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## Report:

### Introduction of Cobalt Ions in $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles by Direct Coprecipitation or Post-synthesis Adsorption: Dopant Localization and Magnetic Anisotropy

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**ABSTRACT:** The influence of cobalt doping on the magnetic anisotropy of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles has been investigated using two different approaches: (i) simultaneous precipitation of Fe<sup>2+</sup>, Fe<sup>3+</sup> and Co<sup>2+</sup> precursors in water and (ii) adsorption of Co<sup>2+</sup> ions onto the surface of preformed iron oxide particles followed by diffusion in the solid phase upon heat treatment. The incorporation of small amounts of Co dopants, less than 1% atomic, was monitored by magnetization measurements combined with X-ray absorption spectroscopy experiments at the Co K-edge. These latter

measurements were carried out in fluorescence mode using a crystal analyzer spectrometer for an enhanced sensitivity. Analyses of the X-ray absorption fine structures allowed for unraveling the differences in local atomic structure and valence state of Co in the two series of samples. A thermally-activated diffusion in the spinel lattice was observed in the 250-300°C range, leading to a substantial increase in magnetocrystalline anisotropy. At higher annealing temperature, magnetic anisotropy was still found to increase due to an enhanced surface contribution associated with deshydroxilation of terminal Fe atoms. This study not only provides direct correlations between magnetic anisotropy and dopant localization in Co doped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> but also demonstrates for the first time that simultaneous coprecipitation of Fe<sup>2+</sup>, Fe<sup>3+</sup> and Co<sup>2+</sup> may actually lead to heterogeneous doping, with a significant part of the Co dopants adsorbed at the particle surface.

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