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Difficult Measurements of Materials Systems at Cryogenic Temperatures: Cryo-EELS and Cryo-4D-STEM

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Scanning/transmission electron microscopy (S/TEM) in materials science has traditionally been accomplished at room temperature due to their solid state in this temperature range and relative insensitivity to radiolysis damage. Cooling to cryogenic temperatures tended to introduce instabilities such as vibration and drift and can lead to the buildup of carbon contamination or ice reducing contrast.[1] The need to expand TEM experimental techniques into new fields such as quantum and battery materials led to new efforts to reduce these instabilities while achieving temperatures at or well below liquid nitrogen (77 K). Further, developments in detector and spectrometer technology brought new capabilities for high resolution electron energy loss spectroscopy (EELS) and scanning nanodiffraction (4D-STEM).[2, 3] These experimental modalities can require even tighter controls of drift, vibration, and exposure time. This presentation will discuss accomplishing difficult experiments at cryogenic temperatures in honor of the late Dr. Lena Kourkoutis who inspired and led many such experiments.

Heterostructures made from mechanically stacked 2D Van der Waals materials provide an exciting new route to developing new material systems with customized, emergent properties. Stacking incommensurate materials or adding a twist angle leads to the formation of a moiré superlattice with optoelectronic properties. Improvements in energy resolution and detector sensitivity have made STEM-EELS an excellent platform for directly correlating the emergent excitonic properties with structural morphology at nanometer scale resolution. The weak excitonic signal requires low temperature measurements and structural encapsulation with hexagonal boron nitride further complicating the experiment. Through cryogenic, monochromated STEM-EELS and ADF-STEM, we correlated the structural reconstruction with exciton confinement with nanometer scale resolution.[4]

Most batteries consist of an anode and cathode separated by a conducting material such as an electrolyte that allows for ionic conduction but not electron conduction. The electrolyte thus allows ions (like lithium) to move from one side to the other while extracting or storing current. Determining the structural order of molecules dissolved in liquid electrolytes could provide insights into properties such as electrical conduction, ion transport, and crystallization properties. Their liquid nature makes TEM observation difficult due to the need to be suspended in vacuum and their extreme sensitivity to radiolytic damage. We thus utilized a liquid cell to contain a model organic electrolyte within the TEM vacuum at sub-freezing temperatures between 273 and 77 K to study the structural order using 4D-STEM and STEM-EELS. We find the system separates into regions of high salt concentration and a liquid with high short-range order.[5, 6]

We will discuss these measurements and their physical significance with an eye towards future developments needed to make these experiments more routine.

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