Chapter

Introductory Chapter: Electron Crystallography

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1. Introduction

The different properties of materials are structure dependent. There are many techniques that are developed for the structure analysis. The most common of them is X-ray crystallography for the structural study of periodic ordered structures at atomic scale level. Few years later, after the discovery of X-ray diffraction, electron diffraction of single crystals was invented. The wave nature of electrons was utilized to discover the state of the art instrument, electron microscope. Since then, electron microscope has been extensively used in many fields for the study of micro-/nanomaterials. Electron crystallography is used to collect different information by electron scattering. This has been used to study crystal structures and defects. After first electron microscopy image taken in 1933, the constant engineering developments from the last 80 years or so made it possible today to record high resolution transmission electron microscopy (HRTEM) images. Moreover, the powerful computers play a very important role in the further improvement of HRTEM images as well as to analyze them quantitatively by using different image processing programs. Modern transmission electron microscope (TEM) can be used for both structure and chemical analysis. The structure analysis is performed by electron diffraction and HRTEM, while the chemical analysis is performed by energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS).

Although X-ray crystallography is known to be the best technique for the structure determination of unknown crystals, but under certain conditions, electron crystallography has some advantages over X-ray crystallography:

- An electron scatters much more strongly than X-rays. Thus, much smaller crystals, million times smaller than those needed for single crystal X-ray diffraction can be studied by electron crystallography. The structure analysis (such as grain boundaries, phases, etc.) of crystals, too small for X-ray diffraction, can be done by electron crystallography.

- HRTEM images of crystals can be recorded in electron crystallography while in X-ray crystallography, imaging is not possible. The phase information remains preserved in the case of HRTEM images.

- The interaction mechanism with the crystal is also different for electron diffraction and X-ray diffraction. Electrons study electrostatic potential distribution in crystals while X-rays study electron density distribution in crystals.

- The X-ray powder diffraction gives results from a sample which may contain millions of small crystals while electron diffraction gives results from a single

or just few crystals. In some materials, where the phases are found to intergrow with each other cannot be solved by X-ray crystallography, whereas in electron crystallography, this problem is eliminated as much smaller crystals are needed for electron diffraction.

- The defects in crystals can be studied using HRTEM images.

Radiation damage is the common problem in X-ray crystallography and electron crystallography. This is especially troublesome in the case of electron crystallography. The proteins and organic molecules are the main sufferers when they are being imaged. Radiation damage can be limited by using electron cryo-microscopy where samples go through cryo-fixation and imaging done at liquid nitrogen or liquid helium temperatures. Due to this, X-ray crystallography is more successful for the structural study of proteins that are more prone to radiation damage. Recently, radiation damage was investigated by MicroED for three-dimensional (3*D*) thin crystals [1, 2]. In the past few years, several protein structures are studied by electron crystallography. The studies on inorganic crystals by electron crystallography were first done by Klug [3] and Hovmöller et al [4]. They used HRTEM images as it is possible to choose thin regions along the edge of the crystal for structure analysis using crystallographic image processing program (CRISP).

In recent years, electron diffraction is widely applied for determining the structure of unknown crystals [5–8]. Electron diffraction is a technique which is well-complementing other techniques, single crystal X-ray diffraction and powder X-ray diffraction for determination of structure. Electron diffraction plays a very important role when crystals are very small for study using single crystal X-ray diffraction or very complex for structure solution by powder X-ray diffraction. The main drawbacks of electron diffraction are the problems in the complete collection of 3*D*-electron diffraction data using standard diffraction techniques and the collection of data is very time consuming. Also, the electron diffraction intensities suffered from dynamical scattering. There are two methods which are developed for the collection of complete 3*D* electron diffraction data: the rotation electron diffraction (RED) and automated electron diffraction tomography (ADT) [8, 9].

With the introduction of advanced methodologies, recently, one of the most important methods for crystal structural analysis in the field of electron crystallography has been discovered. This software-based method is named as rotation electron diffraction (RED), which is capable of overcoming the drawbacks and reducing the dynamical effects [8]. There are two computer programs in a software package, that is, RED data collection and RED data processing. The program for collection of 3*D*-electron diffraction data used the combination of goniometer tilt and electron beam tilt in a transmission electron microscope (TEM). A fine step in the range 0.05–0.20° of electron beam tilt combined with a coarse step in the range 2.0–3.0° of goniometer tilts at common tilt-axis allowed to cover a crystal in a large range of tilt. At every combination, electron diffraction frames are collected. With the collection of about 1000–2000 electron diffraction frames, a complete 3*D* data set is obtained. Thus, a complete 3*D*-electron diffraction data set from a submicrometer sized single crystal can be collected in about 2 hours.

The program processes 3*D*-RED electron diffraction data created by the program RED data collection. It consists of correction of shift in electron diffraction frames, peak search in individual electron diffraction frames for diffraction spots, and identifying diffraction spots as reflections in 3*D*. The program containing RED data processing used to view and analysis of 3*D* reciprocal lattices which are reconstructed from electron diffraction frames. RED method is more capable for determination of structure and identification of phase of crystals which are not

known. It is faster, easier, and more straight-forward than powder XRD and other techniques based on electron microscopy. The configuration used in RED is similar to the technique involving rotation as used in X-ray diffraction. Along one rotation axis, the sample is rotated continuously. Instead of doing continuous crystal rotation, coarse crystal rotation and fine electron-beam tilt on the same axis of rotation are combined in TEM. At every combination of crystal rotation and beam tilt, electron diffraction frame is collected. The 3*D*-reciprocal lattice is reconstructed from the collected electron diffraction frames with the help of RED data processing program.

RED has been used in the recent years to solve large number of crystal structures. These include the most complex zeolites ever solved, open-framework compounds, and quasicrystal approximants, such as the pseudo-decagonal approximants [10–13]. The quasicrystal approximants are dense intermetallic compounds and consist of heavy elements. Thus, they are usual to have higher dynamical scattering. It is more challenging to solve the structure of quasicrystal approximants using RED. Quasicrystalline phases are having forbidden rotation symmetry in their electron diffraction pattern, which are not compatible with periodic translation. Quasicrystals are discovered in 1982 by D. J. Shechtman. A new idea of ordered but non-periodic arrangement of atoms exhibiting sharp diffraction peaks (with icosahedral symmetry) is created due to the breakthrough experiments by Shechtman et al. [14] on rapidly quenched alloys (AlMn) using TEM. Due to the aperiodicity, these materials can be used for applications in industries as they are having properties different from that of conventional metallic materials [15–24]. Quasicrystals are known by a group of different properties, for example, higher hardness, low friction, low-surface energy, and thermal expansion which is as good as metals [25–29].

After the quasicrystals discovered in rapidly quenched AlMn alloys [14], the most important part of their studies has been related to their structure solution. The structure of quasicrystals has not been yet solved. A number of crystalline phases have been observed which are having crystals made up by the same clusters as found in quasicrystals, and they are named as quasicrystal approximants. These approximants are often found to co-exist with quasicrystals. They have similar electron diffraction patterns and similar chemical compositions as that of quasicrystals [30–35]. The local atomic structures are similar in both quasicrystals and quasicrystal approximants. Thus, the structural study of quasicrystal approximants is an efficient way to understand the quasicrystalline structure. Many quasicrystal approximant series have been observed which are closely related on the basis of their structures. Out of the many quasicrystal approximants that are found till yet, only small number of them has been solved to atomic resolution. In this context, RED method is used to solve two very complicated alloy structures of pseudo-decagonal quasicrystal approximants PD2 and PD1 in Al-Co-Ni alloy system [12, 13]. These are built of characteristic 2 nm wheel clusters with five-fold rotational symmetry [36].

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