Structure solution by electron diffraction

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Introduction

X-ray diffraction is the mainstream technique for the determination of crystal structures. However, recent advances in electron diffraction techniques lead to the development of new electron diffraction techniques and data analysis methods, which result in the possibility to solve and refine crystal structures using electron diffraction data. The key advantage of this approach is the possibility to obtain electron diffraction patterns from very small crystals, down to X0 nm.

The most important difference between the x-rays and electrons used as a radiation for diffraction experiments lies in the strength of their interaction with matter. Electrons interact roughly thousand times more strongly than x-ray photons. This is the reason why moderate doses of electrons can be used to obtain diffraction patterns from nanocrystals, while similar doses of photons cannot. The downside of the strong interaction is the occurrence of so-called dynamical scattering in electron diffraction. Dynamical scattering effects arise, when an electron gets scattered in the crystal more than once (Fig.1).

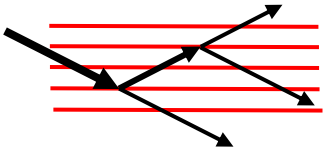

Figure 1. Schematic representation of double diffraction on a set of crystal planes. Part of the incident beam is diffracted, and part of the diffracted beam is diffracted again in the direction parallel to the incident beam. In real diffraction, such multiple scattering usually occurs with more than one diffracted beam simultaneously.

In absence of dynamical scattering effects (*i.e.* when a so-caled kinematical approximation is valid), the diffracted intensity is proportional to the square of the structure factor amplitude of the crystal structure. This relationship is very well fulfilled for x-ray (and also neutron) diffraction, and is the basis of all methods for solution and refinement of crystal structures. In electron diffraction, however, the dynamical scattering breaks this relationship and solving and refining crystal structure from electron diffraction requires special considerations. Traditionally, electron diffraction patterns were taken on oriented crystals. Thanks to the short wavelength of high-energy electrons (~0.0X Å), such patterns display an almost undistorted reciprocal lattice plane and carry a direct information on the geometry of the crystal lattice (Fig. 2).

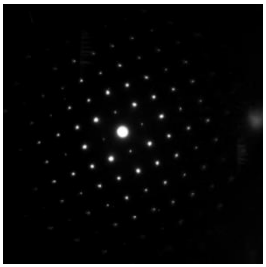

Figure 2. Diffraction pattern of the 001 zone of kassiterite SnO2 exhibiting the four-fold symmetry.

A set of zone axis patterns can be used for the determination of lattice parameters, point group symmetry and, to certain extent, space-group symmetry The downside of this approach is that in oriented patterns the dynamical effects are the strongest, and they can be used for structure determination only with difficulties.

Precession electron diffraction

Precession electron diffraction (PED) was developed in 1994 by Vincent and Midgley (1994). This technique meant a true breakthrough for applications of electron diffraction in structure analysis. The scheme of the technique is shown in Fig. 3.

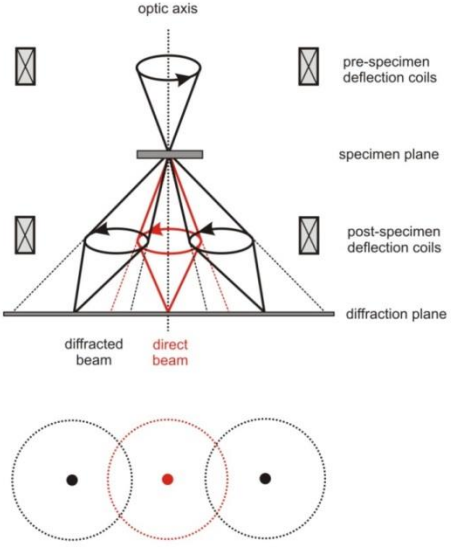

Figure 3. Scheme of precession electron diffraction.

Instead of keeping the incident beam static and parallel to the optical axis of the microscope, the beam is tilted away from the optical axis by a small angle. Then the beam is precessed around a surface of a cone with vertex fixed on the specimen. The movement of the beam in the diffraction plane during the precession cycle is then compensated by an opposite tilt of the diffracted electrons. The resulting pattern is a spot pattern that has the same appearance a standard electron diffraction pattern. However, precession diffraction pattern exhibits a number of characteristics that make it different from a standard

electron diffraction pattern, the most important being that the intensities are closer to kinematical reflection intensities than in a pattern without precession.

Electron diffraction tomography

Another technique, which is crucial for structure solution and refinement from electron diffraction data, is electron diffraction tomography (EDT). The principle of the method is identical to the rotation crystal method used to collect diffraction data on an x-ray diffractometer with area detector. The crystal does not have a special orientation, but diffraction pattern is collected at random orientation, then the crystal is rotated by a small angle and another diffraction pattern is collected. Diffraction patterns are collected in the maximum tilt range allowed by the goniometer are collected. Different flavors of this method have been developed, but the basic principle remains the same (Kolb et al. 2007., Zhang et al. 2010, Gemmi et al. 2015). EDT can be aso combined with PED (Mugnaioli et al. 2009). Because the patterns are collected in random orientation, the dynamical character of the diffraction is suppressed. The dynamical character is further suppressed by using EDT in combination with PED. EDT data can be used for ab-initio structure solution of unknown crystal structures with a high degree of success.

Structure refinement

It is a common practice to refine the structures against electron diffraction data using the kinematical approximation, i.e. assuming that the intensities can be calculated as the squares of the structure-factor amplitudes. This assumption is, however, only a very rough approximation. These *kinematical refinements* cannot be therefore taken as unbiased accurate structure models. They provide a useful tool for completion and validation of the structure solution and for obtaining approximate structural information, but the accuracy of the refined parameters is much lower than the precision indicated by the estimated standard deviations. Nevertheless, the kinematical refinement is still a very useful tool – in many cases there is no other approach available for at least an approximate optimization of the structural model. The problem with the kinematical refinement can be overcome by including dynamical effects in the structure refinement (*dynamical refinement*). This approach is computationally involved and more time consuming than dynamical refinement, but allows for very accurate determination of structure parameters. Recent tests showed that the application of dynamical refinement to EDT data combined with precession yield structure models with accuracy exceeding that attainable by powder x-ray diffraction and approaching the accuracy of single-crystal x-ray diffraction

Conclusions

Electron diffraction techniques evolved in the past decade to the stage that allows an essentially routine determination of unknown crystal structures from single micro- and nanocrystals. The main limitation of the technique is the instability of some crystalline solids, especially organic substances, under the electron beam. However, even this limitation is becoming less and less strict the advent of with new detectors of electrons and with the use of low-dose techniques.

References

Gemmi M, La Placa M. G. I., Galanis A. S., Rauch E. F. and Nicolopoulos, S. (2015), *J. Appl. Cryst.* **48**, 718-727

Kolb U., Gorelik T., Kübel C.,Otten M. T. and Hubert D. (2007), *Ultramicroscopy* **107**, 507–513

Mugnaioli E., Gorelik T. and Kolb U. (2009a), *Ultramicroscopy* **109**, 758–765

Vincent R. and Midgley P.A. (1994), *Ultramicroscopy* **53**, 271–282

Zhang D., Oleynikov P. and Hovmöller S., Zou X. (2010), *Z. Kristallogr.* **225**, 94–102