

Phase transitions and magnetic structures in Epsilon-Fe₂O₃ nanoparticles

A. Romaguera¹, Z. Ma¹, J. Herrero-Martín², C. Popescu², J. Ángel Sans³, M. Gich¹, J.L. García-Muñoz¹

¹Institut de Ciència de Materials de Barcelona, ICMA-B-CSIC, Bellaterra, Spain, ²CELLS-ALBA synchrotron, Cerdanyola del Vallès, Spain, ³Instituto de Diseño para la Fabricación, Universitat Politècnica de València, Valencia, Spain

garcia.munoz@icmab.es

The epsilon phase of Fe₂O₃ (ϵ -Fe₂O₃, its least known polymorph) has gained considerable interest due to its intriguing properties and great application potentials. In the last few years this rare polymorph has received extraordinary attention due to its unique physical properties: it stands out for its huge coercive field (up to 2 T at room temperature), millimeter-wave ferromagnetic resonance, magneto-electric coupling, room temperature ferroelectricity, non-linear magneto-optical effect and photocatalytic activity [1-4].

ϵ -Fe₂O₃ presents a complex noncentrosymmetric structure (*Pna2₁*) with four distinct Fe sublattices: two positions in distorted octahedra (Fe1 and Fe2), one in regular octahedral environment (Fe3r), and one in a distorted tetrahedron (Fe4t). This work examines the structural and magnetic phase transitions in ϵ -Fe₂O₃ nanoparticles (~20 nm) combining synchrotron X-ray and neutron diffraction measurements in the range 2-900 K. Complemented with X-ray absorption spectroscopy (XAS) and angle-dispersive X-ray diffraction under pressure up to 34 GPa.

The origin of the spin frustration was studied in the context of the rich magnetic phase diagram (with four different successive magnetic states) and its relationship with the magnetostructural transitions observed as a function of temperature. The successive magnetic transitions have been thoroughly studied in the whole temperature range, and commensurate ones have been fully described using the magnetic space groups approach. We have found that spin frustration at the Fe³⁺ tetrahedral-site (Fe4t) not only is responsible for the unexpected different FIM1 (soft) and FIM2 (super-hard) commensurate ferrimagnetic phases [5], but it is also at the origin of the singular FIM2-to-ICM magnetic phase transition that disrupts the super-hard ferrimagnetic state of *Pna'2₁*' magnetic symmetry.

The structural evolution of ϵ -Fe₂O₃ is investigated across the magnetic transitions, putting the emphasis on the FIM1 (soft) to FIM2 (super-hard) phase transition at \approx 480 K. The observed magnetostructural coupling at that temperature explains the changes between the magnetic structures associated to respectively the soft and super-hard phases. Puzzling successive changes are also observed between 150 and 100K under cooling, which are the signature of a non-conventional mechanism behind the commensurate-incommensurate magnetic phase transition (FIM2-ICM). The spiral magnetic structure previously proposed below 100 K does not match our neutron diffraction data. Incommensurate (ICM) collinear solutions compatible with neutron data are presented and contrasted. This transition reduces the coercivity of ϵ -Fe₂O₃ from 20 kOe to 0.8 kOe and the final ICM magnetic order (ground state) involves the creation of magnetic antiphase boundaries.

Finally, we report on the structural phase transition under pressure associated to the volume collapse reported in [6]. The transformation of the pristine octahedral and tetrahedral environments above 27 GPa is presented based on synchrotron X-ray diffraction experiments. The observed pressure transition is analyzed in connection with the mechanism for switching the ferroelectric polarization in ϵ -Fe₂O₃ thin films.

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