Atomic resolution spatially-resolved inversion parameter in spinel oxides

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Spinel materials are characterized by an AB_2Z_4 structure, where A and B are divalent and trivalent cations, respectively, and Z is a divalent anion, typically oxygen. The A cations occupy the octahedral positions (O_h) in the structure, whereas the B cations occupy the tetrahedral (T_h) ones. However, depending on the nature of the A and B cations and the external conditions, the distribution of the cations in the structure can be altered. This distribution is characterized by the inversion parameter, x, where the structure is represented as $(A_{1-x}B_x)[A_xB_{2-x}]Z_4$, where "( )" denote O_h positions in the structure and "[ ]" T_h positions, respectively.

The estimation of the degree of inversion with spatial resolution in nanostructured spinel oxides remains a challenge. Several techniques exist that can assess the coordination of chemical species in a crystal, such as x-ray diffraction refinement, neutron diffraction or nuclear magnetic resonance. Yet, these techniques yield averaged information, typically from rather large volumes. Nonetheless, when dealing with complex systems such as core/shell nanoparticles, a few unit cells can determine the resulting overall properties of the system.

Taking advantage of the spatial resolution of electron energy loss spectroscopy (EELS) and its ability to identify different chemical species, the oxidation state and cation inversion parameter in Fe_3O_4/Mn_3O_4 core/shell nanoparticles have been characterized. Interestingly, coordination inversion is determined atomic column by atomic column, a measurement unprecedented in such small nanosystems, which proves important in the understanding of the magnetic behavior of the nanoparticles.

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