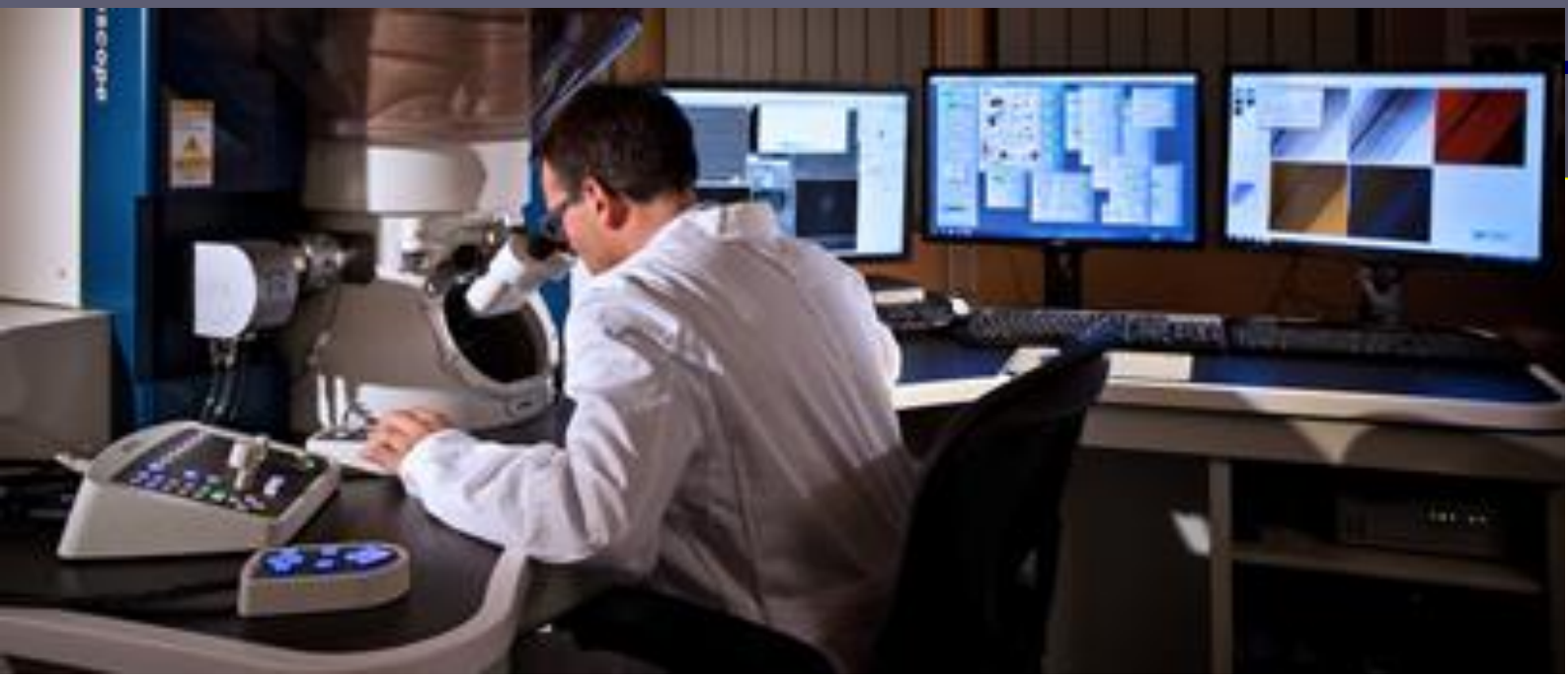
esteem3

Enabling Science through European Electron Microscopy

Report on diffraction methods

Deliverable D4.2 – version 1.1

Estimated delivery date:	April 30th 2022 (M40)
Actual delivery date:	April 29th 2022
Lead beneficiary:	UCAM
Person responsible:	John Walmsley
Deliverable type:	☒ R ☐ DEM ☐ DEC ☐ OTHER ☐ ETHICS ☐ ORDP
Dissemination level:	☒ PU ☐ CO ☐ EU-RES ☐ EU-CON ☐ EU-SEC



Grant Agreement No:	823717
Funding Instrument:	Research and Innovation Actions (RIA)
Funded under:	H2020-INFRAIA-2018-1: Integrating Activities for Advanced Communities
Starting date:	01.01.2019
Duration:	54 months

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Revision history log

Version number	Date of release	Author	Summary of changes
V0.1	26 April 2022	John Walmsley Joonatan Laulainen Petr Vacek Ton Van Helvoort	First Draft
V1	27/04/2022	Peter van Aken	Approval of report
V1.1	27/04/2022	Aude Garsès	General review

Introduction

This report will focus on Task 4.3, Development of Scanning Electron Diffraction and Scanning Precession Electron Diffraction (SED/SPED) for orientation mapping and strain mapping, and Task 4.4, Crystal structure determination of unknown phases using SED/SPED/Convergent Beam Electron Diffraction (CBED) and diffraction tomography. Consortium members directly involved in both tasks are Cambridge (CAM), Norwegian University of Science and Technology (NTNU), Nanomegas (NM) and Quantum Detectors (QD). This report describes background and recent general activities of the consortium members. Examples are given of work that has been carried out within ESTEEM3 and an overview is provided of ongoing activities and plans. Generally, the activities in other parts of the work package are covered by other deliverables.

4.3: Development of SED/SPED for orientation mapping and strain mapping

By acquiring tens / hundreds of thousands of diffraction patterns in a single fast scan, a remarkably rich crystallographic data set provides unique information about the local orientation and strain of the region of interest, Figure 1.

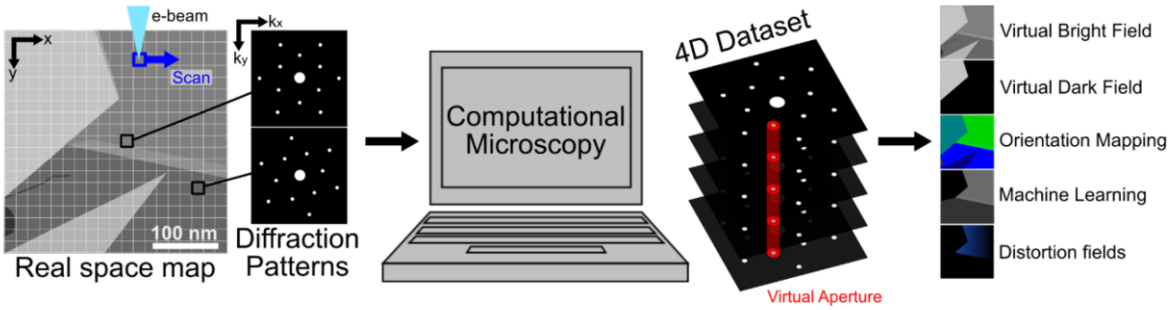

Figure 1 Overview of Scanning Electron Diffraction. Two-dimensional electron diffraction patterns, are recorded at each probe position in a two-dimensional scan to obtain a four-dimensional (4D-SED) dataset that may be analysed computationally in various ways. Taken from[1]

Methods are being developed to perform orientation imaging experiments of nanocrystalline samples within in-situ reaction cells, where electron diffraction intensities appear weak/blurred because of protective silicon nitride windows and the presence of a gaseous or liquid of liquid background medium. This activity is in collaboration with WP6.

Small fast direct electron detectors have revolutionised STEM imaging and SED in recent years, enabling the rapid acquisition of high-quality diffraction patterns, thereby enabling applications including lattice strain mapping, imaging of 3D periodicity in crystals, among others. Scanning precession electron diffraction (SPED) has meanwhile emerged as a critical tool for mapping crystal phase and orientation distributions, and for strain mapping up to length scales measured in microns.

SPED has previously been limited by the noise on the detector system used – a fast video camera (Stingray working at 8/12 bits) imaging the phosphor screen of the microscope. Thus, upgrading to a direct electron counting detector (Merlin from QD) as the recording device became the obvious next step for the technique to improve both acquisition speed and reduce the number of electrons needed for an acceptable quality set of diffraction patterns for quantitative evaluation.

NM have collaborated with QD and University of Glasgow to interface ASTAR (NM) and Merlin (QD) to drive experiments with hybrid pixelated counting detectors.[2] A suitable hardware /software interface to integrate the MerlinEM camera into the imaging framework using 4D-STEM with scanning precession electron diffraction has been established. Direct electron detection together with the higher number of pixels (256 x 256 or 512 x 512) and the high dynamic range (24-bit counting) have been used in conjunction for improved results with precession electron diffraction. The successful integration of a direct electron counting detector into a scanned precession electron diffraction system has been demonstrated.

In the last few years, this configuration has been implemented in a significant number of new TEM installations, within the ESTEEM3 consortium and more widely. This has facilitated an increasing level of technique development and applications in the field of multidimensional electron diffraction.

The large and information-rich multi-dimensional datasets that are generated require extensive computation infrastructure and, in particular, the development of advanced processing algorithms. HyperSpy is an open-source Python library, which provides tools to facilitate the interactive data analysis of multi-dimensional datasets that can be described as multi-dimensional arrays of a given signal (e.g. a 2D array of spectra a.k.a spectrum image). It aims at making it easy and natural to apply analytical procedures that operate on an individual signal to multi-dimensional arrays, as well as providing easy access to analytical tools that exploit the multi-dimensionality of the dataset. Its modular structure makes it easy to add features to analyze different kinds of signals. As a consequence, Hyperspy has become the main framework for the processing of multidimensional TEM datasets.[3] PyXem is an open-source python library for multi-dimensional diffraction microscopy as an extension of the Hyperspy library for multi-dimensional data analysis.[1,4] Pyxstem is a library for analysing pixelated scanning transmission electron microscopy data acquired using a fast pixelated electron detector that is currently being merged with pyxem.[5]

New algorithms are being developed to measure the morphological changes in each diffraction pattern and relate that back to structural distortions, which may be linked to strain or to rotations of the crystal lattice as the beam crosses a boundary (e.g. high angle or sub-grain). Critical to the performance of the algorithm is to understand the likely errors involved and the precision with which the diffraction pattern morphology can be determined. The project will also consider the issues of how best to extend both orientation and strain mapping to 3D, how to interpret 'projected strain' (with e.g. transverse ray transforms) and optimisation of 3D reconstructions of the strain tensor.

Johnstone *et al.* have applied analysis of crystal orientation clustering to visualize any preferred orientations or special orientation relationships present in a dataset.[6] The data used in the analysis are orientation maps gathered using scanning electron diffraction, backscattered electron diffraction, or X-ray microLaue diffraction. The Orix python library was designed to perform calculations for three-dimensional rotations, apply crystal symmetry operations and visualise the results in neo-Eulerian vector spaces. Capabilities of this approach are demonstrated on orientation data from deformed pure titanium. Examples of grain segmentation and misorientations at grain boundaries are shown.[7]

Local crystal orientation is identified by matching the diffraction pattern with a library of simulated diffraction patterns from all the possible zone axes. From all the possibilities, the best match is chosen as the correct orientation. The library of diffraction patterns needs to include not only all diffraction patterns from all possible zone axes, but also their full rotation about the viewing direction. Due to the number of diffraction patterns to analyse and many possible orientations, large amounts of computational resources are necessary. This is addressed by using GPU acceleration, since the algorithm can take advantage of efficient parallel computing capabilities of GPUs. Recently accepted

work allows for fast template matching of spot electron diffraction patterns preformed in the open-source package pyXem. Large (at least up to 25 Gb) data sets as collected by direct electron detectors can be conveniently handled.[8] Based on this open code, further refinements of the matching parameters are made, for example the pixel size calibrations. Further, a standardized export function (crystalmap) is created so that results from template matching can be used by other open packages such as orix and MTEX. These package focus on orientation visualization and calculations. Orientation mapping and data analysis is extended to work with small tilt series. Primary goal is to evaluate the template matching accuracy and precision. Recent updates in template matching routines have been applied to nanoparticle samples, semiconductor devices, light metals and thin film solar cell samples by different facility users in Trondheim.

Beside with a model-based analysis of 4D scanning precession electron diffraction data as described above, analysis based on machine learning is systematically explored.[6] Machine learning can be advantageous, as these 4D data sets collected on new direction electron detectors can be large and complex. A comparative study including supervised as well as unsupervised machine learning (i.e. factorization and neural network based), vector-based matching and template matching is under way, using a 2xxx aluminum alloy as practical model system. All analytical approaches use, or will contribute to, the open-access package pyXem.

One example of addressing the practical issue of associated with the application of SPED have been addressed in an ESTEEM3 Transnational Access activity. SPED data from nanocrystalline materials commonly contain some PED patterns in which diffraction is measured from multiple crystals. To analyse such data, it is important to perform nanocrystal segmentation to isolate both the location of each crystal and a corresponding representative diffraction signal.[9]

Figure 2 shows an image and selected diffraction patterns from a scanned area that includes several partially overlapping MgO particles supported on a carbon film.

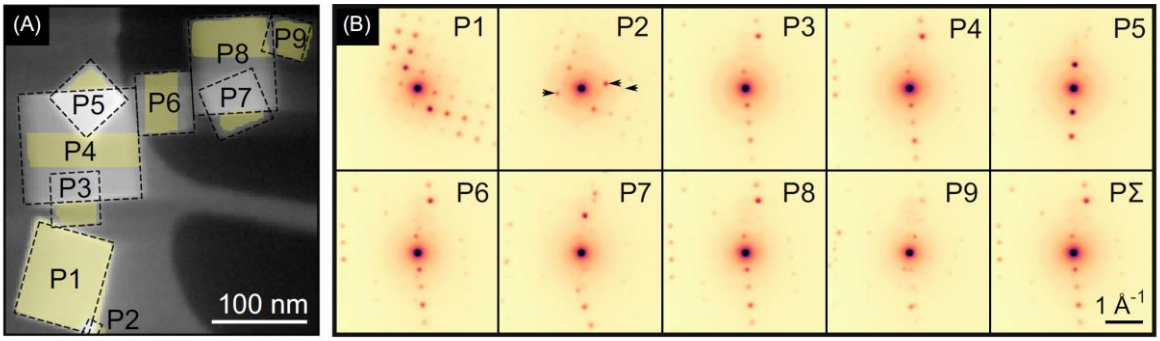

Figure 2 Annular virtual dark-field (VDF) image showing nine magnesium oxide (MgO) particles (grey), labelled P1–P9, lying on top of a holey amorphous carbon film (dark grey) or over vacuum (black). The outlines of the MgO particles are indicated by dashed rectangles. (B) Sum of PED patterns within the yellow areas in (A). The detected diffraction vectors of P2 are marked by black arrows. PΣ is the sum of P3, P4, P6 and P8 taken from[9].

Two approaches to nanocrystal segmentation are presented, the first based on virtual dark-field imaging and the second on non-negative matrix factorization. Relative merits and limitations are compared in application to SPED data obtained from partly overlapping nanoparticles, and particular challenges are highlighted associated with crystals exciting the same diffraction conditions. It is demonstrated that both strategies can be used for nanocrystal segmentation without prior knowledge of the crystal structures present, but also that segmentation artefacts can arise and must be considered carefully. The analysis workflows associated with this work are provided opensource.

Imaging and diffraction tomography in liquid cells is being developed. Nanomegas have been working with collaborators in Ireland, Spain and Switzerland to demonstrate the application of a custom designed e-chip that allows imaging of the sample over a tilt range of +/- 60 °, that allows tomographic investigation of a sample in a liquid environment, based on a Nanomegas patent.[10]. An abstract has been accepted for presentation at M&M 2022.[10] Collaboration between Nanomegas and DENSsolutions for in-situ SPED and electron tomography is ongoing and will be published in the future.

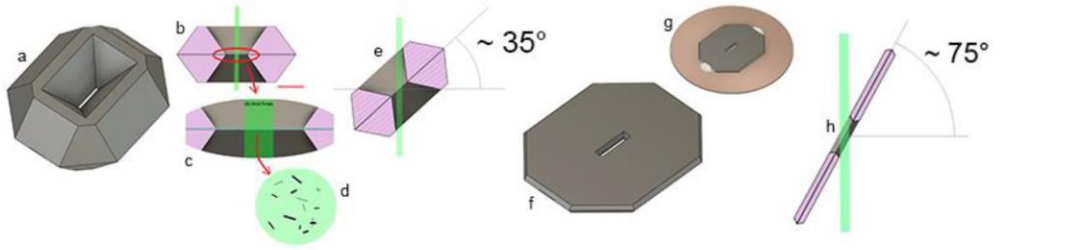

Figure 3 Specially developed liquid cell chip. Relevant dimensions 300 x 25 µm window, 800 µm thickness, (b, c, d) schematic process for TEM observation, (e) maximum tilting range limited to ±35°, (f, g) tomochip thinned to approx. 80 µm with standard 1mm diameter single hole grid that supports it, (h) the Tomochip tomographic LC can be tilted more than ±70°

4.4: Crystal structure determination of unknown phases using SED/SPED/CBED and diffraction tomography

Great progress has been made in using precession electron diffraction to solve crystal structures. There is now almost universal recognition that PED can provide excellent model structures, but there remain uncertainties over refinement and confidence in the structure solution. Orientation imaging will be tested with novel pixelated detectors (QD) in order to obtain detailed phase maps on complex materials, such as those having similar unit cells, but different atomic arrangements, e.g. Li based battery samples or new phases with superstructure, where reflections are often too weak to detect.

An ongoing activity is to consider alternative refinement procedures (e.g. rank refinement and dynamical refinement) and to better understand the robustness of the final structure solution. Several reference materials using new pixelated detectors will be tested with 3D PED tomography to perform dynamical refinements. Such approaches can in principle refine all atomic positions (including H atoms) down to 1 pm level, atomic occupancies and may reduce R-factors to comparable values to single crystal X-ray refinement.

An enormous benefit, it has become possible to do phase identification and characterisation in beam-sensitive organic and inorganic materials through the use of novel pixelated detectors (QD). Such work has enabled the characterisation of defective and non-crystalline materials, such as in defective MOFs [11], Figure 3, lead-halide perovskites [12] and amorphous-amorphous composites.[13] A full journal manuscript has been submitted for the latter. Organic materials have also yielded expectedly complex microstructures, defects, and polymorphs, due to their molecular packing units, resulting in dislocations, twists, strains and other features. Their characterisation is underway.

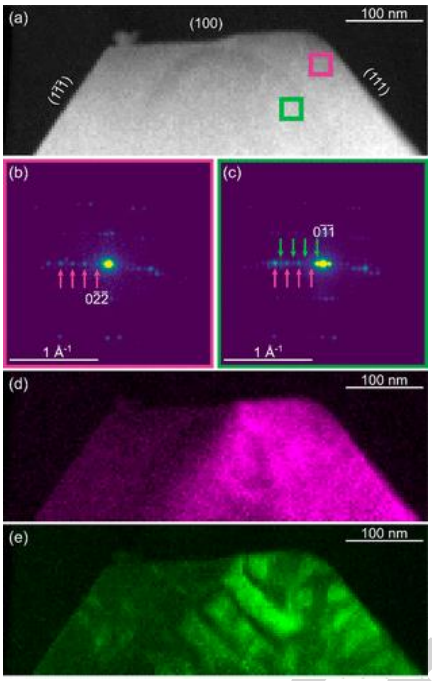

Figure 4 SED analysis of defect nanodomains in a 6(Hf):5(BDC) UiO-66(Hf) particle with high defect density. (a) ADF-STEM image indicating regions where integrated electron diffraction patterns (b, c) were selected. (b) Diffraction pattern from the magenta region, marked in in a, containing only parent reflections indicating the fcu phase. (c) Diffraction pattern from the green region, marked in a, containing both parent and superlattice reflections indicating the reo phase. (d) VDF image formed using integration windows centered on the parent reflections, marked in b. (e) VDF image formed using integration windows centered on superlattice reflections, marked in c, to directly image reo defect nanodomains.

Work has been done to define the complex theoretical framework for 3D strain tensor tomography, which highlighted the need for PED to accurately reconstruct 3D strain.[14] In addition, 3D-ED has been used for diffraction tomography[1], with work on incorporating dynamical refinements into such procedures currently underway. In addition, work is currently underway on spatially-separated 3D diffraction tomography through SED of twisted organic co-crystals.[15]

In Cambridge, a postdoctoral researcher was recruited in 2021, who will have a strong focus on Task 4.4 with funding from ESTEEM3. Current work is focused on development of strain tomography based on the initial work described above. Two approaches are being pursued. First is a real space approach, where a three-dimensional map of atoms is reconstructed from a series of high-resolution images. The strain can be determined from varying interatomic distances. The second approach is a reciprocal space approach, where the strain is determined from positions of reflections in a diffraction pattern using SED combined with beam precession and monitoring positional changes of reflections to determine strain. A tilt series can be performed, and the data used for tomographic reconstruction to get information about strain in three dimensions.

Conclusions

Background and ongoing activities of consortium members active in WP4.3 and WP4.4 have been summarized above. Work that is in progress will be reported during the remaining part of the project. SED/SPED is an active and expanding aspect of TEM technique development and application. The interaction between the academic and industrial partners in ESTEEM3 is an important in realizing its potential.

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