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Complete 3D electron diffraction data collection - new methods and applications. <u>Xiaodong Zou</u>, Peter Oleynikov, Daliang Zhang, Tom Willhammar and Sven Hovmöller. *Inorganic and Structural Chemistry, Department of Materials and Environmental Chemistry, and Berzelii Center EXSELENT on Porous Materials, Stockholm University, Sweden.*
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Electron crystallography is a unique technique for structure analysis of crystals too small to be studied by single-crystal X-ray diffraction, even using a synchrotron radiation. Many different structures including the most complicated zeolites and quasicrystal approximants have been solved by electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) combined with crystallographic image processing.[1] Even though, electron crystallography is not widely used for structure analysis compared to X-ray diffraction. The main reasons for this are 1) dynamical scattering; 2) incomplete data and 3) the techniques are not feasible and highly skilful operators are needed. The later often requires a long and hard training period. We have developed several new methods to tackle those problems.

Dynamical scattering may be reduced when the incident electron beam is tilted off the zone axes. This is achieved in precession electron diffraction (PED). We have developed a new software-based method – the digital sampling method to automatically collect a series of ED frames while the electron beam is precessed.[2] Several different post-processing strategies are developed for extracting the ED data and combining them to a PED pattern. The intensity data obtained by the digital sampling method were used for structure refinement of $K_2O \cdot 7Nb_2O_5$. The data quality is shown to be comparable to, and in some cases even better than that obtained using a hardware-based electron precession device.

We have combined digital electron beam rotations with goniometer tilts for collecting complete 3D electron diffraction data.[3] A 3D electron diffraction dataset with an tilt range of $\pm 70°$ can be collected automatically from a nano-sized crystal on a JEOL JEM2100 TEM. More than one thousand electron diffraction patterns can be collected within 1-2 hours, with a step of $0.05°$ -$0.1°$ for each ED frame. There is no need for pre-alignment of the crystal. The ED patterns are combined into a 3D reciprocal lattice, from which the unit cell parameters and space group can be determined. ED intensities of all reflections can be extracted and used for structure solution and refinement. Diffuse scattering and diffraction streaks caused by crystal defects can be quantified and used for studying the defect structures in the crystals.

The power of the new methods for structure analysis is demonstrated on several inorganic structures and zeolites. The automation procedure for collection of complete 3D ED data from nano-sized crystals opens new possibilities and applications of electron diffraction for structure analysis.

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DFT Versus Accurate Experimental Measurements of Charge Density in Aluminium. <u>Philip N.H. Nakashima</u>[a], Andrew E. Smith[b], Barrington C. Muddle[a]
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The term "density" in density functional theory (DFT), refers to the ground state charge density, which is the basis of this and other *ab initio* models of predictive chemistry. Therefore, the most effective test of all such models is a comparison between the bonding charge density that they predict for a particular material and a corresponding set of accurate experimental measurements.

Quantitative convergent beam electron diffraction (QCBED) is a well-matured technique for the absolute (scale and extinction free) measurement of Fourier coefficients of crystal potential (structure factors) in highly perfect crystals with small units cells [1]. Crystal potential structure factors are directly related to those of the electron density via the Mott formula and it is in the low orders that the conversion process further enhances the intrinsic precision and accuracy of QCBED. The low order structure factors are also those that are most sensitive to chemical bonding and are therefore the ones that should be compared with *ab initio* calculations, such as those based on DFT.

The present work summarises the most recent advances in QCBED, which have produced new modes of analysis that further improve the precision of structure factor measurements [2–4]. Application to pure aluminium in conjunction with a detailed DFT study has allowed a rigorous comparison of the bonding charge density measured by QCBED and that predicted by a variety of DFT calculations, in a material that is, theoretically, ideally suited to DFT.

The general view, that most of the bonding charge density resides in the octahedral interstices of aluminium [5–7], is called into question. The present results show that the main concentration occurs in the tetrahedral interstices instead. The latter configuration presents a number of strong correlations between the nature of bonding in pure aluminium and the nature of strengthening precipitates that form in aluminium alloys. This is an example of how detailed knowledge of a precursor charge density distribution can, at least in part, help explain the route of phase transformations that occur in the environment of a particular electronic structure.

Furthermore, the ability to chose the variant of *ab initio* modeling that best matches an accurate experimental determination of the ground state charge density in a material, will lead to a more educated reliance on solid state theory for the prediction of materials properties. This is a particularly important step for atomistic modeling of phase transformations in aluminium alloys and is one of the main reasons for the present study of pure aluminium.

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