# Automated Crystal Orientation and Phase Mapping of Iron Oxide Nano-Crystals in a Transmission Electron Microscope

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## ABSTRACT

A recently developed automated technique for the mapping of crystal phases and orientations of polycrystalline materials in a transmission electron microscope has been applied to a mixture of iron-oxide nano-crystals.

**Keywords:** precession electron diffraction, TEM, automatic crystal phase and orientation mapping

## INTRODUCTION

The development of novel materials for micro- and nano-electronics requires reliable characterizations of structures, sizes, and orientations of thin polycrystalline films and ensembles of nanocrystals. The electron backscatter diffraction technique (EBSD) in a scanning electron microscope (SEM) [1] is often employed for structural characterization of these kinds of materials. EBSD in SEM is based on backscattered Kikuchi lines. It is therefore highly sensitive to the plastic deformation state of the crystallites as well as to structural damage or contamination of the crystal surfaces.

Electron diffraction in a transmission electron microscope (TEM), on the other hand, delivers a significantly higher spatial resolution as compared to EBSD in a SEM. It is also less sensitive to the plastic deformation state and the surface of crystallites. In short, in cases of small crystallite sizes and foil thicknesses, crystal orientation and phase mapping by this technique is intrinsically more reliable than by its EBSD/SEM counterpart.

An automated technique for the crystal phase and orientation mapping of polycrystalline materials in a TEM has recently been developed [2,3]. This technique is based on template matching of experimental electron diffraction spot patterns to their pre-calculated theoretical counterparts. Very promising results have so far been obtained with this technique for precipitates in heavily deformed austenitic stainless steels [2,3].

It has also been demonstrated that precession [4] of the primary electron beam around the microscope's optical axis during the recording of the spot diffraction patterns improves the reliability of this technique significantly [5]. This is because more reflections are excited in precession electron diffraction spot patterns. For nanocrystal sizes of below approximately 50 nm, the intensities of these reflections are nearly kinematical (i.e. proportional to the square of the structure factors) [6]. Such precession electron diffraction patterns are, therefore, very useful for structural fingerprinting of nanocrystals in a TEM [7,8].

This paper illustrates the application of this technique to a mixture of iron oxide nano-crystals of magnetite and maghemite.

## EXPERIMENTAL DETAILS AND RESULTS

A mixture of magnetite ($Fe_3O_4$, $Fd\bar{3}m$, a = 0.832 nm) and maghemite (gamma-$Fe_2O_3$, $P4_132$, a = 0.833 nm) crystallites with sizes in the range of approximately 3 to 200 nm was used for the automated crystal orientation and phase mapping at a JEOL 3010 TEM equipped with NanoMEGAS' ASTAR system in Grenoble [5].

Complementary high-resolution phase contrast transmission electron microscopy (HRTEM) imaging of individual nanocrystals (of this mixture) in major zone axis orientations were performed at an analytical FEI Tecnai $G^2$ F20 TEM at Portland State University (PSU) [9-11]. Both microscopes are equipped with a "Spinning Star" electron precession add-on from NanoMEGAS*.

Figure 1 shows typical TEM and HRTEM images of these iron-oxide nanocrystals. The determination of individual nanocrystal orientations and phases by

means of HRTEM is currently, however, too time-consuming. Consequently, automated crystal phase and orientation determination techniques are required in order to obtain statistically meaningful results.

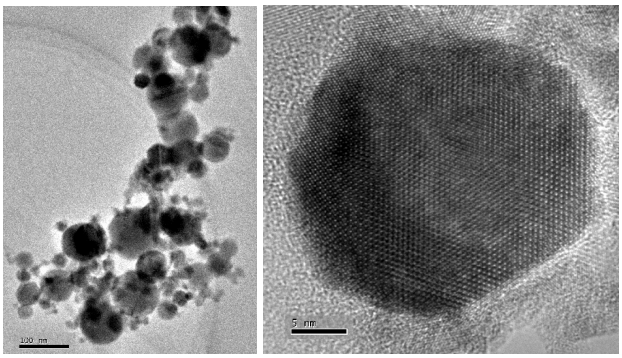

**Figure 1:** TEM (left) and HRTEM (right) images of iron oxide nano-crystals. The magnetite nanocrystal on the right is orientated close to the [110] zone axis.

Note that this mixture of iron-oxide nanocrystals cannot be fingerprinted structurally by powder X-ray diffractometry because the crystallites are too small [12] and both crystal structures are very similar [13]. Automated crystal orientation and phase mapping in a TEM on the basis of precession electron diffraction patters is, therefore, the method of choice for structural fingerprinting of this mixture [5]. A few technical details of this novel technique are described next.

The analysis procedure comprises the automated collection of electron diffraction patterns by an external digital camera while the area of interest is scanned with a nanometer-sized electron beam. The data collection step is followed by automatic data processing, Figure 2.

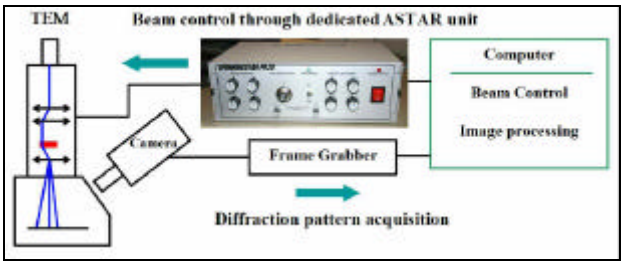


**Figure 2:** The experimental set up of the ASTAR system (from NanoMEGAS) for crystal orientation and phase mapping at a JEOL 3010 TEM in Grenoble [5].

The orientation and phase identification is performed by the matching of each experimental diffraction pattern to a limited number of templates, which are computer calculated diffraction patterns for all orientations over the stereographic triangle. For example, a 1° angular resolution of a highly symmetric cubic crystal structure (such as magnetite) requires fewer than 2,000 templates, Figure 3.

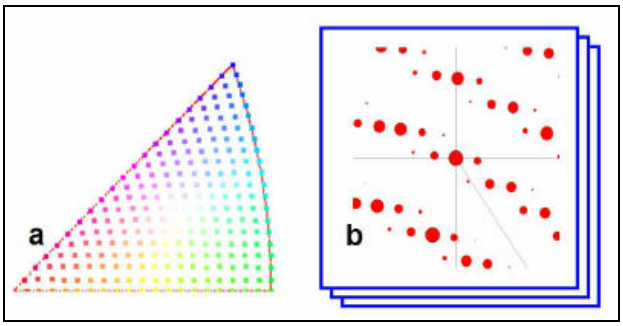


**Figure 3:** (a) The stereographic triangle for cubic crystals with point groups m3m and $\bar{4}$3m; (b) Sketches of templates that are calculated for all orientations over this stereographic triangle.

Figure 4 shows the matching procedure schematically. A typical rate for the matching of electron diffraction spot patterns of magnetite nanocrystals is approximately 100 patterns per second. The degree of matching between the experimental electron diffraction spot patterns (Fig. 4a) and the calculated templates (Fig. 4b) is given by a correlation index [3].

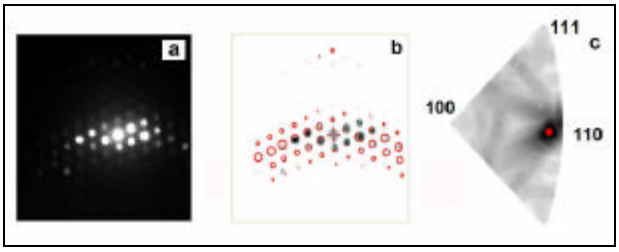


**Figure 4:** Electron diffraction pattern matching: an experimental nano-electron diffraction spot pattern from a crystallite acquired by an external digital camera (a) is compared to each simulated template until the best match is found (b). The correlation index map (c) reflects the degree of matching between experimental patterns and templates. The red dot in (c) shows the most probable orientation of the crystallite that led to the electron diffraction spot pattern of (a).

The correlation index is calculated for every orientation and plotted on a map that represents two standard stereographic triangles for the above mentioned two point groups, Fig. 4c. The resulting


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map reveals the most probable crystal orientation for every experimental diffraction pattern. The highest value of the index corresponds to the appropriate crystal orientation and phase [3,4].

This brief introduction to the automated crystal phase and orientation mapping technique is complemented by a presentation of some results of our study on nanocrystalline iron oxides. Thousands of electron diffraction patterns have been recorded and analyzed automatically in order to generate the crystal orientation and phase maps of the ensembles of iron-oxide nanocrystals in Figs. 5 to 8.

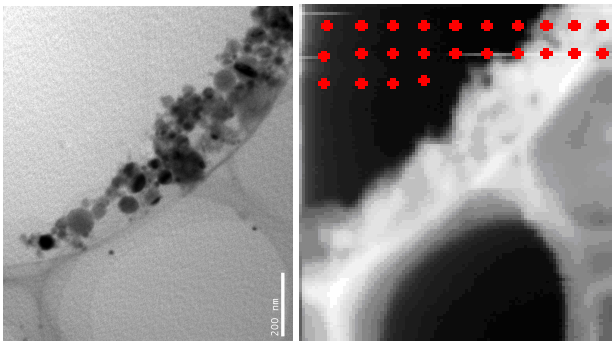

**Figure 5:** Iron oxide nano-crystals in a transmission electron microscope: (**left**) bright field image and (**right**) map of the fluctuations of the primary electron beam intensity in the electron diffraction patterns. A few positions of the primary electron beam at which electron diffraction patterns were automatically recorded by the external digital camera are illustrated by red dots on the left hand side.

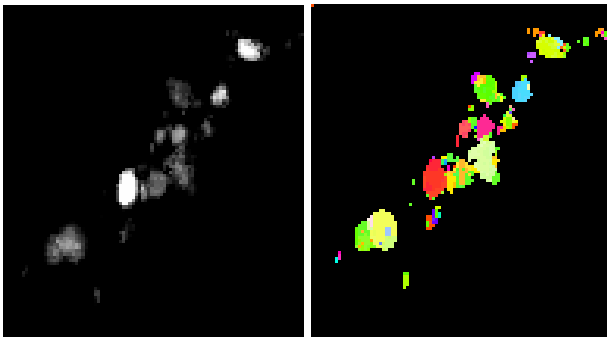

**Figure 6:** Crystal orientation mapping of iron oxide nanocrystals: correlation index (left) and orientation (right) maps, derived from ordinary (not precessing) electron diffraction spot patterns.

The spatial resolution of the crystal orientation and phase maps depends on the primary electron beam step size. In our study, this step size was approximately 30 nm while the primary electron beam had a diameter of about 20 nm.

In order to demonstrate the effect of a precessing primary electron beam on the reliability of the technique, the analysis was performed twice for the same ensemble of nanocrystals. The same scanning step sizes were used first with an electron beam that was not precessing, Fig. 6, and then with an electron beam that was precessing at approximately 0.3º around the optical axis of the microscope, Fig. 7.

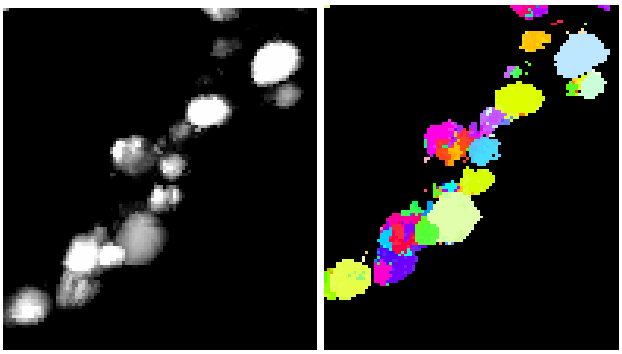

**Figure 7:** Crystal orientation mapping of iron oxide nanocrystals: correlation index (left) and orientation (right) maps, derived from precession electron diffraction spot patterns.

The comparison of figures 6 and 7 shows clearly that a precessing primary electron beam improves the correlation index and crystal orientation maps significantly. Fig. 8 (left hand side) shows the corresponding crystal phase map for magnetite. A comparison with the correlation index map (right hand side of Fig. 8) shows that the majority of the crystals are of the magnetite phase. The same conclusion was also reached from our earlier studies of HRTEM images and precession electron diffractograms of individual crystallites of this mixture [8-11].

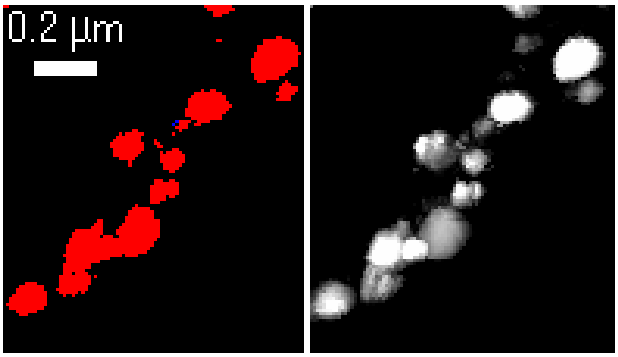


**Figure 8:** Crystal orientation mapping of iron oxide nanocrystals: phase map for magnetite (left) and correlation index (right) map of the whole ensemble of nanocrystals, derived from precession electron diffraction spot patterns.

Automated crystal phase and orientation mapping in a TEM complements both HRTEM image-based structural fingerprinting [9-11] and structural electron crystallography [14]. The crystal orientation maps can be used for the selection of individual nanocrystals that are oriented close to major zone axes for further crystallographic analyses.

## SUMMARY AND CONCLUSIONS

An automated crystal phase and orientation mapping technique enables fast and reliable analyses of ensembles of nanocrystals. Since it is well known that the precession of the primary electron beam increases the number of diffraction spots in electron diffraction patterns while dynamical electron diffraction effects are suppressed for crystal thicknesses of less than approximately 50 nm, it is no real surprise that automated crystal phase and orientation mapping benefits from precession electron diffraction. Nevertheless, the effect needed to be demonstrated experimentally.

Our study shows also that this transmission electron microscopy based electron diffraction spot pattern technique is capable of solving problems for which there are no solutions by electron backscattering techniques of scanning electron microscopy.

## ACKNOWLEDGMENTS

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* Peter Moeck's "Laboratory for Structural Fingerprinting and Electron Crystallography" at Portland State University serves as the first demonstration site of the NanoMEGAS company in the Americas. A first generation "Spinning Star" precession electron diffraction device is interfaced there to an analytical field-emission TEM and can be demonstrated on request (to pmoeck@pdx.edu or tel.: 503 725 4227) together with the whole suite of electron crystallography software from Calidris and AnaliTEX.