Precession Electron Diffraction for the structure solution of unknown crystalline phases

Following the discovery of X-rays by Roentgen, W. H. Bragg and W. L. Bragg used these waves to perform diffraction experiments on crystals and to determine the atomic positions within their ordered structures. X-ray crystallography has been hugely successful in elucidating the structures of minerals, metals and intermetallics, of biological molecules from small molecules to proteins and the DNA double helix. Later, neutron diffraction came in support of X-rays for detection of light elements or for distinguishing elements with similar atomic numbers. The importance of techniques to determine structure can be understood from the fact that knowledge of their structure is paramount to the understanding (and enhancement) of the properties of materials. Here we show the power of electron diffraction for structure solution in the case of nano-scale materials.

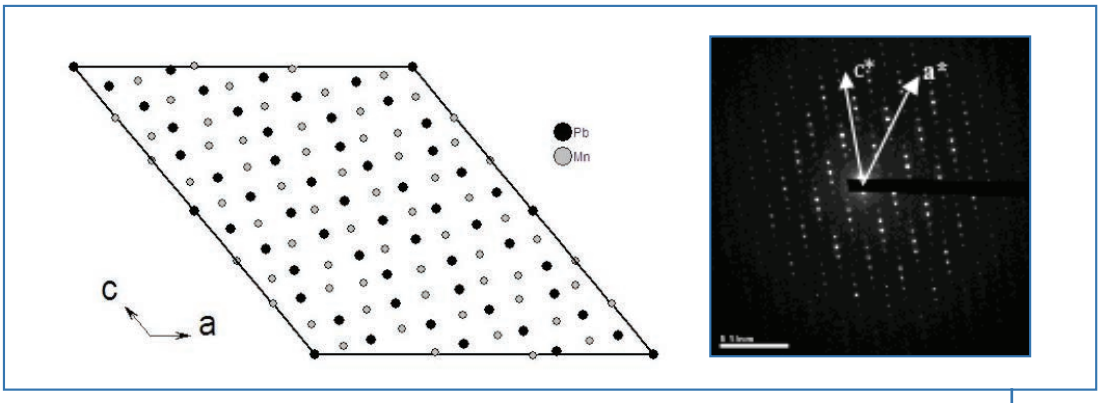

Figure: At left, projection of the cations of PbMnO2.75. At right: Precession Electron Diffraction pattern. The PED data allowed us to obtain all 29 independent cation positions.

Electrons, though they have been used for diffraction experiments in a transmission electron microscope (TEM) since 1933, have for a long time been regarded as inadequate for the solution of unknown crystal structures. This is linked to the strong interaction of electrons with matter. The approximation (routinely done for X-rays and neutrons) that a particle is scattered only once inside the crystal is no longer true for electrons. Even in the thinnest samples, many electrons undergo multiple diffraction. As a result it is extremely difficult to extract from the diffracted intensities meaningful values of the crystal "Structure Factors" used in the procedure for solving a crystal structure.

On the other hand, the strong interaction of electrons with matter is an asset when we study nano-particles. In these cases, X-ray diffracted intensities are very weak, inhibiting structure solution, while electrons are still diffracted to a considerable extent. X-ray diffraction then remains possible on powder samples, but this only yields the mean information for the sample. In the case of powders containing several different crystalline phases, this is insufficient for structure solution. It is therefore interesting to find a way to use electron diffraction for structure solution in the case of nano-structured materials.

The Precession Electron Diffraction (PED) technique, introduced in 1994, considerably relieves the problems linked to multiple diffraction. In this technique, a standard TEM is modified such that the electron beam can be tilted with respect to a crystallographic direction of the sample and precessed around a conical surface, having a common axis with the optical axis of the TEM. Even though PED reduces multiple scattering it does not eliminate it completely. Therefore, the crystallographic community has been very doubtful as to the real possibilities for solving structures by PED, even after the first successful solutions had been published.

In recent work we have studied systematically the influence of several parameters on the success of a structure solution from PED data. Our main result is that the number of measured reflections seems to be the most important parameter. To improve the chance of finding the structure solution, we need a high number of reflections, which in turn is determined by the number of zone axes accessible and the resolution that can be achieved in the reciprocal space. Surprisingly, the efficiency of this technique is not influenced by the precision of measuring the intensities of the reflections or the precision of extracting structure factors from these intensities, provided that strong reflections remain strong and weak reflections remain weak.

In order to test this hypothesis, we used experimental precession electron diffraction data that had previously been used for structure solution. We classified the reflections into just three categories: strong, medium and weak reflections. In each class we attributed the same intensity (the mean intensity of that class) to all reflections. We "deteriorated" the data in this way, for several different crystalline structures, going from simple to complex structures, structures showing low or high symmetry and crystals containing heavy or light elements or both. The structure solutions obtained from these voluntarily deteriorated data were (almost) as good as those obtained previously from the as-measured data. We still obtain the same accuracy of the cation positions; only the accuracy of the light atom positions is sometimes slightly reduced. The effects of multiple diffraction, which are the main hindrance to a precise determination of the structure factors in electron diffraction, are therefore no obstacle to structure solution.

In conclusion we have shown that the data quality obtained by Precession Electron Diffraction is quite sufficient to solve even complex structures in the case of nanometre sized particles. This technique will surely establish itself as an alternative to X-ray diffraction in the next few years.

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FURTHER READING

PRECESSION ELECTRON DIFFRACTION OF MN2O3 AND PBMNO2.75: SOLVING STRUCTURES WHERE X-RAYS FAIL

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THE QUALITY OF PRECESSION ELECTRON DIFFRACTION DATA IS HIGHER THAN NECESSARY FOR STRUCTURE SOLUTION OF UNKNOWN CRYSTALLINE PHASES

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