a CETCOR probe aberration corrector from CEOS to provide a spatial resolution better than 1 \AA in STEM mode, and a Gatan Imaging Filter 866 ERS for spectroscopic analysis. Z contrast imaging has been carried out in high angle annular dark field (HAADF) with a probe convergence angle of 25 mrad and an inner collection angle of approximately 58 mrad. The specimens analyzed correspond to different lamellae extracted from the samples by focused ion beam (FIB) milling in a FEI Helios Nanolab 600 using a 5 kV ion beam for the final thinning to reduce the surface amorphization layer.

In Figure S5 we show two STEM images of different regions of a sample deposited by PLD at 600°C . The arrows indicate the presence of defects, like APBs, which extend across the whole thickness of the films. We did not observe any obvious increase in the number of APBs in the sample synthesized at the higher temperature, with respect to those deposited at 600°C .

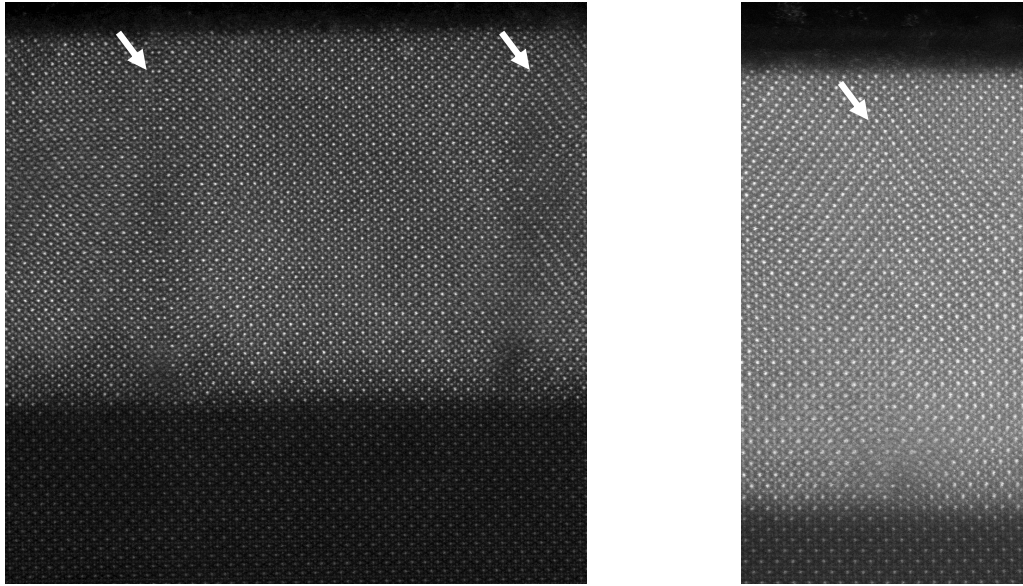


Figure S5: High-resolution STEM images of cross-section lamellae of CFO film deposited by PLD at 600°C.

References

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