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In situ oxidation kinetics of magnetite nanoparticles by total scattering

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Iron oxide nanoparticles (NPs) show different structures as a function of oxidation state. In particular, magnetite (Fe3O4) NPs are easily oxidized in air at moderate temperatures, eventually yielding maghemite (Fe2O3). Oxidation proceeds via the creation of iron vacancies. While the vacancies may be created with a random distribution throughout the octahedral Fe sites, they eventually order over a specific subset of these sites, lowering the symmetry from F-centered (magnetite) to P-centered (cubic maghemite). By ex situ X-ray Total Scattering studies of magnetite-maghemite NPs in different oxidation states[1] we have recently studied, by the DFA method[2], the correlation between particle diameter, stoichiometry and lattice parameter in polydisperse NP samples unraveling also the size dependence of lattice parameter and composition. Moreover, we have shown indirect evidence of the formation of a polycrystalline surface layer of maghemite on a magnetite core in the intermediate oxidation states. Motivated by the excellent ex-situ results, we have also performed in-situ studies where magnetite NPs were oxidised in air at moderate temperatures (50-200 C). We present here an in-situ study performed at the X04SA-Materials Science beamline of the Swiss Light Source synchrotron[3]. Total Scattering X-ray diffraction patterns were collected every few minutes, while the oxidation was completed within several hours. The mechanism of NPs oxidation - whereas a surface oxidised layer is formed by outwards diffusion of Fe, then the vacancies so created order themselves giving rise to the maghemite-magnetite phase transition, will be examined in great detail. We will discuss, on robust statistical basis, the calculation of kinetic and diffusion constants, the temperature effect on the lattice constant and on the thickness of the surface oxidised layer; the different possible structural models for the cubic-maghemite NPs. We thank for support Fondazione Cariplo (2009-0289).

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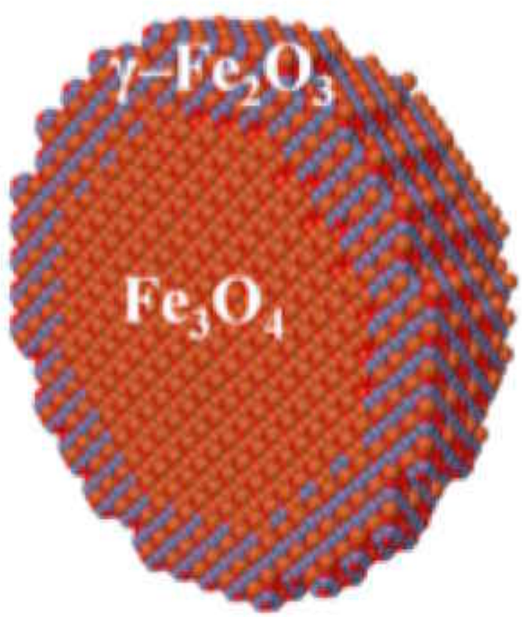

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