High spatial resolution semi-automatic crystallite orientation and phase mapping of nanocrystals in transmission electron microscopes

P. Mocek*¹, S. Rouvimov¹, E. F. Rauch², M. Véron³, H. Häusler⁴, W. Neumann⁴, D. Bultreys⁵, Y. Maniette⁵, and S. Nicolopoulos⁵

¹ Nano-Crystallography Group, Department of Physics, Portland State University, Portland, OR 97207-0751, U.S.A. and Oregon Nanoscience and Microtechnologies Institute, U.S.A.
² SIMAP/GPM2 Laboratory, CNRS-Grenoble INP, 101 rue de la Physique BP 46, 38402 Saint Martin d'Hères, France
³ SIMAP (Science et Ingénierie des Matériaux et Procédés) Laboratory, CNRS-Grenoble INP, 1130 rue de la Piscine, BP 75, 38402 Saint Martin d'Hères, France
⁴ Institute of Physics, Humboldt University of Berlin, Newtonstraße 15, 12489 Berlin, Germany
⁵ NanoMEGAS SPRL, Boulevard Edmond Machterns No 79, Saint Jean Molenbeek, Brussels 1080, Belgium

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A semi-automatic technique for the mapping of nanocrystal phases and orientations in a transmission electron microscope (TEM) is described. It is based primarily on the projected reciprocal lattice geometry, but also utilizes the intensity of reflections that are extracted from precession-enhanced electron diffraction spot patterns of polycrystalline materials and multi-material composites. At the core of the method, experimental (precession-enhanced) electron diffraction spot patterns are cross correlated with pre-calculated templates for a set of model structures. The required hardware facilitates a scanning-precession movement of the primary electron beam on the polycrystalline and/or multi-material sample and can be interfaced to any newer or older mid-voltage TEM. The software that goes with this hardware is so flexible in its intake of experimental data that it can also create crystallite orientation and phase maps of nanocrystals from the amplitude part of Fourier transforms of high resolution TEM images. Experimentally obtained crystallite orientation and phase maps are shown for a clausthalite nanocrystal powder sample, polycrystalline aluminum and copper films, fine-grained palladium films, as well as MnAs crystallites that are partly embedded in a GaAs wafer. Comprehensive open-access and commercial crystallographic databases that may provide reference data in support of the nanocrystal phase identification process of the software are briefly mentioned.

1 Introduction

The development of novel materials for micro- and nano-electronics requires reliable characterization of crystallite phases, sizes, shapes, and mutual orientations in thin polycrystalline films, composite microelectronics structures, and powder ensembles of nanocrystals. The electron backscattered diffraction (EBSD) technique (that is also known as orientation imaging microscopy) in a scanning electron microscope (SEM) [1] is often employed for structural characterization of these kinds of materials. EBSD in an SEM is based on back-scattered Kikuchi lines [2]. It is, therefore, sensitive to the plastic deformation state of the crystallites as well as to structural damages and/or contaminations of the crystal surfaces.

The spatial resolution of that technique ranges from 20 to 80 nm in dependence of the atomic numbers and levels of a sample’s internal strains [1-3]. There is also a claim that the spatial resolution of the above discussed technique is inherently better than 10 nm [3], but those authors felt compelled to add that obtaining such resolutions is “... thwart with difficulties in the SEM because of specimen drift, contamination and poor pattern resolution”. Obtaining such spatial resolutions on a routine basis has, therefore, to wait for further
instrumental improvements of SEMs. EBSD in SEM was recently used to determine the lattice constants of a crystal [4]. This opens up the way of using this technique for structural fingerprinting of unknowns on the basis of comprehensive crystallographic databases. Such developments are very timely because there is now a widespread realization that many nanocrystals cannot be fingerprinted structurally from their powder X-ray diffraction patterns [5].

There are also ongoing efforts to develop orientation imaging microscopy in a transmission electron microscope (TEM) [3,6,7]. A technique that works on the basis of approximately 65,000 reconstructed electron diffraction spot patterns per mapped sample area has been developed during the last 15 years. These patterns are reconstructed by software from some 5,000 automatically collected conical dark field images. Only the projected geometry of the reconstructed diffraction patterns is utilized. The technique is marketed as “Automated Crystallography for the TEM” (ACT) by the company TSL-EDAX. Further improvements of this technique that include utilizing the intensity of the reconstructed diffraction spots in the two-beam dynamical diffraction limit and a Blackman correction have recently been proposed [7].

In the fall of 2008, an alternative system for crystallite orientation and phase mapping that works on the basis of precession-enhanced electron diffraction spot patterns has been demonstrated for the first time. Heavily deformed Cu foils with grain sizes on the order of 20 nm, mineralogical Ca₁₂Al₁₄O₃₃, and stainless steels were used as examples [8]. Since then crystallite orientation and phase maps have also been recorded from synthetic Fe₃O₄γ-Fe₂O₃ powder mixtures, WC/Co composites, and Si/Cu microelectronics device structures [9-11]. There are also soon to be published results by other customers of NanoMEGAS on carbides and nitrides in stainless steel, Si/SiC composites, thin films and nanoscale powders of Pt, heavily deformed Al and Cu, Al/Cu alloys, Pa/Au alloys, Ti/Nb-alloys, and Zr alloys.

The new technique is based on template matching of experimentally obtained (precession-enhanced) electron diffraction spot patterns to their pre-calculated theoretical counterparts. Such template matching has been utilized before for the crystallographic characterization of heavily deformed low carbon steels and shown to be a robust procedure [12-14]. The utilization of the precession electron diffraction (PED) mode [15,16] proved beneficial to the success of the technique on the above mentioned samples [8-11]. In particular, the PED mode typically results in higher template correlation and matching reliability indices. Combinations of both indices with the orientation resolution of the pre-calculated templates and the utilized precession angle may be considered as representing measures of the “accuracy” and “precision” of the mapping process.

The advantages of a precessing primary electron beam for structural electron crystallography in both the diffraction and imaging modes of transmission electron microscopy were already realized in the mid 1970s [17]. Many TEMs do allow for an “electronic” hollow cone illumination with small semi-cone angles [18], but not for a “proper descanning” below the sample that results for a single crystallite in a stationary electron diffraction spot pattern. This “un-precessing” of diffracted rings and arcs that result from the hollow cone illumination into stationary spots is one of the hallmarks of the commercially available precession electron diffraction add-ons to (older and newer) mid-voltage TEMs from NanoMEGAS.

There has also been a “double-rocking” technique [19] for the imaging of zone axis patterns in both the direct and reciprocal spaces. This technique uses a similar “do” (above the specimen) and “undo” (below the specimen) scheme. Rather than a precessing primary beam that produces a hollow illumination cone with apex on the sample, a double rocking movement of the incident beam produces a “(full) square pyramid” with apex on the sample. Below the sample, this kind of sequential off-axis illumination is “doubly un-rocked” so that stationary bright/dark field images or diffraction patterns result.

Brussels/Belgium based NanoMEGAS offers a semi-automatic (i.e. partly on line, partly off line) turn-key solution to PED enhanced crystallite phase and orientation mapping. Their (analog) first generation of PED instrumentation and its operation are described in more detail in ref. [16]. The prospective automated on-line processing of automatically recorded electron diffraction spot data will eventually make their system fully automatic. (Note that NanoMEGAS’s PED system is already available in its second (digital) generation.) The current lack of automation of the data processing step of the method is not to be misunderstood as a serious limitation. It constitutes, in effect, opportunities in many other respects!

While it is true that EBSD/SEM allows for fast and fully automatic crystallite orientation and phase mapping (after decades of development), the analytical capabilities of TEMs are far superior to those of SEMs. As the new method is performed in a TEM, the automatically collected data, i.e. thousands of precession-enhanced electron diffraction spot patterns with a spatial resolution on the order of nanometers to tens of nanometers from square-micrometer to tens of square-micrometer sized regions of a crystalline sample, may be utilized in combination with many other pieces of information that are obtainable in this kind of instrument.
There are also significant economic benefits to the off-line processing of experimental data from a TEM. That TEM can simply be used by others while one of the users processes the automatically recorded diffraction data off line.

This paper describes NanoMEGAS’ digital semi-automatic crystallite orientation and phase mapping system briefly and illustrates the application of the technique on a selection of suitable examples. These experimental examples were chosen primarily in order to illustrate different functionalities of the software of the new crystallite orientation and phase mapping system. The corresponding crystallite phase and orientation, virtual bright and dark field, correlation and reliability index maps are, therefore, not always of the highest obtainable quality since typical data collection and processing artifacts have frequently not been removed. Since the paper concentrates on methodical and technical aspects of the new crystallite orientation and phase mapping technique, we will provide only a minimal amount of materials science background on the samples.

The software that goes with this hardware can also be used for the creation of nanocrystal orientation and phase maps from sections of high resolution TEM (HRTEM) images. This will be demonstrated for a powder of clausthalite nanocrystals that was imaged in an objective-lens aberration-corrected TEM.

### 2 The new crystallite orientation and phase mapping system and method

The new technique produces crystallite orientation and phase map also for plastically deformed polycrystalline materials (which do not produce back-scattered Kikuchi lines of a sufficient quality in an SEM). Also there are no “special crystal surface” preparation steps necessary for the application of this technique. The often required crystal surface preparation methods for EBSD/SEM are simply replaced by standard TEM preparation techniques in order to obtain sufficiently thin and electron transparent crystallites. The new system should therefore, allow for the solving of materials science problems for which there are no solutions by EBSD/SEM.

![Experimental set up of the ASTAR/DigiSTAR system (from NanoMEGAS) for high-resolution crystallite orientation and phase mapping, modified after [8]. The system consists of hard- and software. The hardware can be interfaced to any older or newer mid-voltage TEM. (No preexisting scanning facility or scanning probe microscopy mode is required.) The bulk of the software runs on an external PC under Windows™. This software also includes routines for the “straightening out” of diffraction spot patterns when the large viewing screen of the TEM is used in its horizontal position and the patterns are recorded under some oblique angle. Courtesy of JEOL Ltd., a typical crystallite orientation map of the distribution of copper grains in a microelectronics device structure (that was recorded at their factory in Tokyo on a JEM-2100F field-emission microscope) and its color code are shown in the bottom-right part of the sketch. The faint “smearing out” of the orientation contrast in the top part of this map is an unimportant artifact. This kind of artifact can be minimized by either lowering the acquisition speed of the raw data or by using a dedicated phosphor screen that is optimized for the high-speed recording camera. (Such a phosphor screen would need to have a very short relaxation/“after-glow decay” time response.) Correlation and/or reliability index thresholding during the data processing removes this and other artifacts. (Online color at www.crt-journal.org)](image-url)
The orientation and phase determination is performed by the matching of each experimental diffraction pattern to a large number of templates, which are computer calculated diffraction spot patterns for all possible orientations within the symmetry-invariant section of the stereographic projection of the corresponding crystal phase. A desired 1° angular resolution of a crystallite orientation map requires for a highly symmetric cubic crystal phase (such as aluminum, copper, and palladium) fewer than 1,100 templates (Fig. 3).

Figure 4 illustrates the matching procedure schematically. A typical rate for the matching of electron diffraction spot patterns of highly symmetric cubic crystallites is approximately 100 patterns per second. The degree of matching between the experimental electron diffraction spot patterns (Fig. 4a) and the pre-calculated templates (Fig. 4b) is given by a correlation index.
The correlation index is defined by the relation
\[ Q_m \sim \sum_{i=1}^{n} P(x_i, y_i) \cdot T_m(x_i, y_i), \]
where \( P(x, y) \) stands for the intensity distribution of a single diffraction spot pattern that is composed of \( i \) pixels (in the \( x-y \) plane) and \( T_m(x, y) \) stands for the \( m \)-th of the \( n \) pre-calculated templates. The correlation indices, thus, reflect the degree of matching between a particular electron diffraction spot pattern and all of the pre-calculated templates. Better overall matchings are simply represented by higher correlation indices. This simple definition of the correlation index has been utilized for a range of successful studies of different kinds of samples [8-14]. It may, however, be modified in the future as the mapping technique is developed further. Different kinds of normalizations may be straightforwardly implemented on the basis of this proportionality relation.

The correlation index is calculated at each crystallite orientation increment (e.g. Fig. 3a) for every crystal phase that needs to be tested in order to achieve certain materials science and/or engineering objectives of the investigation of a given sample. The obtained set(s) of correlation indices may be plotted into the symmetry-invariant part(s) of the stereographic projection of the corresponding crystal phase(s). In figure 4c, such a part of the stereographic projection is shown for crystallites that belong to the three lower symmetric cubic point groups. The resulting plot of \( Q_m \) reveals by its maximum (\( Q_{\text{max}} \)) the most probable crystallite orientation (for the selected crystal phase) for an experimental electron diffraction spot pattern such as shown in figure 4a. Darker areas in a plot of the correlation index versus crystallite orientation increments (Fig. 4c) represent higher correlation indices.

The experimental parameters of the electron diffraction spot pattern acquisition process are typically set so that correlation index maxima on the order of several hundreds are obtained. For the obtaining of high correlation indices, it is important that diffraction spots with Bragg angles of up to about 1.5 to 2 degrees are collected.

The calculation of the templates is currently based on the kinematical diffraction theory and also neglects individual crystallite size and shape effects. Modeling the whole polycrystalline sample in the software as a thin plane-parallel film, all (kinematically allowed) reciprocal lattice nodes are extended into Laue/Ewald reciprocal lattice spikes (that some textbooks refer to somewhat loosely as “relrods”).

These spikes are considered to be centrosymmetric and shaped “like cigars”. Although side maxima of the spikes are ignored, they approximate the effect of the shape transform of a thin film (that is transmitted in the direction of its thickness) sufficiently well. The spike’s most important parameter with respect to producing a finite section of an infinite 2D translation net by accounting for the curvature of the Ewald sphere is their total length, which is inversely proportional to the film’s thickness. The long (rotation-symmetric) axis of the spikes is oriented parallel to the normal of the film. The spikes are fixed with their center at the positions of the exact reciprocal lattice nodes. All spikes have the same size and shape. The integrated intensity of a particular reflection is distributed evenly over the whole volume of the corresponding spike. For the purpose of the cross correlation index calculation, the intensity of a reflection in a template is currently approximated by the relation
\[ I_i = I_{\text{max}} \cdot (1 - s / s_{\text{max}}), \]
where \( I_{\text{max}} \) is the reflection’s integrated intensity as obtained from a kinematical calculation, \( I_i \) its “local” intensity at the (reciprocal space) position \( s \) of the intersection of the Ewald sphere with the corresponding spike, and \( s_{\text{max}} \) is one half of the total length of the spike. The total length of the spike is currently adjustable as a free parameter of the template generation software. This parameter needs to be adjusted by the user so that high maxima of the correlation index are obtained on the basis of either prior knowledge about some calibration sample or presumably correctly identified crystallite orientations and phases of the sample under investigation. Both reciprocal lengths \( s \) and \( s_{\text{max}} \) are measured along the rotation-symmetric axis of the corresponding spike from the position of the center of the given reciprocal lattice node. (For \( s \geq s_{\text{max}} \), the respective spike has lost contact with the Ewald sphere and the local intensity of the corresponding reflection is set to zero.) For all reflections in all templates, the circular areas that the reflections occupy are set proportional to their local intensity.

Although dynamical electron diffraction effects and the PED geometry are not taken into account in the calculation of the templates, the above mentioned approximations proved sufficient for a range of experimental studies [8-14]. Similarly, the individual crystallite shapes and sizes (that result in certain distributions of electrons in the reflections) have been ignored so far without rendering the technique impractical. Better
approximations for the calculation of the reflection intensities in the templates may, however, be utilized as the technique is developed further. The Lorentz factor of the PED geometry [20] tends to enhance the intensity of reflections in the vicinity of the primary electron beam and may also be taken into account in the future.

Since the geometry of the reflections in the templates is to a good approximation equivalent to the geometry of experimental electron diffraction spot patterns, the success of the cross-correlation indexing procedure relies primarily on the identification of the correct projected reciprocal lattice geometry. As the intensities of the reflections in the templates may match to some lesser degree also the intensities in experimental electron diffraction spot patterns, the success of the cross-correlation identification may also rely somewhat on the reflections’ intensities.

The success of the new technique on a variety of samples [8-14] demonstrates that reasonably accurate crystallite orientation and phase mappings are possible under highly idealized assumptions that concern the underlying electron diffraction processes. These assumptions do, however, require not much more prior knowledge about a sample than what is readily available in comprehensive crystallographic databases. Such databases will, therefore, be briefly mentioned in the final section of this paper. An (crystallite orientation) reliability index is calculated for each \( Q_{\text{max}} \) by the relation

\[
R = 100 \cdot (1 - \frac{Q_{2\text{nd} \_ \text{highest \_ peak}}}{Q_{\text{max}}}),
\]

so that high reliabilities are obtained for “rather flat” \( Q_{m} \) plots. Such a flat \( Q_{m} \) plot is shown in figure 4c. Since this plot has no strong second highest peak, the possibility of a mis-identification of the crystallite’s orientation and/or phase from its electron diffraction spot pattern \( P(x,y) \) (Fig. 4a) is very low. Note that reliability indices in the two digit range signify high reliabilities per definition. A reliability index in the lower one digit range, on the other hand, indicates an ambiguous indexing. For the mapping of two crystallite phases, a “phase reliability index”

\[
R_{\text{phase}} = 100 \cdot (1 - \frac{Q_{\text{max} \_ 2\text{nd} \_ \text{phase}}}{Q_{\text{max} \_ 1\text{st} \_ \text{phase}}}),
\]

needs to be utilized. When there are more than two phases to be considered, a modified phase reliability index is used. Whenever the primary electron beam transmits two crystallites at once, e.g. adjacent grains that are separated by a grain or phase boundary, all of the corresponding reliability indices will be low. Maps of these indices will, therefore, ideally possess the useful feature that grain and phase boundaries will be outlined by (what is in an image processing context know as) “tonal undershoot (dark halos)” around the corresponding crystallites.

To produce typical crystallite orientation (see, e.g., the bottom-right part of figure 1) and phase maps, 50,000 to 250,000 experimental diffraction spot patterns are collected with an external digital camera that is placed outside of the microscope in front of the TEM viewing screen (Figs. 1 and 2c). The diffraction spot patterns are then stored in a dedicated file format. The acquisition frequency is synchronized with the primary electron beam scanning and precession movements at typically 100 Hz so that less than 15 minutes to half an hour is sufficient to acquire the required structural information from the sample for the subsequent mapping procedures. The primary electron beam scanning and precessing movements are both controlled by the dedicated precession hardware (add-on to the TEM) that is connected to the microscope’s sets of deflecting coils and controlled by a dedicated remote computer. Since the scanning movement of the primary electron beam is entirely controlled by this hard/software add-on, the microscopy itself does not need to possess a scanning facility or a scanning probe mode†.

The data analysis, as currently performed off-line, consists of compensating for all kinds of distortions of the experimental electron diffraction spot patterns, detecting of the location of the transmitted electron beam, and identifying of crystallite orientations and phases through the template matching procedure as described above. The distortions are assessed on the basis of known reference electron diffraction spot patterns for certain sets of experimental conditions and are caused by various influences such as systematic distortion effects of the projector lens, the inclination of the external optical camera with respect to the viewing screen, and the uncertainty in the knowledge of the exact camera length of the TEM.

For highly symmetric small unit cell crystals, e.g. face- and body centered cubic (FCC and BCC) metals, 100 to 200 patterns may be analyzed per second. The spatial resolution limit of the mapping technique depends on both the obtainable minimal spot size of the primary electron beam in the microscope and the freely adjustable scanning step size. The minimal spot size depends on both the type of the electron gun used and the

† If a scanning probe facility or mode does exist on the TEM to be interfaced to a second generation (fully digital) ASTAR/DigiSTAR system or a first generation (semi-analog) ASTAR/Spinning Star system, it will not be utilized during the recording of the experimental data and also does not interfere with this process.
size of the aperture utilized in the second (or if present third) condenser lens. In a TEM with a field emission electron source and a sufficiently small aperture, the minimal spot size can be on the order of 1 to 10 nm. When nearly parallel illumination conditions can be somewhat relaxed to allow for a small primary beam convergence, e.g. for the mapping of FCC and BCC metals, the minimal spot size might even be in the sub-nanometer range. The scanning step size, on the other hand, is adjustable down to the order of magnitude of the smallest obtainable spot size and can also be smaller than a nanometer.

Ideally, a nearly parallel illumination setting should be used as one wants to avoid the expansion of the diffraction spots into disk that would result from a significant convergence of the primary electron beam. The electron transparent area of the sample may set a limit to the size of the maps that can be obtained by the technique. Also the specifics of the materials science and/or engineering problem that one needs to address may impose a certain size requirement on the recorded maps.

While we usually map sample areas of less than 5 μm times 5 μm into 500 by 500 pixels, we have also collected data for maps of up to 15 μm times 15 μm. This required comparatively large step size of 50 nm for materials science problem adequate maps of 300 by 300 pixels.

The crystallite orientation resolution of the method depends on the angular resolution increment of the pre-calculated templates and the precession angle. Typically this resolution is one degree or a few tenths of a degree. The precession angle needs to be chosen judiciously in order to suppress typical thin TEM film specimen “buckling” effects that may stem for the necessity of preparing an electron transparent film. At the same time, higher precession angles imply lower obtainable crystallite orientation resolutions.

Experience so far has shown [8-11] that precession angles of a few tenths of a degree are often sufficient to increase the accuracy of the method significantly while also removing thin TEM film specimen buckling artifacts. Precession angles of up to one degree (or even somewhat larger if additional reflections from higher order Laue zones are to be utilized) may only be beneficial for the mapping of simple inorganic materials with very small unit cell volumes.

PED of individual crystallites results in spot patterns with more reflections with partially or fully integrated intensities. If the crystallites are not too thick and the precession angle is sufficiently large, the intensities of PED spots may also be “less dynamical” [15,16] because “few beam” conditions [21] may have prevailed during the precession diffraction experiments. This may result in quite effective suppressions of dynamical diffraction effects. Few beam conditions may be approximated to two beam conditions and it is well known that the kinematical diffraction theory is a small crystallite thickness, small electron wavelength, and small structure factor modulus approximation to the two-beam dynamical diffraction theory when the unit cell volumes are large [9,22,23]. For sufficiently thin crystals, PED spot intensities may, therefore, be used for advanced structural fingerprinting in the transmission electron microscope in addition to the projected reciprocal lattice geometry and symmetry of individual crystallites [5,9,22,23]. Since the new crystallite orientation and phase mapping technique uses currently templates that are pre-calculated on the basis of the kinematic diffraction theory, it is well suited to work with experimental PED data from sufficiently thin crystallites.

For the same electron wavelength, PED brings a larger section of the Ewald sphere in contact with a crystal’s reciprocal lattice than the conventional selected area electron diffraction technique. This is advantageous for dealing with the so called “180° ambiguity” in the indexing of electron diffracting spot patterns. That ambiguity arises from the fact that a particular diffraction spot in the zero order Laue zone may be indexed as either \((hkl)\) or \((\bar{h}\bar{k}\bar{l})\) [24]. While one will obtain the same zone axis indices for both sets of indexed reciprocal lattice vectors, an ambiguity will exist as to the azimuthal orientation of the crystal around the zone axis. Two azimuthal orientations that differ by 180° will be equally likely. For non-centrosymmetric cubic crystals, one may reformulate this ambiguity as being one between indexing non-symmetry equivalent zone axes as either \([uvw]\) or \([\bar{u}\bar{v}\bar{w}]\).

Although the 180° ambiguity is irrelevant for many applications, it becomes important for the unambiguous determination of grain and phase boundary parameters. Methods to tackle this ambiguity are discussed in ref. [25]. We will discuss the origin and details of this ambiguity elsewhere and also give more information there on how we deal with it at present. Here we just mention that we have experimental evidence for the fact that the cross correlation indexing of reflections from higher order Laue zones, as present in many precession-enhanced electron diffraction spot patterns, is one feasible way of dealing with the 180° ambiguity.

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1 More reflections are observed experimentally in the PED mode even when the morphologies of the crystallites are highly anisotropic such as in the case of nano-wires.
With purpose written software, the second (digital) generation precession device (DigiSTAR) of NanoMEGAS could possibly be run in a manner that emulates either the “double-rocking” technique [19] or alternative “tilted but nearly-parallel illumination” schemes that avoid some of the shortcomings of classical precession electron diffraction, e.g. the unavoidable simultaneous excitation of systematic rows and the need to go twice through the Bragg condition during one precession cycle for each reflection. If the templates in the cross-correlation procedure were to take the Lorentz factors of such tilted but nearly-parallel illumination techniques into account, high cross correlation and reliability indices may result.

This brief introduction to the semi-automatic crystallite phase and orientation mapping technique is complemented below by a presentation of some recent experimental results. The data for the corresponding studies were recorded at three different microscopes, each of which equipped with PED instrumentation by NanoMEGAS, see figures 2a,b and 2c for two of these TEMs. We show below results of our mappings of undeformed (Figs. 5 and 6) and tensile stress deformed aluminum (Fig. 7), fine-grained palladium (Fig. 8), polycrystalline copper (Figs. 9 and 10), and MnAs crystallites in a GaAs wafer (Figs. 11 to 13).

**3 Experimental examples**

The data for the crystallite orientation maps in figures 5 to 7b,c were collected at the Free University of Brussels with a Philips CM20 TEM that was operated at 200 kV. This microscope features a LaB₆ electron gun and an interfaced PED device ASTAR/DigiSTAR from NanoMEGAS. Polycrystalline aluminum before (Figs. 5 and 6) and after (Fig. 7) tensile stress deformation experiments served as samples.

In order to demonstrate the effect of the PED mode on the accuracy of the technique, the analysis was performed twice for the same ensemble of nanocrystals (Figs. 5 and 6). While the data of figure 5 were recorded with a non-precessing primary electron beam, their counterpart data in figure 6 were recorded with a precession angle of 0.9°. The step size was in each case 10 nm. The diameter of the primary electron beam was
orientations of certain structures may be corrected by some kind of a “structure dependent” normalization. This processing step has been omitted on purpose in order to clarify its importance in removing artifacts. The “essentially black” areas (around the figure labels in the bottom-right corners) of the correlation index maps (Figs. 5b and 6b) possess a correlation index of essentially zero. This means that these areas represent the edge of the sample to the vacuum within the microscope. There is again a faint and rather unimportant “smearing out” artifact in both of these maps for the reasons discussed in the caption of figure 1. However, enforcing a suitable correlation index threshold on the crystallite orientation and reliability maps (Figs. 5a, 6a, 5c, and 6c) would, reveal the sample edge to the vacuum (in the bottom-right corners of these maps) as well.

Comparing the first three panels of figures 5 and 6 with each other, one can see that the crystallite orientation map which is based on PED data is much “clearer”, that the corresponding correlation index map is “much brighter”, and that the corresponding reliability index map is both “brighter and clearer”. “Clearness” in the crystallite orientation and reliability index maps corresponds to pixel value homogeneity throughout some neighboring areas. Higher brightness in both the correlation index and reliability index maps means simply that the numerical values of the indices are higher on average.

In the sense discussed in the introduction of this paper, it is clear that the crystallite orientation map on the basis of PED data represents “more accurately” the true orientation distribution in the sample. Note that some crystallites show a rather significantly different color in the crystallite orientation maps of figures 5a and 6a. One such crystallite with an orientation difference between the two crystallite orientation maps of roughly 20° is marked in both maps by the tip of an arrow. One may, thus, say that a part of the crystallite orientation map for the zero precession angle (Fig. 5a) is in error. The PED-data based reliability index map of Fig. 6c shows that precession results in a significant increase of the reliability index throughout the area of this particular crystallite so that the “interior” of the crystallite and the surrounding grain boundaries are both clearly revealed. This is not the case for this particular crystallite in the reliability index map for zero precession angle (Fig. 5c) so that the advantage of the PED mode for crystallite orientation mapping has been clearly illustrated.

Simulations by other authors for zero precession angle data have shown that the immediate orientation environment of certain low indexed zone axis patterns, e.g. [112] and [013] in FCC metals (such as aluminum), are particularly difficult to index by cross-correlation techniques, see ref. [26] for more details. While [112] roughly corresponds to the color of the crystallite that is marked by the tip of the arrow in figure 6a, [013] corresponds roughly to a bright shade of the color yellow. At some later stage of the development of the cross correlation software, such predictable difficulties in obtaining high correlation indices for certain crystallite orientations of certain structures may be corrected by some kind of a “structure dependent” normalization.

For now it is probably more than sheer coincidence that the application of the PED mode reveals an approximately [112] oriented grain in a crystallite orientation map of a FCC metal clearly, see tip of the arrow in figure 6a, while it seems to have been mis-indexed on the basis on data that were recorded with a (scanning) parallel-to-optical-axis primary beam, see corresponding area in figure 5a. Also the color of the very small crystallite underneath the “m” of the “μm” annotation in figure 5a changed from bright yellow for the scanning parallel-to-optical-axis primary beam data to light blue in figure 6a for the PED data. The corresponding area also appears rather dark in the reliability index map (Fig. 5c) in agreement with the above mentioned simulations [26], while it is rather bright in the counterpart map that is based on PED data (Fig. 6c).

The comparison of the two electron diffraction spot patterns in the last panel of figures 5 and 6 from the crystallite underneath the scale bar in figures 5a and 6a (where the arrows start) illustrates not only the main advantage of the PED mode, i.e. more reflections, but also reveals evidence for the suppression of multiple electron diffraction effects. Such effects resulted for this particular crystallite in the formation of Kikuchi lines in the zero precession angle pattern of figure 5d.

Figure 7a shows the negative of a conventional bright field TEM image of a tensile stressed aluminum sample. The data for the crystallite orientation mapping of this sample were recorded with a precession angle of 0.9° (Fig. 7b). The step size for the recording of this map was 10 nm. The diameter of the primary electron beam was approximately 8 nm. Note that a larger sample area than visible on the conventional TEM negative was scanned-precessed for this purpose. Also shown is the superposition of this crystallite orientation map with the corresponding reliability index map (Fig. 7c). Some of the grains that are oriented close to [112] possess again a low reliability index as marked by arrows in figure 7c. Other grains close to this orientation do, however, possess low reliability indices only at their clearly visibly grain boundaries, i.e. do not appear dark in their interiors in figure 7c. It might, therefore, be the case that some of the “dark grains” in figure 7c are due to superpositions of more than one grain in the direction of the transmitted electron beam. The hole in the sample...
appears in a green color in figure 7b due to the above (in the caption of figure 1) mentioned slight smearing out effect of a fast data acquisition process. Figure 7c clarifies that the orientation reliability within that particular sample area is very low. That area may be removed from the crystallite orientation map by a suitable reliability index thresholding.

At the JEOL JEM 2200FS of Humboldt University Berlin that possesses both a field-emission gun and an in-column Ω energy filter, the data for the maps of figure 8 were collected at 200 kV within three minutes from a fine-grained palladium sample. A PED device ASTAR/DigiSTAR from NanoMEGAS is interfaced to this microscope and it serves as demo site for this company for middle Europe. While the scanning-precessing step size of the primary electron beam was for these experiments set to 0.4 nm, the full widths at half maximum of the primary electron beam was approximately 0.5 nm. Such a small-size nearly parallel primary electron beam is possible in this microscope due to its field emission source and a 10 μm diameter aperture in the condenser.

For the applied mapping technique, one may infer a maximal spatial resolution of approximately 1 nm from the “crystallite mis-orientation versus line scan direction” plot in figure 8d. This inference is based of the very faint visibility of a “partially enclosed” crystallite (of roughly that width) within a clearly visible (about 6 nm wide) crystallite that appears blue in the crystallite orientation map (Fig. 8a) and is marked there by a thin straight bar.
crystallite orientation map, one would probably need a sampling at twice or thrice as many scanning-precession increments. A maximal spatial resolution of 1 nm, thus, may correspond to a “more readily discernable” spatial resolution of 2 to 3 nm.

Two crystallites in twin orientation in a FCC metal share a {111} plane and are mis-oriented with respect to each other by a rotation of 180° around the normal of the twin plane. This normal is a <111> zone axis with point symmetry 3m. Symmetry equivalent directions within a {111} plane possess, therefore, a multiplicity of 6, with mis-orientations of 60° (and multiples of 60°) around the corresponding zone axis directions.

One may, for example, consider a specific twin plane in a FCC metal, e.g. (111), viewed edge on. If one crystallite is oriented with its [112] direction parallel to the optical axis of the TEM, its twin will be oriented with its [211] direction with respect to this axis. The orientations [121], [211], [121], and [211] are all symmetry equivalent to these two orientations and also lie in the (111) plane so that the cross correlation software cannot distinguish between them.

If the (111) twin plane is not viewed edge on, the multiplicity of crystallite orientations with respect to the twin plane is 12. This would result in “four sets” of symmetry equivalent crystallite orientations which are mis-oriented with respect to each other by 120° (and multiples of 120°) around the [111] zone axis.

When these basic crystallographic facts are combined with the 180° indexing ambiguity, mis-orientations of 60° (i.e. the difference between 180° and 120°) are likely to be observed for inclined (111) twin planes as well. In conclusions, mis-orientations of approximately 60° between two FCC crystallites that share a more or less straight grain boundary are often associated with twinning, but there can certainly be other grain boundaries with this characteristic that are not twin boundaries.

Thin polycrystalline copper films were analyzed at the FEI Tecnai G² F20 ST analytical field-emission microscope of Portland State University. This microscope is also equipped with an ASTAR/DigiSTAR system of NanoMEGAS and serves as demonstration site for this company for the USA. Due to its field emission source, nanometer sized primary electron beams with small convergence angles can be utilized in this microscope (with a 10 μm diameter aperture in the second condenser lens) in conjunction with suitably small step sizes.

While the step size was set to 150 nm in the analyses of the polycrystalline copper films in order to cover wide sample areas, a primary electron beam with a diameter of approximately 20 nm was used. A low precession angle of 0.15° was used for the analyses, although the unit cell volume of copper is smaller than that of aluminum and palladium. The virtual bright field (Fig. 9a), crystallite orientation (Fig. 9b), correlation index (Fig. 9c), reliability index (Fig. 9d), and virtual dark field maps in the bottom row of figure 10 may, therefore, contain some thin film buckling artifacts. The crystallite orientation map (Fig. 9b) shows nevertheless sufficient pixel value homogeneity throughout many of the crystallites.

Virtual dark field images of individual crystallites or crystallite areas are obtained with the ASTAR software by a simple (computer) prompt after a suitable “virtual aperture” has been set around a particular reflection spot in one of the automatically recorded electron diffraction patterns from that crystallite. The corresponding dark field map then shows the crystallite or crystallite areas with bright contrast together with all of the various sample areas that contribute to the diffracted intensity within the virtual aperture.

The experimental electron diffraction spot patterns that form the basis for the crystallite mapping process can simply be displayed by clicking with the mouse on a crystallite in either the virtual bright field map or the crystallite orientation map. In the top row of figure 10, four such electron diffraction patterns are shown.

Due to the comparatively small precession angle, resemblances of “dynamical diffraction contrast” should be present in the virtual bright field map (Fig. 9a) and the virtual dark field maps, bottom row of figure 10. This is indeed the case as marked by arrows in figure 9a and the virtual dark field image in the first column of the bottom row of figure 10. While thickness fringes (of classical diffraction contrast) are a sequence of bright and dark stripes at the edge of a crystallite in the virtual bright field image of the marked crystallite, the contrast is reversed in the corresponding virtual dark field image. This kind of quasi-classical diffraction contrast at low precession angles will have its usage in more thorough off-line analyses of polycrystalline materials. Large precession angles, on the other hand, tend to average such contrasts out.

As a “rule of thumb”, crystallites that appear dark in a virtual bright field map are for sufficiently thin samples often associated with electron diffraction spot patterns that possess many reflections. These crystallites in turn tend to possess high correlation indices and appear, therefore, bright in a correlation index map. For an illustration of these relationships, compare individual crystallites and their contrast in figures 9a and 9c, their experimental electron diffraction spot patterns, and their contrast in the virtual dark field maps of figure 10.
More precisely, the intensity in virtual bright field maps depends on the local sample thickness as well as on both the number and type of reflections. Each type of reflections possesses a certain extinction distance and it will be the combined effect of all reflection intensities that have been removed by the “software equivalent” of an aperture (i.e. a virtual aperture) around the primary electron beam that determines the brightness in a virtual bright field map.

![Image of crystallite orientation mapping](image_url)

**Fig. 9** Crystallite orientation mapping of polycrystalline copper, 0.15° precession angle. (a) Virtual bright field map, (b) crystallite orientation map, (c) correlation index map, and (d) reliability index map from the same sample area. The color code of (b) is the same as in Figs. 1 and 7b. Note that the “microscope’s vacuum area” is clearly visible at the top of both the virtual bright field and the correlation index maps and was set to appear “light orange” in the crystallite orientation map. The numbers in round brackets in (a) and (b) identify individual crystallites that are correspondingly labeled in the virtual dark field maps in the bottom row of Fig. 10 below. Note that the microscope’s vacuum area appears in “dark gray” in the virtual bright field map (a), although it would possess the highest brightness in a real (parallel illumination) bright field image. This is a rather unimportant processing artefact that can be straightforwardly removed by the software. (Online color at www.crt-journal.org)

![Image of crystallite orientation mapping](image_url)

**Fig. 10** Crystallite orientation mapping of polycrystalline copper, continuation from figure 9. Top row: Experimental diffraction spot patterns of selected crystallites (that appear brightest and largest in the bottom row). The positions of a 5 pixel diameter aperture that was imposed as mask on the diffraction spot patterns in order to create the dark field images (in the bottom row) are indicated by circles. Bottom row: Corresponding virtual dark field maps. The numbers in round brackets identify individual crystallites in these maps that are correspondingly labeled in the virtual bright field map (Fig. 9a) and the crystallite orientation map (Fig. 9b) above. The horizontal stripes in some of the virtual dark field maps are artifacts that are related to the after-glow effect that was discussed in the caption of figure 1 (and can be removed by thresholding).

Self-assembled MnAs crystallites in a GaAs wafer were analyzed at the above mentioned JEOL JEM 2200FS of Humboldt University Berlin (Figs. 11 to 13). While the scanning-precessing step size of the primary electron beam was for the phase and crystallite orientation map data collection experiments set to 5 nm, the full widths at half maximum of the primary electron beam was approximately 2.4 nm. A precession angle of 0.9° was utilized. Virtual bright field, correlation index, reliability index, and MnAs crystallite / GaAs matrix phase map are shown for such a sample in figures 11 and 12. The maps in figure 11 show that essentially all of the identified MnAs crystallites possess the orthorhombic crystal phase. The small “blue area” of the MnAs
crystallite that has been marked by an arrow in figure 11d may not necessarily be convincing proof that hexagonal MnAs is actually present. The corresponding crystallite orientation maps of figure 12 were, therefore, only calculated for the two phase system orthorhombic MnAs and (cubic) GaAs.

**Fig. 11** Crystallite phase mapping of MnAs in a GaAs matrix, [001] plane view (0.9° precession angle) from the same sample area. (a) Virtual bright field, (b) correlation index, (c) phase reliability index, and (d) crystallite/matrix phase map of both orthorhombic MnAs (in green) and hexagonal MnAs (in blue) on a (red) GaAs background. Note that the outlines of phase boundaries around five larger MnAs crystallites (that are marked by numbers) are clearly visible in the phase reliability map due to the above mentioned tonal undershoot (dark halos) artifact. The arrow in (d) is explained in the text. (Online color at www.crt-journal.org)

**Fig. 12** Crystallite orientation mapping of orthorhombic MnAs in a GaAs matrix, [001] plan view (0.9° precession angle, same sample area as in figure 11). The GaAs orientations in both (a) and (b) are mutually perpendicular and belong to the (001) zone of the wafer. The red “background” color in (c) signifies the [001] orientation of the GaAs wafer. In the second row of this image, (d) represents the color code of these maps for GaAs and (e) for the orthorhombic MnAs crystallites, respectively. (Online color at www.crt-journal.org)

**Fig. 13** Ordinary TEM bright field images of self-assembled, surface contactable, partially embedded MnAs crystallites in a GaAs wafer. (a) [001] plan view and (b) [110] cross section. (Online color at www.crt-journal.org)

Figures 12a to 12c indicate that at least the “five larger” MnAs crystallites are well ordered/textured in all three spatial dimensions, i.e. in the two mutually perpendicular directions that are within the thin sample film and in the one direction that is parallel to the GaAs wafer normal (which was adjusted to be parallel to the optical axis of the microscope).

For comparison and in order to illustrate that at least some of the MnAs crystallites are only partially embedded in the GaAs wafer (Fig. 13) shows both conventional plan-view and cross-section bright field TEM images of such a sample (from different areas than shown in figures 11 and 12). While the plan view of figure 13a illustrates the fact that the MnAs crystallites possess some size distribution, it is clearly revealed in the cross section of figure 13b that at least some of the MnAs crystallites are exposed to the free sample.
surface, which is more or less perpendicular to the GaAs wafer normal. These MnAs crystallites are, thus, only partially embedded in the GaAs matrix and, therefore, “surface contactable”.

4 Nanocrystal phase and orientation mapping from HRTEM images

The projected reciprocal lattice geometry and Laue class\(^{§}\) diffraction symmetry of a nanocrystal are (with some modifications due to the prevailing contrast transfer function of the microscope) revealed in the amplitude part of the Fourier transform of its (parallel-illumination) HRTEM image. This part of the Fourier transform is typically displayed in conjunction with a HRTEM image and considered to be its “digital diffractogram”.

The extension of the high-resolution crystallite orientation and phase mapping procedure to digital diffractograms of nanocrystals is illustrated in figure 14. The method works well since an HRTEM image can after crystallographic image processing\(^{**}\) be utilized for advanced structural fingerprinting in the TEM [5,27-30] just as well as a PED spot pattern [5,9,22,23]. Note that the former type of structural fingerprinting in the TEM is often possible without a correction of the effects of the prevalent contrast transfer function of the microscope. The experimental HRTEM data for the crystallite orientation mapping in figure 14 were recorded with the internal slow-scan CCD camera of an objective-lens aberration-corrected TEM.

While nanocrystals with relatively large unit cells, i.e. magnetite and maghemite (\(\alpha \approx 0.83 - 0.84 \text{ nm}\)), can be fingerprinted structurally in the HRTEM imaging mode with modern analytical TEMs or older “dedicated mid-voltage HRTEMs” [27-30] (with typical point-to-point resolutions of 0.24 to 0.19 nm), other inorganic nanocrystals require the utilization of aberration-corrected microscopy (with typical point-to-point resolutions of better than 0.1 nm) for the recording of the experimental data. The same applies to the application of the new crystallite orientation and phase mapping technique to sections of HRTEM images.

![Fig. 14](image-url) Processing of HRTEM images of PbSe (\(\alpha \approx 0.61 \text{ nm}\)) nanocrystals with the software of the ASTAR system in order to create a crystallite orientation map, adapted from ref. [9]. (a) Overview screenshot of the analysis program window with an HRTEM image for the selection of individual nanocrystals for the calculation of fast Fourier transforms (FFTs). (b) Simulated template that matches a particular FFT best (upper part of panel) and location of that template close to [001] in the symmetry-invariant part of the stereographic projection for the lower symmetric cubic point groups 4\(_3\)2, \(m_3\), and 2\(_3\) (as inset). (c) Color-coded nanocrystal orientation map of PbSe nanocrystals (top) with stereographic-triangle color-key for point groups 4\(_3\)m and \(m_3\)m (bottom). (Online color at www.crt-journal.org)

5 Wider utility of the mapping technique and comprehensive crystallographic databases

Besides its obvious utility for a wide range of materials science applications, high-resolution crystallite orientation and phase mapping in a TEM from either single crystallite PED patterns or sections of HRTEM

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\(^{§}\) The Laue class in two dimensions consists of the point groups 2, 2\(_m\), 4, 4\(_m\), 6, and 6\(_m\). All of these point groups contain a two-fold rotation point [9]. Some other authors refer to the Laue class as the Patterson group.

\(^{**}\) Crystallographic image processing was pioneered in the electron crystallography community and allows for the extraction of good estimates of the phase of structure factors for weak phase objects. It, thus, provides a solution of the well known phase problem of diffraction based crystallography. A popular computer program for crystallographic image processing is commercially available from Calidris, http://www.calidris-em.com/, S. Hovmöller, Ultramicroscopy 41, 121 (1992).
images complements (and enhances) advanced structural fingerprinting from individual nanocrystals [5,9,22, 23,27-30], structural electron crystallography [31,32], and transmission electron microscopy in general. Structural identification of crystallites in a TEM must be based on reliable crystallographic data and we give below information on comprehensive sources of such data. The solving of new structures by electron crystallography often proceeds from a powder mixture of known and unknown phases [32].

A preliminary unit cell and rough approximation of the structure of an unknown phase that coexists in a mixture with a known phase can frequently be derived from a powder X-ray diffraction pattern. The approximate structure of the unknown might even be very coarse, e.g. all structure factor amplitudes may be set to unity. Preliminary crystallite orientation and phase maps can then be obtained from a powder mixture of both phases in the TEM. These maps may be used for the selection of individual crystallites of the unknown that are oriented close to major zone axes. Structural electron crystallography may then proceed on the basis of these crystallites in suitable orientations.

Crystallite phase and orientation mapping as demonstrated in the previous two sections of this paper may rely on data from the Powder Diffraction File [33], the Crystal Data database of the National Institute of Standards and Technology (NIST) [34], the Inorganic Crystal Structure Database [35], the NIST Standard Reference Data Bases 83 and 84 [36], as well as Pearson's Crystal Data [37] database. As an alternative to these well established commercial databases, one may use now comprehensive open-access databases.

Comprehensive datasets are available in open access at the web sites of the Crystallography Open Database (COD) [38], the COD’s mainly inorganic and educational subsets [39], the American Mineralogist Crystal Structure Database [40], and the AtomWork database of the National Institute for Materials Science, Tsukuba, Japan [41].

Note that the COD alone has currently more than 135,000 entries and is rapidly growing [42]. All of its entries (and all of the entries of its subsets [39]) can be visualized interactively at the atomic level at the Portland/Oregon based web portal [43]. All datasets of the COD are in the form of Crystallographic Information Files (CIFs), i.e. the preferred format for the electronic dissemination of crystallographic data as endorsed and promoted by the International Union of Crystallography [44,45]. More information on crystallographic databases can be accessed at the corresponding wikipedia entry, ref. [46].

6 Summary and conclusions

The new semi-automatic (high spatial resolution precession-enhanced electron diffraction spot pattern based) crystallite orientation and phase mapping technique enables fast and reliable analyses of polycrystalline materials. The software of this mapping system is flexible in its intake of experimental data so that crystallite orientation and phase mappings can also be performed on the basis of HRTEM images. The utility of the single crystallite precession electron diffraction mode for the increasing of the accuracy of the method has been demonstrated. Comprehensive open access crystallographic databases that can be used in conjunction with the mapping system have been mentioned. As our experimental studies suggest, the novel transmission electron microscopy based (PED enhanced) spot pattern technique should be capable of solving problems for which there are no solutions by the electron backscattering techniques of scanning electron microscopy. This should in parts be due to both the much higher achievable spatial resolution of the novel mapping technique and its reliance on electron transmission diffraction rather than backscattering from a specially prepared crystallite surface.

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References

http://nanocrystallography.net (in Oregon, USA) where all entries of the COD and of its subsets can be visualized interactively at the atomic level. www.cdt-journal.org

http://www.fiz-karlsruhe.de/icdd.html
http://www.cif-ibt.lt (in Lithuania), mirrored at: http://www.crystallography.net and http://cod.ensicaen.fr/ (both in France), as well as at: http://nanocrystallography.org (in Oregon, USA). Also accessible under a different search surface at: http://fireball.phys.wvu.edu/cod/ (in West Virginia, USA). There is also a web portal at http://nanocrystallography.net (in Oregon, USA) where all entries of the COD and of its subsets can be visualized interactively at the atomic level.

http://nanocrystallography.research.pdx.edu/CIF-searchable/, data on some 20,000 mainly inorganic crystals.
http://rruff.geo.arizona.edu/AMS/amcsd.php, data on some 10,000 minerals.
http://www.fiz-karlsruhe.de/icsd.html.