Identification of Defects in Lepidocrocite Nanoparticles and Correlation with Their Magnetic Properties

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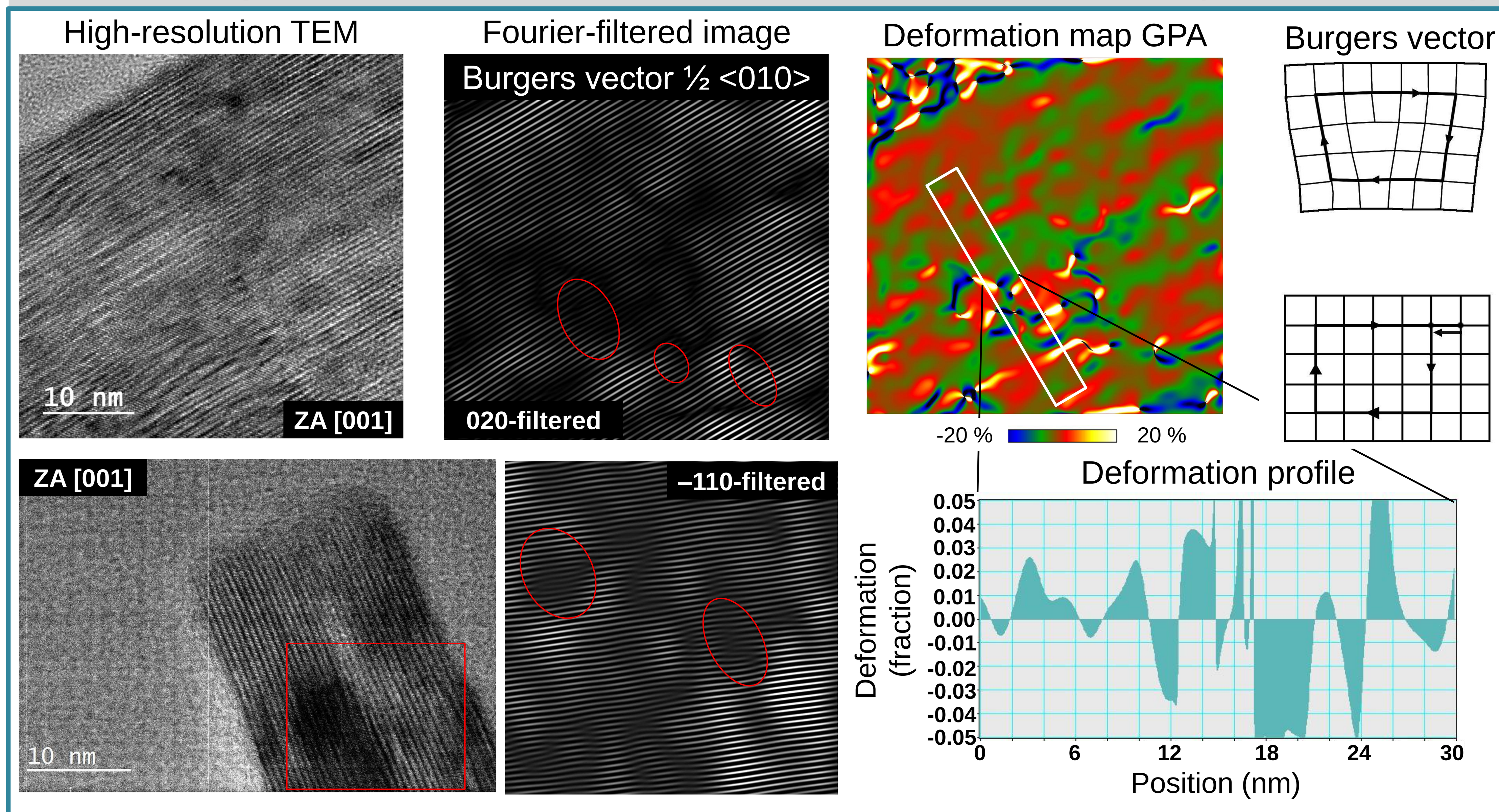
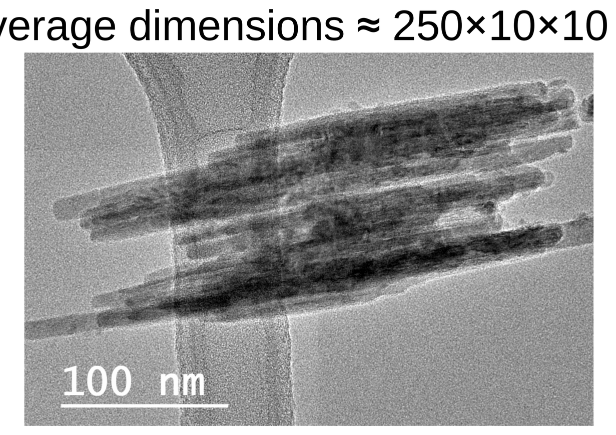
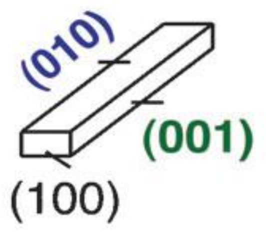
Iron oxide nanoparticles can be used in a variety of industrial applications such as pigments, magnetic recording media, adsorbents in different fluids, etc. However, the properties of nanoparticles can be often altered significantly by the presence of defects present on the surface or within the volume or both. In this work we show the characterization of defects in lepidocrocite (γ-FeOOH) nanoparticles using high-resolution TEM, Fourier filtering analysis and geometric phase analysis (GPA). The presence of defects results in anomalous magnetic properties such as ferrimagnetism despite being antiferromagnetic in the bulk. This anomalous behavior is likely due to changes in the cationic order around the defects.

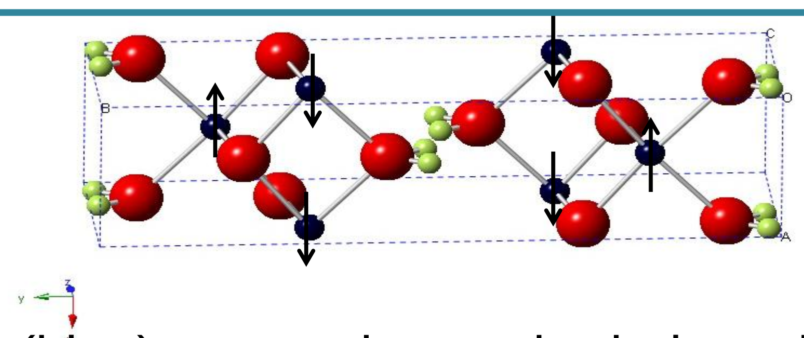


High-resolution images (left), Fourier-filtered images (center), and deformation map together with a deformation profile (right) obtained using geometric phase analysis (GPA [1]) were used to identify the defects in lepidocrocite. Dislocations were found in (020), (004) and (-110) planes, Burgers vectors (magnitude and direction of the lattice distortion) are ½ <010>, ¼ <001> and ½ <-110> respectively. Deformation of (020) lattice fringes is rather uniform (± 5 %). Lattice distortion along deformation profile line can be ascribed to dislocations. Negative deformation corresponds to the shorter lattice parameter.

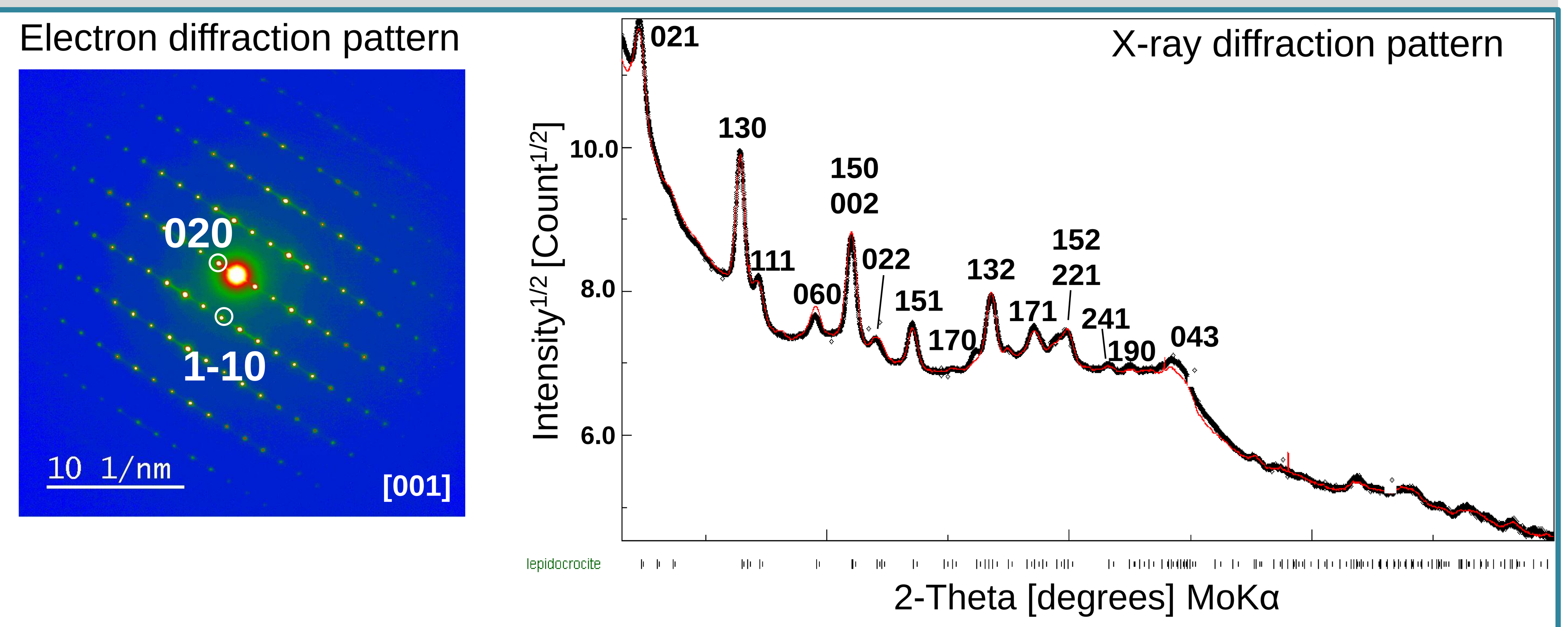




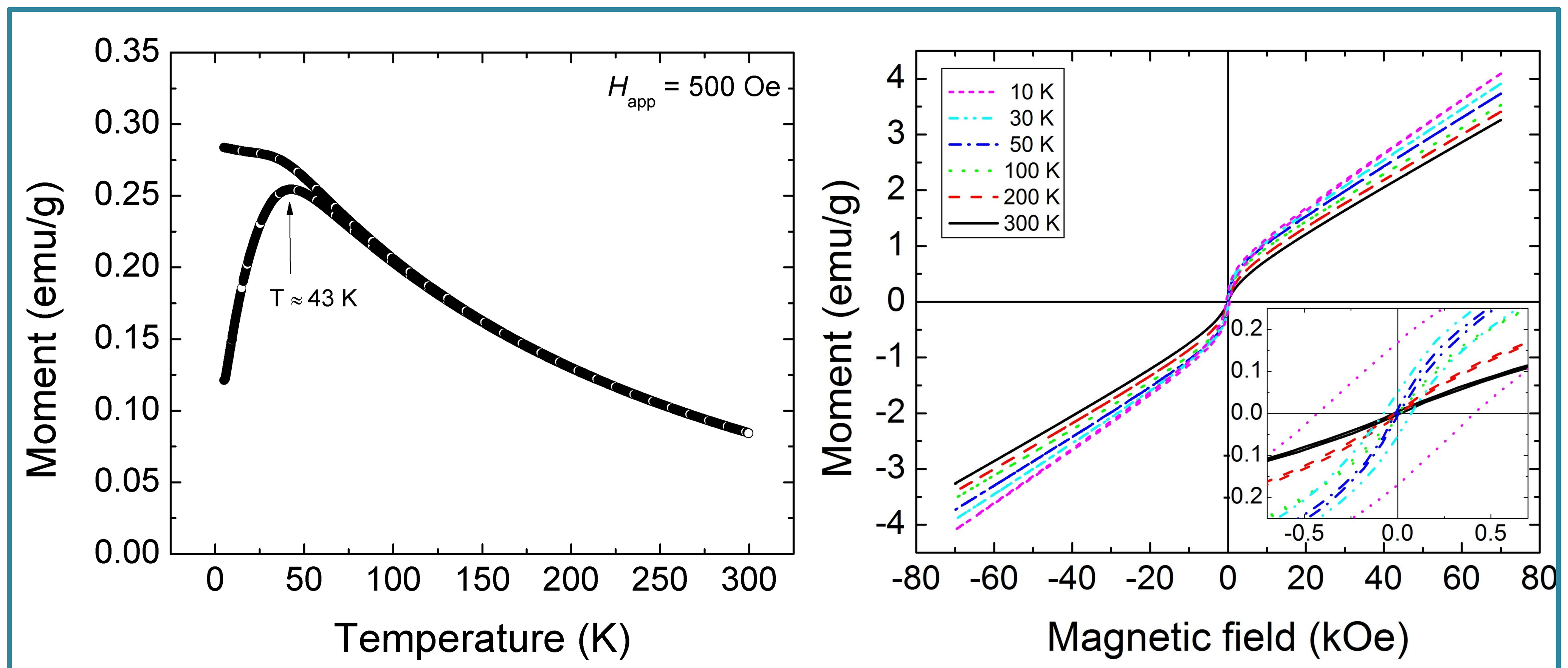
Song and Boily, Phys. Chem. Chem. Phys. 14 (2012) 2579.



Iron (blue) atoms in octahedral positions has superexchange interaction via oxygen (red) atoms



The diffuse intensity, which can be related to defects (dislocations, anti-phase boundaries, etc.), was detected along <010> direction from electron diffraction patterns. Rietveld refinement using Popa algorithm shows an enhanced strain on (002) and (022) planes.



Lepidocrocite is paramagnetic at room temperature and becomes antiferromagnetic below ≈ 77 K (Neel temperature, T_N). Our low temperature magnetic characterization indicates the presence of a ferri- or ferromagnetic component with a blocking temperature of ≈ 43 K, similar to earlier reports [2]. The cationic order around the defects is likely to be responsible for the presence of the hysteresis loop. Indeed, the converse behavior has been observed in nominally ferrimagnetic nanoparticles where the defects result in an antiferromagnetic component [3].

Conclusions

- Strain analysis methods (in HRTEM images and PXRD patterns) was used to find defects in lepidocrocite nanoparticles. Defects were identified as dislocations (Burgers vectors ½ <010>, ¼ <001> and ½ <-110>) in (020), (004) and (-110) planes and in (021), (111) and (004) planes for this work
- Diffuse scattering, which can be related to defects (dislocations, anti-phase boundaries, etc.), was detected in [010] and [110] directions
- Presence of ferrimagnetic domains due to cationic distortion in antiferromagnetic lepidocrocite was observed

Acknowledgements

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[1] Hÿtch et al., Ultramicroscopy 74 (1998) 131; [2] Hirt et al., J. Geophys. Res., 107 (2002) ECM-5; [3] Wetterskog et al., ACS Nano, 7 (2013) 7132.