# Commission on Electron Crystallography

## ELECTRON CRYSTALLOGRAPHY – SEEING IS BELIEVING

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## Abstract

The Commission on Electron Crystallography (CEC) of International Union of Crystallography (IUCr) is active in promoting electron crystallography science. Electron crystallography bridges two communities: electron microscopy and crystallography. General definition of electron crystallography science is usage of electron scattering and imaging to study the structure of matter. Amazing development of the instrumentation and computerization, transformed electron microscopes into unique tools providing information on: atomic structure at nanoscale by electron diffraction; ultra-high resolution images; local chemical composition, including construction of 2D/3D maps of composition and of electromagnetic fields. Moreover, time-resolved phenomena at the sub-picosecond timescale can also be studied using these machines. Furthermore, electron diffraction itself has also dramatically evolved giving rise to amazing awaking of the field evidenced by exponential increase in number of publications per year written on this subject. Taking into the account wide spread of materials` types and variety of structural complexity being studied by these methods, the sky is not a limit for electron crystallography.

## Introduction

In the era of nanoscience, electron crystallography, which is defined as the branch of science that uses electron scattering and imaging to study the structure of matter, can be considered as a powerful and sometimes the only possible tool for the structural study of materials. Since most physical properties of matter depend on its atomic structure, such study is of detrimental importance.

X-ray crystallography was founded in 1912 and until today it is still the most important and widely used technique for studying atomic structures of materials. However, this method is limited by the requirement of specific (adequate) size of crystals (single crystal X-ray diffraction) or peak broadening and overlapping (powder X-ray diffraction).

Electron diffraction (ED) was discovered fifteen years later and in 1933, the first transmission electron microscope (TEM) was presented by Ruska. These discoveries were revolutionary and gave birth to electron microscopy science. Usage of electron radiation for structural analysis provides an advantage over X-ray, since data can be collected from areas of a few tens of nanometers, as the charged electron undergoes about $10^4$ times stronger interaction than X-ray. Moreover, electron microscopy delivers the only method capable of acquiring imaging and diffraction data from the same (nano-sized) sample volume. Electron diffraction, in comparison to high-voltage high-resolution TEM (HRTEM) imaging, provides as well sub-Ångstrom structural information with good signal-to-noise ratio in reciprocal space but imposes a significant lower dose onto the sample, thus causing less beam damage. Today, less than 100 years after their discovery, modern HRTEMs and scanning transmission electron microscopes (STEMs) combine structure analysis by ED and HREM imaging with chemical analysis by energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). With the advent of aberration correctors, monochromators and computer control, the electron microscope is able to form not only ultra-high resolution images but also 2D and 3D maps of composition (using EELS or EDS) and of electromagnetic fields (through electron holography), and can follow time-resolved phenomena at the sub-picosecond timescale [1,2]. It should be underlined that in nanoscience there is no alternatives for attaining structural information but electron crystallography. Electron diffraction in STEM (D-STEM) presented an ability to sample individual electron diffraction patterns from nanostructures as small as ~3 nm [3]. This makes electron microscopy a powerful and complete analytical tool for studying materials, defining more broadly the concept of electron crystallography as method allowing study of perfect crystal structures as well as defects and interfaces.

## Crystal structure determination using electron crystallography

Structure analysis of crystals by electron diffraction (ED) was first pursued in 1937-1938, by a group of crystallographers in the former Soviet Union (taken from [4]). Using electron diffraction data, they developed electron diffraction into a complete and independent structure analysis method. Vainshtein wrote in his book (1956) [5]: “There is no doubt now that electron diffraction may be used for the complete analysis of crystals whose structure is unknown”. This pioneering work was summarized in a review article by Vainshtein, Zvyagin and Avilov (1992) [6].

Despite the enormous advantages of electrons over X-rays with regard structural study, strong interaction of electron with matter is not only an advantage it is also a disadvantage. In X-ray diffraction, the diffracted amplitudes are, to a very good approximation, proportional to the squared amplitude of the corresponding structure factors. In other words, the kinematical diffraction theory applies. Electron diffraction, in general, does not obey the kinematical diffraction theory, and, therefore, the diffracted intensities are not, under general conditions, proportional to the square of the structure factor. Such

diffraction is called dynamical. This problem was, for a long time, considered an almost unsurmountable obstacle in the attempts to solve and refine crystal structures against electron diffraction data. There are, in general, two basic approaches to this problem: suppressing the dynamical effects by experimental approaches and including the dynamical effects in the calculation. These approaches are not exclusive and can be combined. Computational approach means that the experimental intensities are not compared with intensities calculated from the structure model using the kinematical approximation, but with intensities calculated using the many-beam dynamical diffraction theory [7, for example]. The experimental approaches to minimizing dynamical effects include: usage of thinnest crystals, avoiding zone-axis patterns and using precession electron diffraction (PED) to integrate intensities [8]. Last method was presented in 1994 [8], and, since its commercialization [9, as an example], the number of papers dealing with crystal structure solution and refinement of materials using electron crystallography increased tremendously. Based on PED data, many zeolites, complex oxides, intermetallides and minerals were solved [10-16, for example].

One of the major drawbacks which discouraged the use of electron crystallography for structure solution was the need for extensive training on electron microscope and time consuming data acquisition. This has changed with the invention of automated electron diffraction tomography [17-21]. Over the past few years automated electron diffraction tomography has become an established technique for structure solution of nano-crystalline material. The intentional choice of an arbitrary tilt axis and thus, the use of non-oriented diffraction patterns (off-zone acquisition) together with fine equidistant sampling of the reciprocal space result in high quality intensity data sets. Coupling automated electron diffraction tomography with precession [8] enables sampling of intensities between the static slices of reciprocal space and, therefore, enhances the quality of intensity data further. Relatively complex structures have been solved using 3D electron diffraction intensities extracted from automated electron diffraction tomography data. A promising alternative experimental setting was proposed in [20]. In this method, called the Rotation Electron Diffraction (RED), mechanical sample tilt is supplemented by beam tilt for a finer reciprocal space sampling. The RED was also successfully applied for the structure determination of many new complex structures.

It is worth-mentioning that other, less widely used, methods exist for extracting structure factors phases from electron data such as quantitative Convergent Beam Electron Diffraction [22] or HRTEM images [23,24].

Parallel development of low dose methods and computerization raised interest to electron crystallography of many scientists working in the areas of inorganic and biological materials. For biological samples, electrons were first used to collect diffraction data from 2D crystals of bacteriorhodopsin to a resolution of 7 Å using TEM [25, 26]. This pioneering work by Henderson and Unwin launched the field of 2D electron crystallography which has since been used to solve the structure of many membrane proteins in their lipid environments [27], with the highest resolution structure resolved to 1.9 Å [28]. Electron diffraction of 3D protein crystals in the TEM has been attempted over the years but none yielded a refined structure [29–32]. One of the major problems was the beam damage associated with data collection, due to radiation sensitivity of the samples [32]. Today, during the collection, data can be gathered so that electron beam damage will be minimized by cooling down to liquid $N_2$ temperature (using a cryo-TEM holder) and/or using low dose conditions (often requires special cameras) [33], nano-beam illumination and/or gathering the data in faster manner (Fast EDT [20], for example). Groups headed by Prof. Abrahams (development of methods and detectors) and Prof. Gonen (invention of MicroED method which was used successfully to determine protein structure by electron diffraction from microcrystals [34]) should be especially mentioned due to their major contribution to the field.

## Commission on Electron Crystallography

Commission on Electron Crystallography was founded by International Union of Crystallography recognizing the importance and scientific impact of this branch of science. The commission bridges two communities: electron microscopy and crystallography. Moreover, as a matter of the type of material being studied another division exists: life and material science. We strive to strengthen links and interactions among electron crystallographers, and to promote a common language for all these communities. In order to push our science forward we encourage the development and dissemination of mathematical and theoretical methods, software and databases for the solution of electron crystallographic problems. We acknowledge scientists who made an outstanding contribution to the field of electron crystallography by Gjønnes Medal which is awarded every three years. The Gjønnes Medal is accompanied by a certificate and funding. The recipient is invited to present a Keynote Lecture at the triennial International Congress of Crystallography.

Commission on Electron Crystallography puts strong emphasis on education. Many courses and international summer schools are being held each year providing teaching platform and financial aid to prospective graduate students and academics at early stages of their careers in order to promote electron crystallography as a science (please follow the updates, published on the web page of the commission https://www.iucr.org/resources/commissions/electron-crystallography/meetings). It is our pride that our schools and courses are widely spread geographically and well attended.

## Summary

Electron Crystallography methods have evolved extensively so that today, atomic structure of wide range of materials such as complex oxides, organic crystals, intermetallic compounds and proteins can be tackled. It is evident that for crystal structure solution EDT/RED and dynamical refinement are the future of electron crystallography. Electron crystallography science is very versatile and has many branches. It can be used as standalone method and in combination with other methods such as XFELs or powder X-ray diffraction. Unfortunately, in this

paper not everything was reviewed (due to the length limitation of the article), but fields as application of Pair Distribution Function (PDF) on electron diffraction data [34, for example], in-situ studies in electron microscopes [35, for example] and time resolved electron crystallography [36, for example] has to be mentioned.

The number of users of electron microscopy and diffraction, always large in the US and Europe, continues to increase as developing countries such as India purchase new instruments to improve their technological base. Thus, it is our strong belief that our community will grow and develop.

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