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Electron crystallography – diverse facets of nanocrystalline materials

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Electron crystallography came on the scientific scene 15 years ago with the introduction of automated procedure for stepwise electron diffraction data acquisition – automated diffraction tomography (Kolb, et al., 2007). Later, diverse instrumental variants of the method appeared (Gemmi et al., 2019, Gruene & Mugnaioli, 2021), including rotation electron diffraction (RED), precession-assisted electron diffraction tomography (PEDT), and continuous rotation electron diffraction (cRED, essentially equivalent to microcrystal electron diffraction, microED). In the meantime, all these techniques are located under an umbrella term of 3D electron diffraction – 3D ED. The success of 3D ED for structure analysis is given by the simplicity of the data acquisition and the possibility to use procedures established within X-ray crystallographic community. Successful structure analysis from 3D ED data were reported for different classes of materials, featuring a structure determination of an unknown protein (Xu et al., 2019), structure analysis of twinned orthocetamol crystals (Andrusenko et al., 2019), MOFs and COFs (Huang et al, 2021a) and zeolites (Su et al., 2014). Potential of the method as high-throughput technique is demonstrated by Bruhn (Bruhn et al., 2021) and Burch (Burch et al., 2021).
Possibilities to automate the data collection have opened a new facet of the method – serial electron crystallography – the collection of series of small datasets with partial completeness or single diffraction patterns from individual randomly oriented crystals. The method has been effectively used to identify and solve structures of inorganic (Smeets et al., 2018) and biological (Buecker et al., 2020) compounds. Cluster analysis of the serial electron diffraction data allowed identifying and analysing individual components in a complex polyphasic system (Wang et al., 2019).
Analysis of electron scattering intensities between the Bragg peaks allows for structure analysis of features beyond the average crystalline structure (Mugnaioli & Gorelik, 2019) of nanocrystalline materials. Models of stacking faults in nanocrystalline layered materials can be constructed from quantitative analysis of diffuse scattering lines within the reciprocal space (Krysiak et al., 2018). Furthermore, 3D ΔPDF maps obtained from 3D ED data (Schmidt et al., 2021), allow for analysis of interatomic distances correlation in materials with high amount of point defects just as it can be done from X-ray or neutron diffraction data.
Crystal size confinement produces extended features in the reciprocal space. In the extreme case of 2D crystals, the reciprocal space consists of continuous lines – relrods – which can be seen as a special case of diffuse scattering. Analysis of scattering intensities distribution along the relrods allows to assign the number of repetition units in a crystal, i.e. determine the number of layers in a 2D crystal (Gorelik et al., 2021).
Finally, the structure of amorphous material on nanoscale can be studied using electron Pair Distribution Function (ePDF) and Fluctuation Electron Microscopy (FEM), where ePDF (Gorelik et al., 2019; Ehrhardt et al., 2021) allows for “bulk” structure analysis of the material, whereas FEM (Voyles & Muller, 2002) provides information on the local atomic arrangement (Huang et al., 2021b).

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