Oral Contributions

[MS17] Combined methods for soft matter and other crystallography

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[MS17-01] Single Crystal Diffraction from Powders

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The best way to do a crystal structure determination is by single crystal diffraction. Traditionally this has been done mainly by X-ray crystallography and sometimes by neutron diffraction. Unfortunately, these methods require crystals several micrometers big. For nanometer sized crystals, electron diffraction and electron microscopy are the only possibilities. While some remarkable results have been obtained on structures ranging from membrane proteins to metal alloys, it required a lot of hard work by highly skilled persons. For the modern world of nanomaterials it has become urgent to develop single crystal electron diffraction for powder-sized samples, i.e. < 0.1μm in all dimensions.

Modern transmission electron microscopes are equipped with the two things that are necessary for turning them into automatic single crystal electron diffractometers; they have CCD cameras and all lenses and the sample stage are computer-controlled. Two methods have been developed for collecting (almost) complete 3D electron diffraction data; Rotation Electron Diffraction (RED) by Zhang et al. 2010 and Automated Electron Diffraction Tomography (ADT) by Kolb et al. 2007.

ADT and RED are both performed in standard transmission electron microscopes (TEM), but with slightly different geometry. ADT is similar to screenless precession in X-ray diffraction, while RED is the equivalent of the rotation method; the sample is rotated continuously along one rotation axis. This can be done either by only goniometer tilt or by a combination of larger steps (2-4º) of goniometer tilts and finer steps (usually 0.1-0.05º) of beam tilt. Typical exposure times are 1 second or less. At +/-60º tilt with 0.1º steps, a complete data collection will be some 1200 frames and take about one hour. There is no need to align the crystal orientation.

The data processing starts with a peak hunt. All peak positions are combined in 3D. The program combines nearby peaks from adjacent frames into diffraction spots and finds the reciprocal lattice including the unit cell dimensions. Unit cell dimensions are correct to within 1% in length and 1º in angle. The reciprocal lattice can be rotated and displayed at any direction of view (Figure 1).

Space group can be determined numerically from a list of extinction conditions or by looking for extinctions in for example the *hk0* and *hk1* reflections. The whole data processing takes one hour.

There will always be a missing cone of data. It can either be filled in by symmetry-related reflections or by collecting another data set on the same crystal after rotating it around another axis than the rotation axis, or by collecting data from a second crystal. The crystal structures are solved by direct methods, charge flipping etc and then refined against all the diffraction data.

3D electron crystallography is very powerful in combination with X-ray powder diffraction. Unit cell and space group determination becomes trivial, as does the indexation of powder peaks. Multi-phasic samples appear as isolated single crystals in the EM and so can be solved one by one. In one case a complicated X-ray powder diffraction pattern turned out to be from a mixture of five compounds, all of which were

solved by RED. Only then could we index the powder pattern. On the other hand, it is necessary to collect X-ray powder patterns of the samples, because only that technique gives a representative picture of the total sample. In EM we investigate only one or a few individual grains out of the millions that are obtained from a microgram of sample. We need to make sure if these crystals are representative of the majority phase of the sample, or are from some minority phase.

Although 3D electron diffraction by ADT and RED are just a few years old, over one hundred structures have been solved already. These include inorganic and organic compounds, many of them quite complex. In fact, the most complex zeolites (porous silicates) are all solved by electron crystallography and not by X-rays.

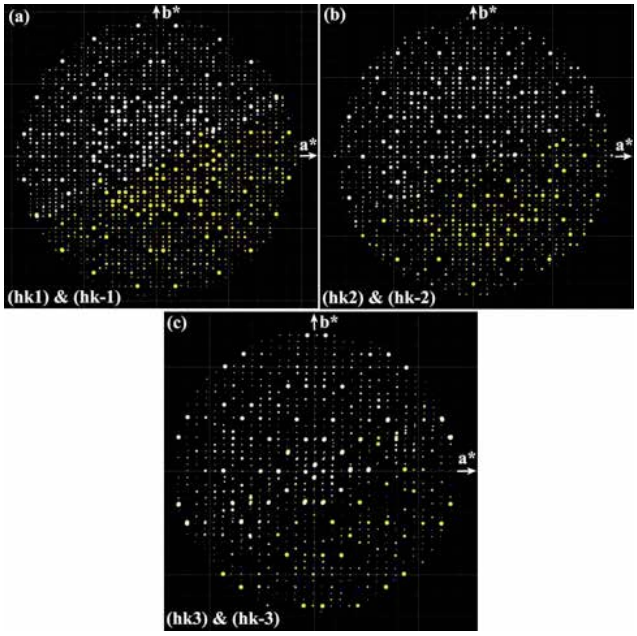

Figure 1. The three layers hk1, hk2 and hk3 cut out from the 3D RED data of the quasicrystal approximant PD2 in Al-Co-NI. From Devinder Singh et al. 2013, in manuscript. Notice the many rings of 10 or even 20 very strong reflections, typical of pseudo-decagonal (PD) approximants.

References:

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