Inversion detection in $CoFe_2O_4$ spinels by EELS and BM3D analysis

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Context

In the domain of catalysis and gas sensing, the size, shape and composition of ferrite nanoparticles can be tuned to adjust their properties [1]. In order to tailor the reactivity and catalytic properties of cobalt ferrites, nano-ferrites with different shapes, e.g. nano-octahedra and nanocubes, can be synthesized using solvothermal methods for which the shape of nanoparticles is governed by the differences in growth velocity of specific crystallographic facets, which in turn can be controlled by the use of specific surfactants. Cobalt ferrites are mixed ferrite spinels, with an inversion degree that varies with the cobalt content, particle size and the synthesis method, so the cation distribution about the tetrahedral and octahedral sites, should also be considered when discussing cobalt ferrite properties. Here we apply both principal components analysis (PCA) and block matching and 3D filtering (BM3D) analysis (see below) to the problem of denoising the Co Fe and O distributions in nanocubes with a view ultimately to measuring the inversion parameter. The main challenge in performing the experiment arises from the beam-sensitive nature of the material, meaning that only hyperspectra with quite poor statistics can be acquired before the damage becomes significant.

Normal and inverse spinel structure

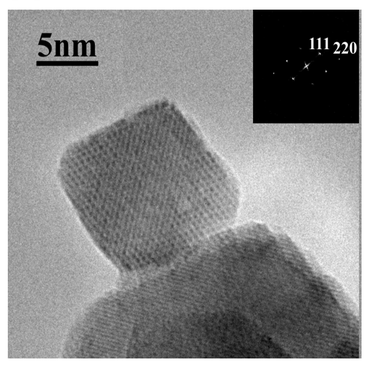
The spinels are any of a class of minerals of general formulation AB_2C_4 which crystallise in the cubic crystal system, with the C anions (typically chalcogens, like oxygen and sulphur) arranged in a cubic close-packed lattice and the cations A and B occupying the octahedral and tetrahedral sites in the lattice respectively. In a “normal” spinel all the A cations occupy tetrahedral sites and the B atoms the octahedral sites, which are twice as numerous. (See figure below) However, the two anions may exchange positions to a degree characterised by the inversion parameter *x*. $(A_{1-x}B_x)(A_xB_{2-x})C_4$ thus represents a structure in which a fraction *x* of the A anions occupy octahedral sites and a corresponding number of B atoms occupy tetrahedral sites. For x = 1 the inversion is said to be complete, although the stoichiometry requires that half of the B anions remain on octahedral sites.

Experiments

Hydrothermal synthesis of $CoFe_2O_4$ nano-octahedra

Typically 2 mmol of $Co(NO_3)_2.6H_2O$ and 4 mmol of $Fe(NO_3)_3.9H_2O$ were dissolved in deionized water. The pH was controlled by adding NaOH, and CTAB (cetyltrimethyl-ammonium bromide) was used as surfactant [2].

HRTEM image of typical $CoFe_2O_4$ nano-octahedrons



EELS experiments

Data was acquired using a Nion UltraStem operating at 100kV. Hyperspectra were recorded typically with <10ms acquisition times and probe currents of about 30pA from [110]-oriented particles on a holey carbon film. Some damage was still visible in most final datasets.

Data analysis

Principal components analysis (PCA) is a well-known dimensionality reduction method often used in EELS to perform denoising of the data [3] by reconstructing the hyperspectrum by keeping only the most significant components, the others being interpreted as noise. However, this method has the disadvantage of not taking into account the spatial correlations present in the hyperspectral image as the initial datacube is flattened into an n (pixels) x m (bands or spectral channels) matrix.

Indeed, for our data the elemental maps obtained by this method remain quite noisy.

Denoising algorithms considering jointly the spatial and spectral correlations are more promising in terms of performance.

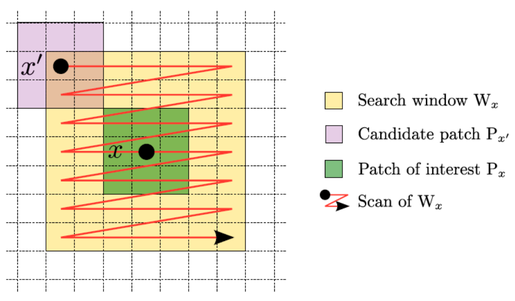
Some algorithms consider directly the datacube as a whole. These techniques are computationaly expensive and require the fine tuning of several hyperparameters.

Therefore, we chose to use a sequential approach that combines successively a change of representation space (with PCA) and a denoising of 2D images (component weight maps).

2D denoising is performed by a patch method. Patch-based filters model images as a collection of patches (i.e., small windows extracted at different positions) and assume that this collection presents redundancy or clusters. This assumption relies on the self-similarity property of images: the same content can be observed at different positions, thus, most of the patterns occur several times. This principle is particularly well suited to atomic resolution images.

We used the state-of-the-art image denoising method **Block matching and 3D filtering (BM3D)** [4].

The denoised spectrum-image is then reconstructed by an inverse PCA.



The patch-filter combines for each pixel x the noisy value of pixels x’ according to the similarity between two patches P_x and $P_{x'}$ centered respectively around the sites x and x’. The pixels x’ are limited to a search window W_x centered around the pixel x.

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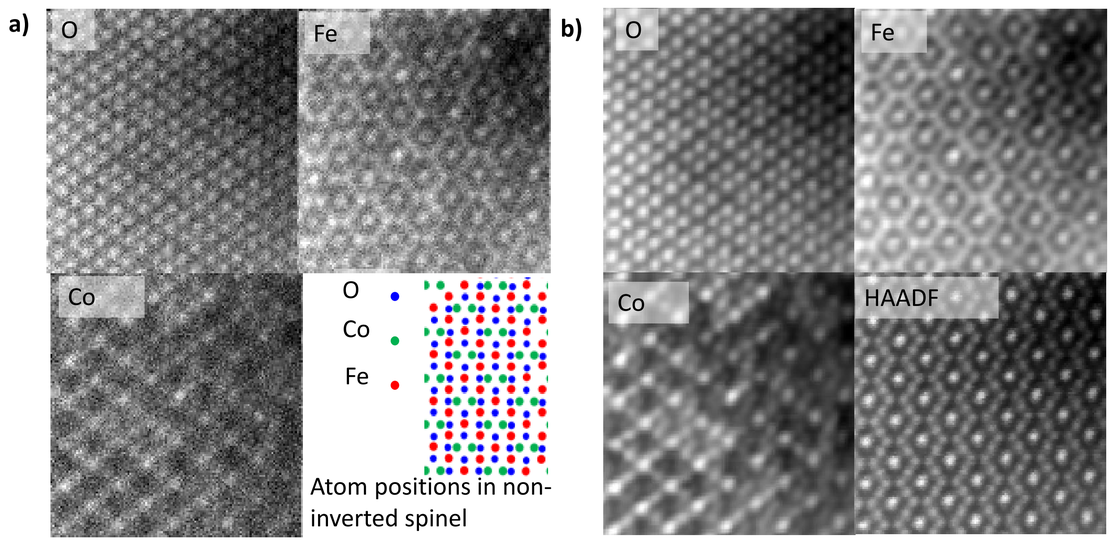
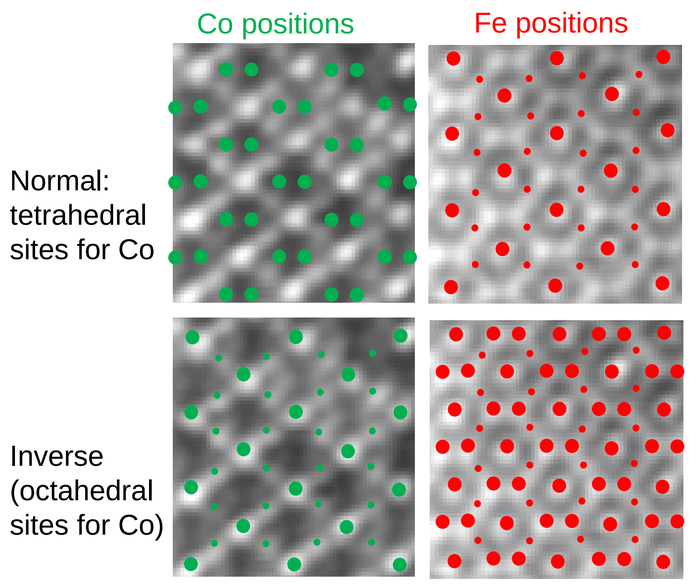
Results

Once the SI is denoised, the chemical maps are obtained by the classical method of background subtraction and integration of the characteristic signal



EELS elemental maps in the [110] direction after a) PCA and b) PCA+BM3D. Also shown are the atomic position projections in the non-inverted spinel and the simultaneous HAADF image. Some beam damage is visible in the top-right of the images.



Fe in octahedral sites:
Smaller dots represent sites which have double the spacing in the z (beam) direction compared to the ‘apex’ sites (large dots) and so only half the number of atoms in the beam path

Fe in inverse spinel :
Here the double z-spaced tetrahedral sites should be of the same intensity as the apex sites which are twice as dense but only 50% Fe-occupied for *x*=1

Bottom-left part of elemental maps with superimposed atom positions for normal and inverse spinels. The intensity distributions correspond much better to the inverse case.

Estimating the inversion parameter *x*

We cannot as yet give a high-precision value for *x*. The Co signal being stronger on octahedral than tetrahedral sites implies *x*>0.5. Quantification of the pixels around the tetrahedral sites gives an average Fe:Co ratio of 75:25 with a variation of around ± 7 for each percentage. Given that there is a large background signal of both elements everywhere in the data (finite probe-size and signal delocalisation effects) the inversion *x*= 0.75 implied by this ratio is very likely an under-estimate. However, the lower Fe intensity in the tetrahedral than in the apex octahedral sites implies incomplete inversion. A somewhat more detailed examination gives *x* = 0,8 ± 0,15 but simulations will be needed to refine this figure.

References

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