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Determination of Ti3C2Tx Mxene few layers stacks architecture using valence EELS and diffraction

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The properties of two-dimensional (2D) materials generally depend on their architecture, e.g. the number of layers in a stack, the interlayer distance or the layer functionalization. Focusing on the most studied MXene compound to date, i.e. Ti3C2Tx 2D layers (where T-groups usually correspond to O, OH, F and/or Cl surface terminations inherited from the synthesis process), it has been shown that physical properties have a significant dependence on the number of layers in few-layer stacks. Beyond their thickness, MXene properties are also very sensitive to the interlayer distance which can be increased by intercalation of ions and/or molecules, or reduced by removing the interlayer intercalated water. In order to evidence the thickness/properties interplay in this rich family of 2D materials, one thus needs to precisely determine the architecture of a given MXene few-layer stack during TEM experiments. In this context, we show that valence EELS (VEELS) which corresponds to the excitation of the materials valence electrons, combined to density functional theory (DFT) simulations, provides a direct way to quantify (i) the number of layers in Ti3C2Tx few layer stacks for thicknesses up to ∼10 layers, and (ii) the average inter-layer distance. [1]

Figure 1 shows a comparison between experimental VEEL spectra recorded on different Ti3C2Tx multilayers and the spectra simulated for different numbers of layers. To push the comparison quantitatively the mean squared error between experiments and simulations has been plotted, allowing to determine the exact number of layers in the thinnest samples. In addition, the position of the main peak, corresponding to the bulk plasmon, is closely correlated with the distance between sheets in the stack. Its shift can thus be used to estimate interlayer distance variations in a MXene multilayer with nanometer scale resolution

Finally, the thickness of a sample can also be obtained through diffraction measurements and intensity profiles STEM-HAADF analysis. Therefore in order to validate the thickness measurements obtained by the VEELS method, position averaged CBED (PACBED) patterns and STEM-HAADF images were recorded on the very same areas of the Ti3C2Tx MXenes. Different families of reflections exhibit different behavior of their pendellösung allowing to determine the sample thickness by comparison between experimental and simulated intensity ratios (Figure 2). PACBED and STEM-HAADF analysis confirm the outcomes of the VEEL spectra analysis.

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Figure 1: (Left) Comparison between experimental VEEL spectra (black and grey curves) and DFT simulations considering thickness effects with the Kröger formula (color curves). Spectra were recorded on a FEI Themis Z microscope, equipped with a monochromator and operated at 80 kV. (Right) Mean squared error between experimental curves and simulations. It shows the very good precision on thickness determination for very thin samples.

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Figure 2 : Pendellösung of the 100 and 110 reflections in the [001] zone axis and intensity ratio between the reflexions as a function of the thickness.

Graphic:

Figure 1:

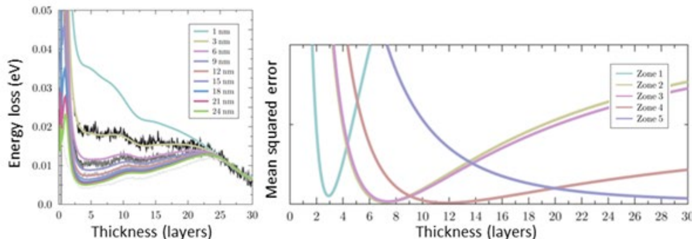
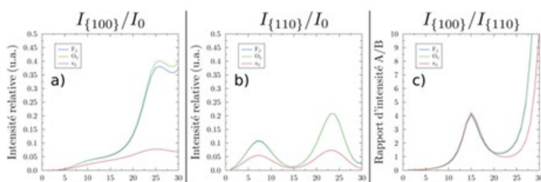


Figure 2:



Keywords:

low-loss, thickness measurement, diffraction

Reference:

[1] T. Bilyk et al., 2D Materials, 9 (2022), p.035017