Quantification of Dynamic Scattering Effects in Molecular Crystals using Large Angle Rocking Beam Electron Diffraction

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Background

Electron crystallography provides a pathway to solve structure of small crystals (< 1um) in size, and thus overcomes difficult synthesis constraints involved in growing large crystals. Generally, electron diffraction data is collected in the form of integrated intensity using continuous rotation or by precession. The measured intensities in 3D are utilized for structure solution. Using this approach, structure solution of difficult crystals, such as small crystals of zeolites, metal-organic frameworks, molecular crystals, and proteins , can be solved by electron diffraction.

However, electron structure solutions are regularly reported with higher R-values than x-ray or neutron diffraction. While similar structures are found despite the high R-values, the differences in the measure intensity and theory calculated intensity limit information that can be extracted by electron diffraction. Previous work demonstrated that including multiple-scattering effects significantly reduce the R-values . Thus, it is critical to be able to quantify the dynamical diffraction effects in molecular crystals.

Aims

Here, we introduce the large-angle rocking beam electron diffraction (LARBED) technique implemented with hardware synchronization for the quantifying dynamical scattering in large unit cell and dose sensitive crystals, such as zeolites. We report LARBED measurement from zeolite-Y crystal. The resulting patterns show the effects of dynamical interactions when scattering through an imperfect crystal. Our aim is to provide an example of the type of interactions which are limiting the statistical accuracy of methods like microED. Furthermore, we suggest that LARBED can be utilized as a complementary method, where solving the LARBED pattern will provide enhanced statistical accuracy.

Methods

The LARBED technique was implemented on an FEI Themis-Z microscope operating in precession mode with a TEM nanobeam diffraction probe. Here we establish a dark field pivot point aligned to the bottom of the sample with the range of the LARBED pattern set as the precession angle, here, 60mrad. This setup allows for a scan generator to drive the scan coils to tilt the beam rather than rastering the beam in real-space as in standard 4D-STEM

techniques. The signal then incrementally tilts the beam with a step size corresponding to the precession angle divided by the integer size of supplied signal grid. The signal was provided using the synchronized scan generator of an electron direct detector. This allows for high-throughput data collection, where 128x128 scans are taken in 17seconds providing high resolution rocking beam curves while maintaining a lower dose. Additionally, dose was minimized using the monochromator slit to 2pA and ~ 0.2mrad convergence angle as a 4.5nm FWHM probe. The Zeolite-Y sample was prepared as a dried powder on an ultrathin lacey carbon grid.

Results

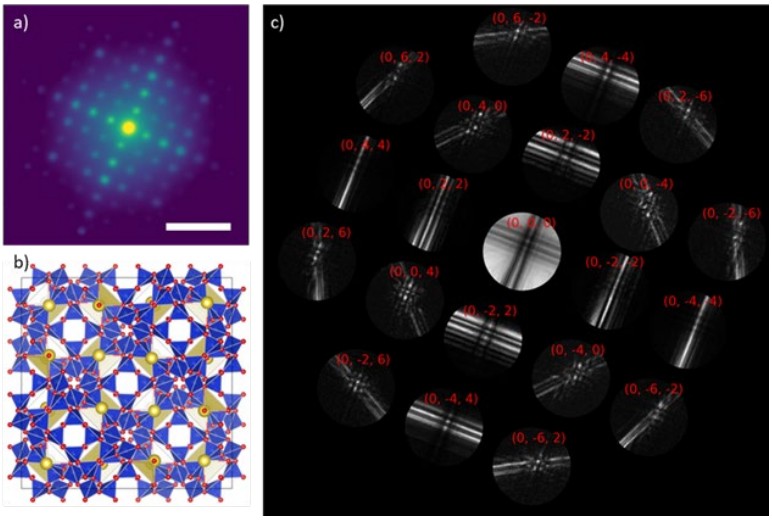
Figure 1 shows the LARBED pattern of a 60 mrad [100] obtained from a Zeolite-Y crystal. The collected datasets are a 4-dimensional stack of diffraction patterns of shape. Here, data are individual point-like diffraction patterns as a 2D array, with one pattern taken at each point on a 2D array grid of tilts. Figure 1a is the average electron diffraction pattern over all tilts, where the intensities are quasi-kinematic due to the averaging of the intensities. Figure 1b shows the expected structure of the Zeolite at the [100] orientation. Figure 1c is the recovered LARBED Patterns for individual selected disks from the incident beam to the (0,2,6) family of reflections. The bright lines perpendicular to the g-vector direction are generally where the Bragg excitation is satisfied. Note the exact zone axis displays the most complex interactions with highly varying intensity in nearly all beams. This is indicative of multiple scattering effects between many beams as they are all in or near excited conditions. This represents, to our knowledge, the first example of this type of pattern on a large unit-cell, dose-sensitive crystal.

The details within the disk excitation lines also show the effects of small crystalline differences. For a perfect Ia-3d cubic crystal we expect each family of reflections to maintain expected mirror and rotational symmetries(4mm1R). In this case, there are several excitation lines with variations in the families of reflections. These deviations will also be present when performing microED and will subsequently affect the intensity integration. These types of deviations are not accounted for by multiple scattering alone.

Conclusions

Our results show unexpected intensity variation relevant to electron diffraction intensity integration. The splitting of excitation lines is the result of dynamic effects from small defects, orientation, or thickness differences in the sampled region of the crystal. These effects are apparent in LARBED patterns and can potentially be utilized to supplement microED data in the future. Careful selection of the intensities from LARBED patterns have the potential to aid statistical analysis of solved crystal structures.

Graphic:



Keywords:

Electron Diffraction, Crystallography, Dynamic Scattering

Reference:

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