Structural fingerprinting of a cubic iron-oxide nanocrystal mixture: A case study

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ABSTRACT

Two novel strategies for the structurally identification of a nanocrystal from either a single high resolution (HR) transmission electron microscopy (TEM) image or a single precession electron diffractogram (PED) are proposed and their advantages discussed in comparison to structural fingerprinting from powder X-ray diffraction pattern. Simulations for cubic maghemite and magnetite nanocrystals are used as case study examples.

Keywords: structure, nanocrystals, transmission electron microscopy, structural fingerprinting

INTRODUCTION

Nanocrystals possess size [1] and morphology [2] dependent properties that are frequently superior to those of the same materials in their bulk form. Any future large-scale commercial "nanocrystal powder-based industry" will need to be supported by structural assessment methods [3]. The quite ubiquitous method of identifying crystal structures is (Cu-tube based) powder X-ray diffraction (XRD) [4], e.g. Fig. 1. That method works best for micrometer-sized crystals and becomes due to peak broadening and (isotropic or anisotropic) shifting less useful to useless for crystals in the nanometer range [5, 6]. XRD patterns of nanocrystals are also made significantly less characteristic by surface relaxation effects [7].

Two novel strategies for the structural identification of nanocrystals in the TEM are, therefore, proposed. Both of these methods are applicable to nanocrystal thicknesses for which the scattering of fast electron can be considered as essentially (quasi-)kinematic. This thickness range is for HRTEM imaging 1 to about 10 nm and for PEDs 10 to 50 nm. In the dynamic scattering limit, these methods become analogous to the well known structural identification methods for single crystals in the TEM that only use information on the projected reciprocal lattice geometry. For a recent review of those methods and more information on the two novel strategies, see ref. [8]. Because cubic maghemite and magnetite possess almost the same lattice constant and "rather similar" atomic arrangements (i. e. nearly cubic densest packings of oxygen with differences in the iron occupancies of the intersites), the XRD patterns are very similar, Fig. 1. Allowing for peak broadening, peak shifting, and surface relaxation, nanometer sized crystals of these two cubic iron-oxide minerals can hardly be told apart and their mixtures can not be quantified by XRD.

Quite independent on the nanocrystal size, there is, however, structure information at the atomic level in a (single) HRTEM image and a (single) precession* electron diffractogram (PED) of a (single) nanocrystal that can be advantageously employed for its structural identification [8-13].

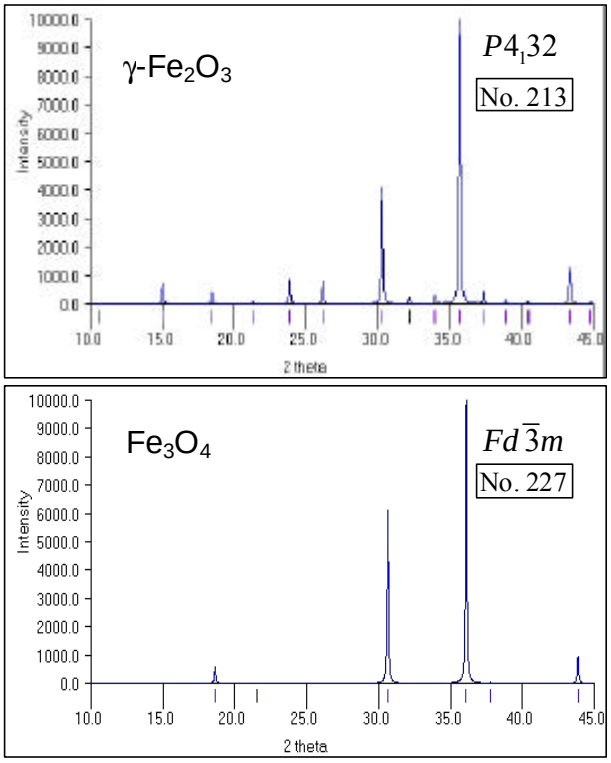

Figure 1: Calculated powder X-ray (Cu-Ka) diffraction patterns for micrometer-sized cubic maghemite, γ-Fe_2O_3, and magnetite, Fe_3O_4, out to the 400 reflections. The space group symbols and their numbers are also given.

This atomic-structure-level structure information is in the case of TEM images after crystallographic image processing [8, 14, 15] structure factor amplitudes and phases out to the point resolution of the microscope, e.g. at least out to 5 nm^{-1} for dedicated (but non-aberration corrected) HRTEMs. In the case of PEDs, this atomic-structure-level information is the structure factor amplitudes and extends to at least twice as far in reciprocal space.

Extracting this kind of information for unknowns, combining it with the extractable projected reciprocal lattice geometry, and comparing it to structural information that is contained for a range of candidate structures in a

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crystallographic database is the basis of our two novel methods for structural fingerprinting in the TEM [8]. The approximately 20,000 entry mainly inorganic subset [16] of the more than 50,000 entry Crystallography Open Database (COD) [17] may be employed for this purpose.

This paper illustrates that for nanocrystals which scatter fast electrons quasi-kinematically much more structural information can be extracted from either HRTEM images or PEDs than is accessible from powder XRD. Simulations for nanocrystals of cubic maghemite, γ-Fe_2O_3, and magnetite, Fe_3O_4, are used as case study examples.

STRUCTURAL INFORMATION FROM HRTEM IMAGES OR PRECESSION ELECTRON DIFFRACTOGRAMS

Table 1 lists theoretical structure factor amplitudes and phase angles for cubic maghemite and magnetite nanocrystals. Their experimental counterparts can be extracted from HRTEM images that were recorded at a microscope with 0.19 nm point resolution. Figure 2 shows a so called "lattice-fringe fingerprint plot" for magnetite for the same point resolution. This plot was calculated over the Internet (on the fly) from data of the mainly inorganic subset of the COD [16]. We call these plots "lattice-fringe fingerprint plots" because the idea to plot two reciprocal spacings and their acute intersecting angle, (i.e. 3 independent entities), into a two-dimensional (2D) plot originated in connection with Fourier transforms of HRTEM images that showed crossing lattice fringes [13].

{hkl}	**γ-Fe_2O_3** |F|	**γ-Fe_2O_3** α	**Fe_3O_4** |F|	**Fe_3O_4** α
011	0.78	90	-	-
111	0.55	135	1.55	0
012	0.90	90	-	-
112	0.60	0	-	-
022	3.25	0	3.29	180
013	0.50	270	-	-
113	4.41	45	4.85	180
222	0.15	90	1.11	0
023	0.63	0	-	-
123	0.43	180	-	-
004	5.65	180	6.47	0
033	0.38	270	-	-
114	0.38	270	-	-
133	0.28	135	0.37	180

Table 1: Theoretical** structure factor amplitudes (|F| in nm) and phase angles (a in degree) for cubic maghemite, γ-Fe_2O_3, and magnetite, Fe_3O_4. The experimental counterparts to these structure factors can be extracted from Fourier transformed HRTEM images that were taken at a microscope with 0.19 nm point resolution. (There are also tetragonal maghemites with similar stoichiometries and variations in the occupancy of the iron intersites, which we do not consider here).

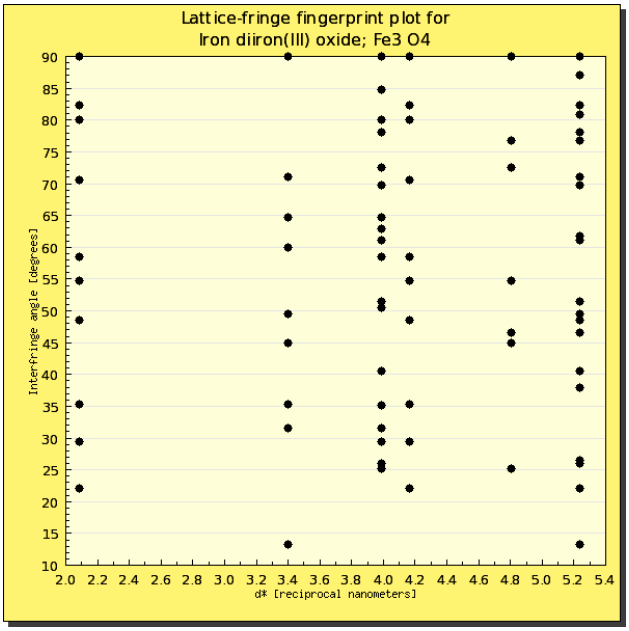

Figure 2: Lattice-fringe fingerprint plot of magnetite for a HRTEM with 0.19 nm point resolution.

The so called "interfringe angle", i.e. the acute angle under which lattice fringes intersect in HRTEM images, is plotted in a lattice-fringe fingerprint plot against the reciprocal lattice vector magnitude. While there are two data points in lattice fringe fingerprint plots for crossed fringes with different spacings, the crossing of two symmetrically related fringes results in just one data point (because the latter possess by symmetry the same spacing). These plots may extend in reciprocal space out to either the point or the instrumental resolution of the microscope. All of the resolvable lattice fringes up to this resolution will be included for a certain crystal structure into these plots.

If derived from PED data, the counterpart to a lattice-fringe fingerprint plot will extend in reciprocal space out to the diffraction limit of the structure. As far as the projected reciprocal lattice geometry is concerned, there is no essential difference between lattice-fringe fingerprint plots that originated from Fourier transformed HRTEM images and their counterparts that originated from PED data.

An initial search in a database of theoretical lattice-fringe fingerprints that is only based on the 2D positions of lattice-fringe data points, Fig. 2, may result in several candidate structures. In the following step, the search can be made more discriminatory by trying to match crystallographic indices to the 2D positions. Because one will always image along one zone axis, all of the indices of the reflections must be consistent with a certain family of zone axes. (As far as the lattice-fringe fingerprint plots are concerned, this follow up search is equivalent to assigning crystallographic indices to the 2D data points.)

Similarly to the classical Hanawalt search strategy of powder X-ray diffraction databases [4], one can divide lattice-fringe fingerprint plots, such as the ones shown in Fig. 2, into 2D geometric data sectors of experimental

condition specific average precisions and accuracies and also allow for some overlap between the sectors. Larger reciprocal spacings and interfringe angles can be measured inherently more accurately than smaller reciprocal spacings and interfringe angles. The location of the respectively more accurate data points will be in the upper right hand corners of lattice-fringe fingerprint plots.

The accuracy and precision of the extracted structure factors will depend on how accurately the contrast transfer function of the objective lens can be determined at every point of interest by crystallographic image processing [14, 15]. The accuracy of theoretical structure factors is not precisely known as it depends on the (not precisely known) accuracy of the atomic scattering factors. Nevertheless, the accuracy of theoretical structure factors is likely to be similar for all structure factors because each of them represents the scattering in a certain direction by all of the atoms in the unit cell.

COMPARISON BETWEEN TEM AND XRD DATA FOR STRUCTURAL IDENTIFICATION OF NANOCRYSTALS

If one takes the peak position and peak height in an XRD diffractogram as two pieces of information, there are just 12 such pieces for magnetite (including those from the very weak 222 peak next to the strong 400 peak and the weak 133 peak which falls just outside the angular range of Fig. 1), which can be used for the structural identification of this mineral. In Fig. 2, there are, however, 74 data points for magnetite out to the family of {133} reciprocal lattice vectors. In addition, each of the 6 families of lattice planes in Fig. 2 possesses both structure factor amplitude and structure factor phase angle, see last two columns of Table 1.

If the counterpart of a lattice-fringe fingerprint is for maghemite constructed from PED data, there will be many more data points in the plot as the resolution of such data is not restricted to the point or information limit resolution of the HRTEM. There will, however, be for each family of lattice planes only the structure factor amplitude available for structural fingerprinting in the TEM.

Due to the primitive cubic space group symmetry of maghemite, its theoretical lattice-fringe fingerprint plot counterpart contains about five times more data points (with distinctively different 2D coordinates in the plot) for the same 0.19 nm point resolution of the HRTEM. In addition, due to this space group being not centrosymmetric, the structure factor phase angles can have any value, see third column in Table 1, while they are restricted to be either 0° or 180° for magnetite, see last column of Table 1. Cubic maghemite and magnetite nanocrystals can, therefore, be reliable distinguished on the basis of HRTEM images when they are part of a mixture, as experimentally demonstrated in refs. [9-11].

Since the indices of the three strongest peaks in XRD patterns out to the 400 reflection, Fig. 1, are for magnetite and maghemite identical, these two iron-oxides can even for micrometer sized crystals not easily be distinguished by the classical Hanawalt [4] approach. Due to XRD peak broadening, peak shifting, and surface relaxation effects, both a distinction between these two minerals and quantification in case of a mixture of these two iron-oxides become for nanocrystals quite impossible.

SUMMARY OF THE KIND OF INFORMATION THAT IS OBTAINABLE FROM TEM FOR STRUCTURAL IDENTIFICATION OF NANOCRYSTALS

The structural information that can be extracted from a HRTEM image is the projected reciprocal lattice geometry, the plane symmetry group, and a few structure factor amplitudes and phases. Except for the structure factor phases, the same kind of information can be extracted from a single PED, but the information that can be used for structural fingerprinting is in this case is not limited by to the point or instrumental resolution of the TEM. PEDs show frequently higher order Laue zones that enable the extraction of structural information in 3D.

More elaborate lattice-fringe fingerprint plots may contain in the third and forth dimension information on structure factor phases and amplitudes. Possibly in a fifth dimension, histograms of the probability of seeing crossed lattice fringes in an ensemble of nanocrystals may be added to lattice fringe fingerprints and may facilitate the structural fingerprinting of a multitude of nanocrystals. The equations for calculating such probabilities for an ensemble of randomly oriented nanocrystals are given in ref. [13]. Instead of employing higher dimensional spaces, one may stick to two-dimensional displays such as Fig. 2 and simply add to selected data points sets of numbers that represent additional information, e.g. structure factor phases and amplitudes with their respective error bars. Because all interfringe angles between identically indexed reflections are the same in the cubic system, space group information can be extracted straightforwardly from lattice-fringe fingerprint plots of cubic crystals even without indexing.

Searching for these kinds of extractable structural information in comprehensive databases and matching it with high figures of merit to that of candidate structures allows for highly discriminatory identifications of nanocrystals, even without additional chemical information as obtainable in analytical TEMs. Structural identification of nanocrystal within the quasi-kinematic electron diffraction limit will be after automation [8] superior to structural fingerprinting from XRD data.

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* The electron precession method is formally analogous to the well known X-ray precession technique (Buerger, M. J.: Contemporary Crystallography. McGraw-Hill, 1970, pages 149-185), but utilizes a precession movement of the electron beam around the microscope's optical axis rather than that of the specimen goniometer around a fixed beam direction. The diffracted beams are de-scanned in such a manner that stationary spot diffraction patterns are obtained. The illuminating beam can be either parallel or focused.

Precession electron add-ons (to newer and older) TEMs have been developed by Dr. S. Nicolopoulos (Tel.: +34 649 810 619, info@nanomegas.com) and coworkers and can be purchased from NanoMEGAS. Prof. P. Moeck's (pmoeck@pdx.edu, Tel.: USA 503 725 4227) Laboratory for "Structural Fingerprinting and Electron Crystallography" at Portland State University's Physics Department is the first demonstration site for this company in the Americas. There is currently only one other commercial precession electron system from NanoMEGAS installed in the USA (at ExxonMobile Research & Engineering Co. Inc, Annandale, NJ), while there are already 26 installations in Europe alone. Profs. S. Hovmöller and X. D. Zou of the Swedish company Calidris, http://www.calidris-em.com, offer IBM-PC compatible software that supports the extraction of structural information from both HRTEM images and PEDs. (This software can also be demonstrated at P. Moeck's lab in Portland, OR.) While Dr. P. Oleynikov is developing dedicated structural-electron-fingerprinting software at the AnaliTEX company, Dr. S. Rouvimov will develop structural-electron-fingerprinting protocols for industrial partners.

Northwestern University (Evanston, IL) possesses a user-built precession electron system. Copies of that system have been installed at the University of Illinois at Urbana-Champaign, Arizona State University, and the National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory.

It is advantageous that the so called "structure-defining" reflections fulfill the quasi-kinematic diffraction approximations sufficiently well even for thicknesses on the order of 20 to 40 nm for crystals that are otherwise known to scatter fast electrons dynamically; C. S. Own, W. Sinkler, and L. D. Marks, *Ultramicroscopy* **106** (2006) 114-122 as well as P. Oleynikov, S. Hovmöller, and X. D. Zou, *Ultramicroscopy* **107** (2007) 523-533. **Precession electron diffraction is, thus, bound to become the "quasi-kinematic electron diffraction fingerprinter's and crystallographer's" preferred operation mode for nanocrystals in the thickness range from approximately 10 to 50 nm.**

** Averaged structure factor amplitude values, calculated with AnaliTEX's program Emap & Simulator from **open-access** data at: http://rruff.geo.arizona.edu/AMS/amcsd.php.