

STEM Analysis of Vacancies in Magnetite Nanoparticles

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Magnetite (Fe_3O_4) nanoparticles (NPs) have attracted a lot of attention due to their widespread applications in ferrofluids, magnetic separation, contrast agents, magnetic resonance imaging and magnetic hyperthermia. Synthesising NPs with a magnetisation value close to that of bulk magnetite is a challenging task due to difficulties in the precise control of their stoichiometry as well as the ubiquitous presence of structural defects [1]. In addition, magnetite nanoparticles have a tendency to transform towards the more stable maghemite (Fe_2O_3) form of iron oxide. We note that maghemite and magnetite share the same inverse spinel structure with the maghemite structure hosting eight (ordered) vacancies, i.e. $8/3 \text{ Fe}_B$ octahedral vacancies per unit formula of Fe_3O_4 . In this work we present a study comparing scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) images with image simulations carried out with the multislice approach and using crystal structures optimised using the crystal structure prediction code ChemDASH [2], as well as ab initio calculations based on density functional theory (DFT).

Fig. 1 shows a STEM-HAADF image of a selected region of a Fe_3O_4 NP observed along the [111] zone axis. The image shows a hexagonal pattern that reflects the Fe octahedral (Fe_B) and tetrahedral (Fe_A) atomic columns viewed along the [111] direction. The difference in intensity between the columns is associated with the relative occupancy of Fe atoms in these columns: in a fully stoichiometric case, the brightest columns have 3 Fe atoms per unit repeat length while the six satellite (less bright) spots have 1 Fe atom per unit repeat length. Although this is qualitatively reproduced in Fig. 1b, which represents an image simulation of fully stoichiometric Fe_3O_4 , careful analysis of the experimental column intensities of magnetite reveals an asymmetric reduced brightness on a number of atomic columns. This is assumed to be due to Fe vacancies in the magnetite NP. In order to confirm this, we have performed crystal structure prediction to determine which structural sites of magnetite were most likely to form thermodynamically stable vacancies,

For a $1 \times 1 \times 3$ supercell of magnetite, we constructed initial structures containing one or two vacancies. For the two-vacancy case, we used the SOD (Site-Occupation Disorder) package [3] to determine the inequivalent configurations of vacancy placements within the magnetite structure. For each of these starting structures, we used ChemDASH to swap Fe^{2+} and Fe^{3+} ions amongst the octahedral sites, considering 1000 arrangements of the ions for each vacancy combination. Each of these arrangements of

the Fe ions was relaxed to its energetic minimum using atomic force fields in GULP [4], with new arrangements accepted or rejected according to the Metropolis criterion: $Rand < exp(-\Delta E/kT)$.

The lowest energy structures from each ChemDASH run lie within ~ 20 meV/atom of the convex hull, indicating thermodynamic stability. Amongst the lowest energy structures, we found one particularly striking example of vacancies on opposite sites, alongside several examples of vacancies in first- or second-nearest neighbouring sites. Image simulations using parameters mirroring the experimental conditions were carried out for the most promising and most stable structures, using the multislice code abTEM [5], Fig. 1c.

Finally, a further DFT optimisation was carried out, aiming to confirm bond angles and Fe-O-Fe distances, with a view to use these results as input for further studies of the role of vacancies in the magnetic dynamics of Fe₃O₄ NPs.

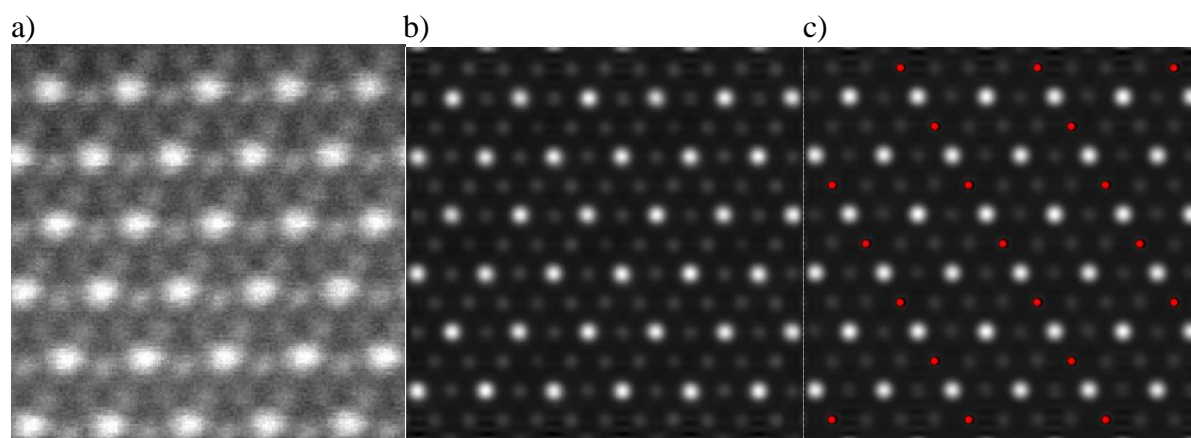


Figure 1. a) STEM-HAADF image from Fe₃O₄ NPs. b) Image simulation of fully stoichiometric Fe₃O₄. c) Image simulation of Fe₃O₄ NPs with presence of vacancies, the positions of the vacancies are denoted by red dots.

References:

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