Quantitative Four-Dimensional Electron Diffraction in the TEM

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BIography
Christoph Koch, after finishing his undergraduate studies at Heidelberg University in Germany, received his PhD from Arizona State University in 2002. He then spent nine years as a staff scientist at the Max Planck Institute for Metals Research in Stuttgart before he was appointed Professor at Ulm University in 2011, a position endowed by the Carl Zeiss Foundation. His research interests include quantitative electron microscopy, diffraction, and inline holography, dynamical electron diffraction theory, electron and light optics, as well as the application of novel TEM methods to solving materials science questions.

Albstract
Conventional electron diffraction patterns are 2-dimensional. Under dynamical scattering conditions, recording such patterns for a range of illumination tilt angles spans another two dimensions, making them 4-dimensional. In this article we will provide examples of diffraction data acquisition techniques suitable for nanocrystals that are based on sampling 4D diffraction space and provide an indication as to what kind of information we expect to be able to extract from such data in the near future.

KEYwords
transmission electron microscopy, electron diffraction, precession electron diffraction, convergent-beam electron diffraction, dynamical scattering, diffraction mapping

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Introduction
Electrons, because of their 10⁴ times stronger interaction with matter than X-rays (and even more in comparison with neutrons) and the possibility to focus them into sub-nanometer areas, are the ideal tool to investigate the structure of nanovolumes. However, dynamical (multiple) scattering of electrons, even in samples which are only a few nanometers thick, poses a serious limitation to existing methods for quantitative interpretation of electron diffraction intensities, thus preventing electron diffraction in the transmission electron microscope (TEM) from establishing itself as a quantitative technique suitable for routine structural crystallography.

In an attempt to reduce the effect of dynamical scattering and to increase the accessible range in reciprocal space limited by the curvature of the Ewald sphere, precession electron diffraction (PED) [1] effectively integrates the diffracted intensities by precessing the incident beam direction around the optic axis and compensating this precession below the specimen again (see illustration in Figure 1a). The number of publications based on the application of PED has grown quite rapidly in the last few years, one of the reasons for which is very likely the fact that, since the original design by Vincent and Midgley [1], a number of different hardware implementations of the PED method have become available [2-4]. Modern TEMs provide access to a number of current settings of lenses and deflection coils by software commands. This has also led to the development of several PED software implementations [5, 6] which do not require the attachment of any additional hardware to the microscope.

As illustrated in Figure 1, the integration of diffraction patterns in PED causes the loss of information about variations in the diffracted intensity due to changes in the illumination tilt angle. Large-angle rocking-beam electron diffraction (LARBED), a technique which has been developed quite recently [7], extends the PED principle by compensating a very well-defined fraction of the illumination tilt angle, but not necessarily all of it. It is thus capable of downsampling arbitrarily large precession circles (as shown in Figure 1b) or other tilt patterns (see, for example, Figure 3) in the diffraction pattern, preserving the rocking curve information while avoiding overlapping diffraction orders.

Since, in contrast to conventional convergent-beam electron diffraction (CBED), this variable scaling of the diffraction disc size allows the range of illumination tilt angles in LARBED experiments to be chosen independently of the distance between Bragg spots, 2D rocking curve patterns may be collected from materials featuring any size unit cell for all Bragg spots simultaneously, making this inherently a 4D technique.

In this paper we will describe the application of our recently developed quantitative electron diffraction (QED) plug-in [8] to Digital-Micrograph (Gatan Inc., Pleasanton, CA, USA)
to the acquisition of PED and LARBED patterns and demonstrate how such information may be used to reconstruct part of 3D reciprocal space from such data. In addition we will give examples of the usefulness of this software for acquiring diffraction maps or for extending the acceptance angle of an energy filter attached to the microscope.

**Materials and Methods**

**Specimen Preparation**

Different sample preparation techniques were applied for this work. The thin SrTiO$_3$ sample (Fig. 4) was prepared by edge polishing followed by a short polish in a low-voltage ion mill; the MgO nanocrystals (Fig. 5) were caught from the smoke of a burning Mg rod using a copper grid covered with holey carbon; the multilayer sample shown in Fig. 6 was cut by a focused ion beam; and the diffraction data shown in Fig. 7 were recorded from a standard TEM grid covered with holey carbon.

**Transmission Electron Microscopy**

Although successful tests of the QED software have been performed on TEMs produced by various manufacturers, for reasons of availability of the equipment, the experiments described here were performed on a 200 kV Zeiss SESAM, a monochromated FEG-TEM equipped with an in-column high-transmissivity Mandoline filter and a Gatan US100 CCD camera, as well as on a 120 kV Zeiss EM912 with a LaB$_6$ source, an in-column Omega filter and a Gatan Orius SC200W CCD camera. The microscopes were operated in standard TEM mode (Köhler illumination). The probe sizes were therefore defined by the smallest condenser aperture and were 120 nm on the Zeiss SESAM and 1 µm on the Zeiss EM912.

**Aberration Compensation**

One very important prerequisite for quantitative LARBED experiments is that all diffraction information stems from exactly the same specimen area, for all angles of incidence of the electron beam. Otherwise it will be impossible to separate the effect of varying specimen thickness from the genuine rocking curve signal. This is particularly challenging if the sample is nanocrystalline and a very small probe must be used, in which case the same requirement applies also to PED. It is thus necessary to keep the probe from wandering about the sample surface during acquisition.

Within the QED software this is achieved by first fitting a set of pseudo-aberration coefficients to the movement of the spot on the sample for a large range of beam tilt angles. These parameters, which include all aberration coefficients up to (and including) 3rd, 5th, or 7th orders, depending on the user’s choice, are then, during the actual data acquisition, used to predict the probe shift corresponding to any beam tilt within (and to some degree also outside) the range of tilt angles sampled during the calibration (see Figure 2).

**Non-Linear De-Scan Calibration**

It turns out that, although much smaller deviations from the optic axis are involved, on most microscopes the diffraction shift does not behave in a fully linear fashion. As shown in the example in Figure 3, recorded on the Zeiss SESAM for a tilt amplitude of 60 mrad (3.4°), assuming the applicability of a simple linear calibration may result in delocalized scan figures in PED patterns and distorted discs in LARBED patterns at large precession angles or LARBED disc radii, respectively. This problem can be overcome by applying a non-linear calibration scheme which is, similar to the illumination aberration compensation, based on a larger number of diffraction tilts, spiraling away from the way up to tilt amplitudes used for acquiring the actual experimental data. Applying such non-linear calibration scheme compensates any residual movement of the diffraction pattern with beam tilt, as demonstrated in the right hand column of Figure 3.

**Results and Discussion**

The fully automated calibrations of the illumination tilt, the diffraction shift and the aberrations of the illumination system is all that is needed for quantitative PED or LARBED patterns to be acquired. If the microscope is operated in imaging mode rather than diffraction (e.g. when acquiring diffraction maps, as explained below) a wide illumination would be used and shifts in the illumination are not important, in which case the calibration of the illumination tilt alone is sufficient.

**Large-Angle Rocking-Beam Electron Diffraction**

Figure 4 shows a zero-loss filtered LARBED pattern of a thin SrTiO$_3$ specimen. This pattern provides dynamical rocking curve information up to an illumination tilt angle of 70 mrad in all directions, i.e. the diameter of each of the diffraction disc is 140 mrad (8°). As for conventional PED patterns, the (partial) compensation of the illumination tilt by the diffraction shift smeared out any detail within the thermal diffuse scattering background, such as Kikuchi bands. This feature increases the accuracy with which quantitative information may be extracted from each of the diffraction discs of a partially compensated LARBED pattern.
However, the data presented in Figure 4 were acquired by recording each of the 1009 individual diffraction patterns, storing these in a single data stack (there is no limit to the size of the data set, since one may also choose to store the data directly on disc). For a diffraction pattern consisting of discrete spots, as is the case in the presented example, this allowed the background to be subtracted under each of the individual diffraction spots present in the diffraction pattern, for each discrete illumination tilt angle separately. The value of each pixel within the individual diffraction discs displayed to the left and right of the LABED pattern in Figure 4 thus represents the integrated background-subtracted diffraction intensity for the selected Bragg spot (see [6] for details).

The large tilt range covered by this data set causes most of the diffracted intensity to be concentrated along narrow Bragg lines whose width decreases with the distance from the origin of the diffraction pattern. The intensity fluctuations along these Bragg lines are due to strong multi-beam dynamical diffraction conditions. For beam tilts closer to the ends of the Bragg lines at the disc perimeter the diffraction conditions are more two-beam like. As discussed in more detail elsewhere [9, 10], the 2D rocking curve information available in LABED patterns may be used to directly invert the dynamical scattering and retrieve amplitudes and phases of the structure factors representing the potential distribution of the diffracting crystal structure. While such numerical analysis is quite complicated, if the specimen is thin enough, it is also possible to fit structure factor amplitudes and specimen thickness to such kind of data using the kinematic scattering approximation [6].

Reconstruction of 3D Reciprocal Space

Whether they are individual LABED patterns or the corresponding data stacks, the large tilt range covered in these kinds of data sets implies direct access to information about at least some section of 3D reciprocal space. This is true independently of whether the data was acquired for a circular or disc-shaped scan pattern, and may be achieved by assigning the intensity at each pixel within every individual diffraction pattern (or every pixel within the individual LABED disc) to the corresponding voxel in 3D reciprocal space, so that each voxel represents the average intensity of all diffraction patterns for which the Ewald sphere has passed through it. For a circular scan pattern, the number of different diffraction conditions being averaged over is at most two (e.g. the two ends of the Bragg lines), whereas for a disc-shaped pattern, a large number of pixels may be averaged over (e.g. the average along the whole Bragg line).

Figures 5a and 5b show energy-filtered PED and LABED patterns for an MgO cube with about 60 nm edge length in the (001) orientation that were acquired on the 200 kV Zeiss SESAM. Figure 5c shows the small sub-region of 3D reciprocal space that was reconstructed from the LABED data stack consisting of 1257 individual diffraction patterns, each having a...
size of $512 \times 512$ pixels (binning 4 on a $2k \times 2k$ Gatan USC 1000 CCD camera). The small unit cell size of MgO allowed only a single Laue zone to be reconstructed, but even this small tilt range was sufficient to allow the reconstruction of the 3D vicinity of all of the Bragg spots in this zone. The observed intensity distribution of any of these reflections corresponds very well to the expected shape transform of a cube, but laterally convoluted with the spatial coherence envelope.

**Precession Electron Diffraction**
Adjusting the proportionality factor controlling the tilt de-scan to 1 will produce a spot pattern, independent of the shape of the scan pattern. Such a spot pattern recorded for our 60 nm MgO cube is shown in Figure 5a. Although the MgO nanocrystal was oriented slightly off its (001) zone axis, the PED pattern is still very symmetric, allowing the symmetry of this zone axis to be determined quite easily.

**Diffraction Mapping**
Operating the microscope in image mode and inserting a small objective aperture, the QED module may also be used to acquire diffraction maps [11]. Just as for a LARBED data stack acquisition the beam is tilted to produce a large number of different illumination tilt conditions. The small objective aperture permits one to work with a large number of diffraction patterns and imaging energy acceptance angle of imaging energy entrance aperture inserted. The radius of the objective aperture determines the access to quantitative (i.e. ideally zero-loss-filtered) imaging energy acceptance, and indicates the mask to be applied during reconstruction, discarding any information outside its boundaries.

**Extending the Filter Acceptance Angle in Energy-Filtered Electron Diffraction**
The final example we want to present, describes how one may easily overcome the limited acceptance angle of imaging energy filters and mimic an ideal beam stop for the central beam, even if the microscope is not equipped with one. We chose amorphous carbon as a test sample, since for the determination of the radial distribution function from diffraction patterns of amorphous materials access to quantitative (i.e. ideally zero-loss-filtered) diffraction information covering a large reciprocal space range out to at least 10 nm$^{-1}$ is necessary [12].

The data acquisition is essentially identical to the acquisition of a precession data stack for a circular tilt scan, but with the de-scan turned off and a large objective aperture or filter entrance aperture inserted. The radius of the precession circle (i.e. the tilt amplitude) should be chosen slightly larger than the angular cut-off imposed by the aperture. This will block the central beam of the diffraction pattern and allow for a large enough exposure time to be chosen for high-quality data to be acquired. The QED plug-in provides a function for automatically reconstructing the complete 2D diffraction pattern from such a precession data stack.

**Conclusion**
We have presented several example applications of the acquisition of four-dimensional diffraction information in the TEM, operating the microscope in diffraction but also in image mode. All these experiments have been facilitated by the functionality provided by our QED plug-in for the Gatan DigitalMicrograph software.

**References**
8. QED is commercially available from HREM research (www.hremresearch.com).

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