MS24 3D electron diffraction

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Frame-based kinematical refinement: a way to quantify dynamical effects in 3D electron diffraction

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Abstract

3D electron diffration (3D ED) is a technique that allows single-crystal structure analysis from submicrometric crystals. However, the acuracy of the structure models is still lower than what is achievable from single-crystal X-ray diffraction. One way to improve the accuracy of the structure model is to use the dynamical theory of diffraction to calculate model intensities (so-called dynamical refinement, [1]). The extent to which dynamical diffraction effects are responsible for the lower accuracy of structure refinements that do not involve dynamical diffraction theory (so-called *kinematical refinement*) is a subject of an ongoing debate.

It is dificult to compare directly the kinematical and dynamical refinement, because they require different data processing. The main difference is that kinematical refinement allows averaging over symmetrically related reflections. In dynamical diffraction, the intensities depend on crystal orientation. Thus, each diffraction pattern (aka frame) needs to be treated separately, and symmetry-related reflections cannot be averaged. As a result of the different treatment of the data, the number of parameters and reflections is not the same in dynamical and kinematical refinement, and the figures of merit cannot be easily compared.

We developed a method to circumvent the problem [2]. The amount of multiple scattering depends on the scattering power of the atoms, and it is thus possible to decrease the dynamical scattering in the model calculation by lowering the occupancy of all atoms. In the limit of almost zero occupancy, the calculation corresponds to the case with essentially no dynamical diffraction effects. Such refinement, while involving kinematical diffraction, preserves the same number of reflections and refined parameters as a full dynamical refinement. As this refinement keeps the frame-specific data treatment, we call it frame-based kinematical refinement.

Figure 1 shows a plot of wRall for an inorganic mineral natrolite and an organic compound limaspermidine as a function of the occupancy reduction. Both structures are non-centrosymmetric, and therefore wRall for both the correct and inverted model are shown.

The results of the calculations lead to the following observations:

- The dynamical effects are present in the data even for organic, weakly diffracting materials. Their description, albeit with an approximate model assuming a perfect crystal, substantially improves the fit to the data.
- The improvement of the fit obtained by dynamical refinement over kinematical refinement is not due to the different data treatment, but indeed due to the description of the dynamical effects.
- Making the data "partially kinematical", i.e. progressively lowering the atomic occupancies, does not improve the fit. Thus, when the dynamical refinement does not fit the data perfectly, it cannot be improved by assuming that the diffraction is not entirely dynamical. Instead, a different, better model of the dynamical effects in an imperfect crystal is needed.

References

[1] Palatinus L., Petricek V., Correa C. A., Acta Cryst. A **71**, 235-244 (2015)

[2] Klar P, Krysiak Y, Xu H, Steciuk G, Cho J, Zou X, et al.,ChemRxiv 2021. doi:10.26434/chemrxiv-2021-4jh14 (2021)

wRall factors as a function of occupancy reduction