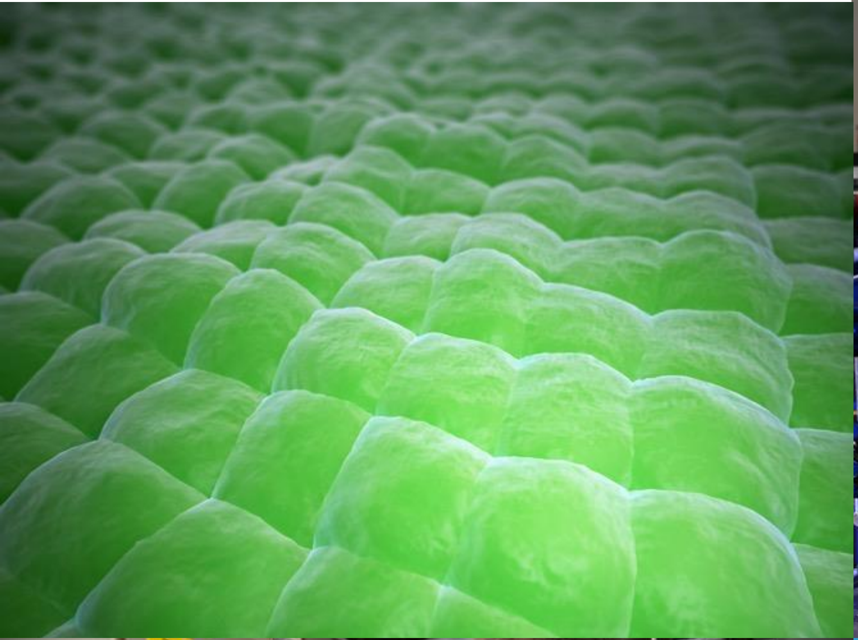
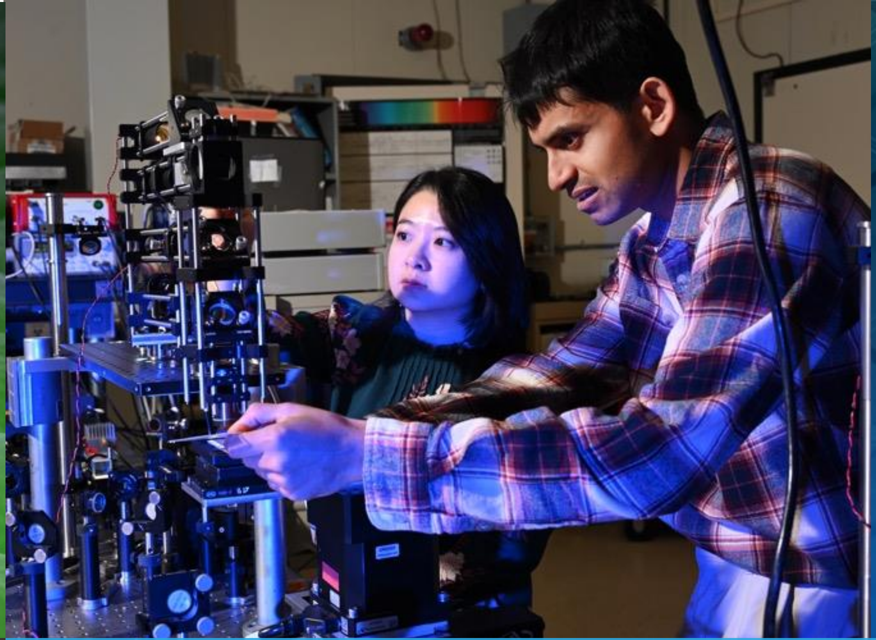


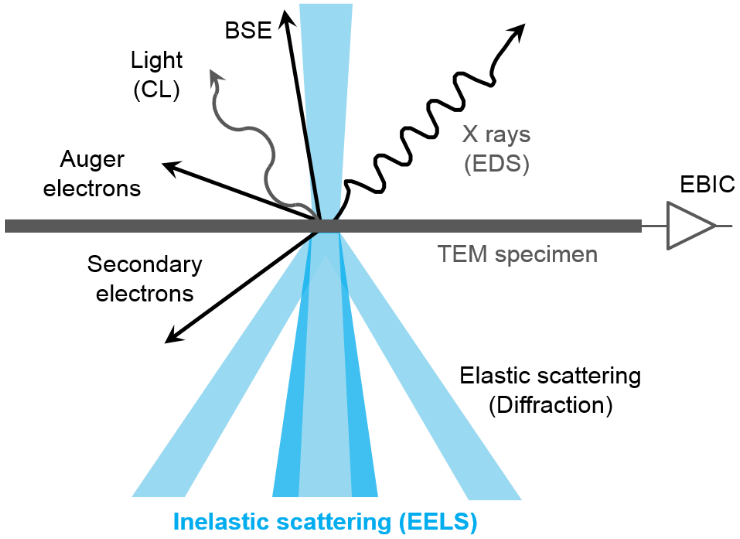


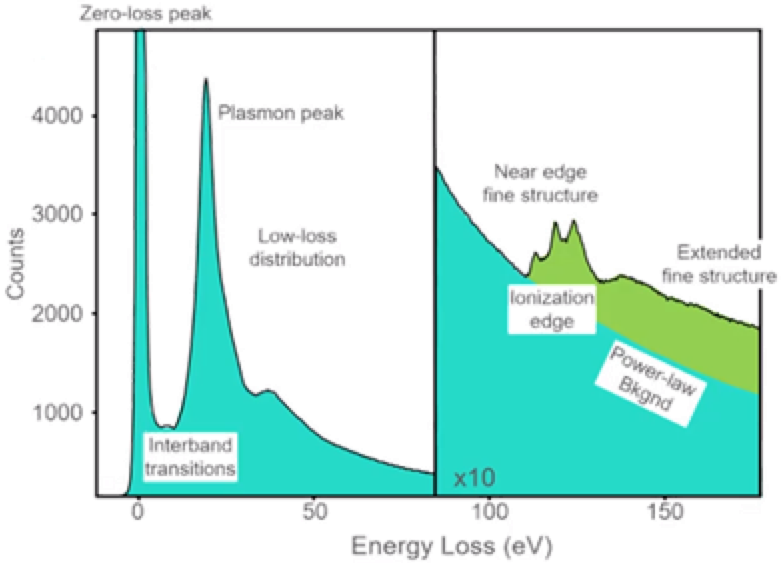
April 17th, 2024

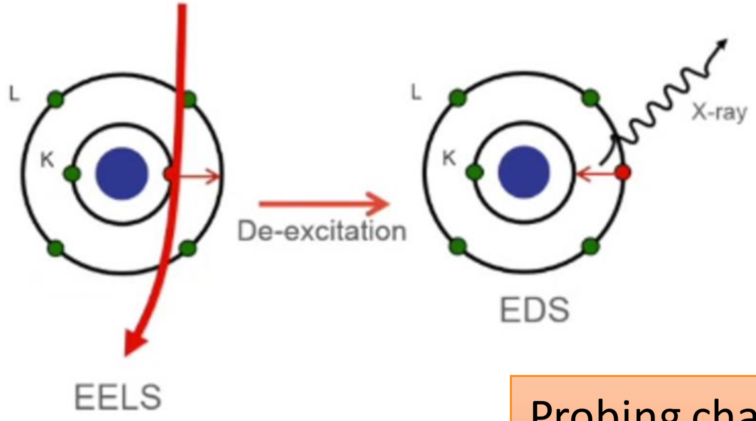
**Kaustubh K. Bawane**
Staff Scientist

# Determining Valence States using Electron Energy Loss Spectroscopy (EELS)

# Electron Beam and Specimen Interactions




**Core loss region – ionization edges**

- Near edge spectrum – Valence states – represent characteristic transitions
- For transition metals – $L_{2,3}$ edges (2p→3d transition), for lanthanides/actinides – $M_{4,5}$ edges (3d→5f transition)

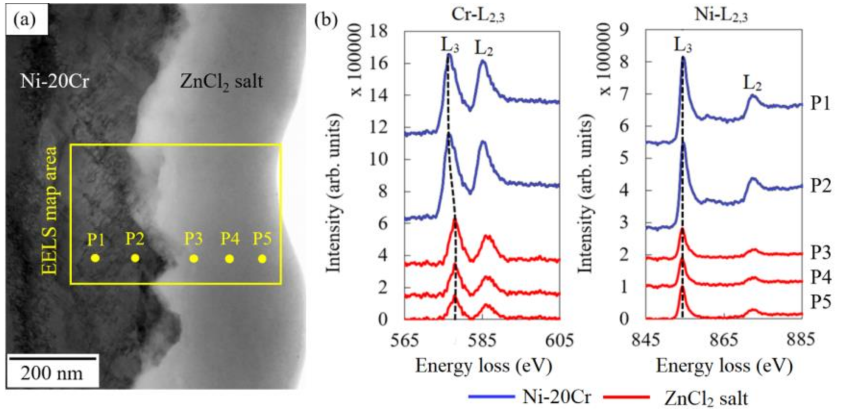
Probing changes in valence states is useful for corrosion, FCCI studies in nuclear materials

eels.info

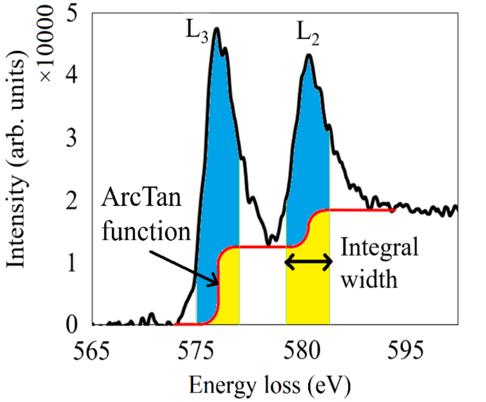
# Valence state analysis:

**Example: Molten salt corrosion of Ni-20Cr**

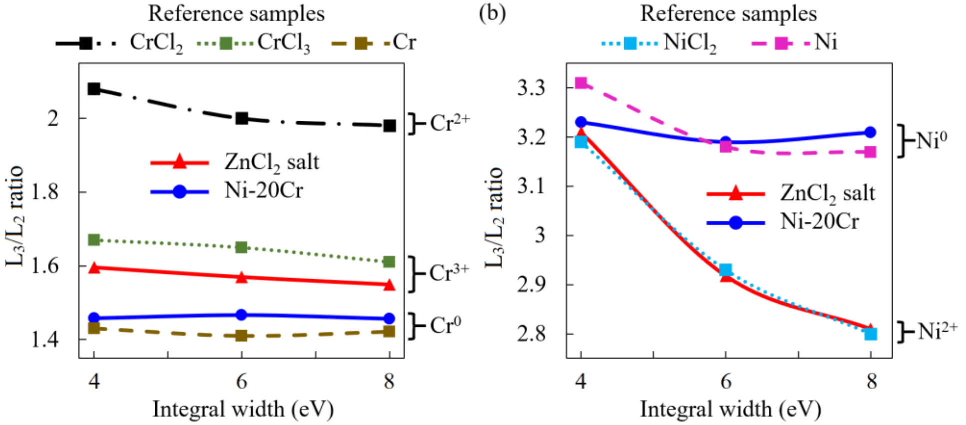
Cr-$L_{2,3}$ and Ni-$L_{2,3}$ EELS spectra at different locations




$L_3/L_2$ ratio to determine valence states




K. Bawane, *Scripta Materialia*, 2021




**Challenges with valence state analysis using EELS:**

(1) EELS analysis is not straightforward – needs a lot of preprocessing. Vendor's software provides only basic functions

(2) Standard reference spectra are needed for each compound

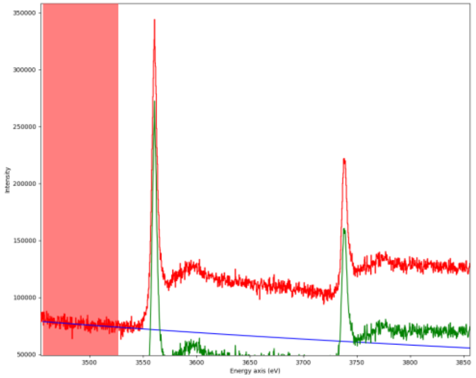
- Depends on instrument and acquisition parameters, sample thickness, calibration issues
- Online EELS database on some nuclear materials is limited

# Overview of NSUF instrument scientist (NSUF-IS) work

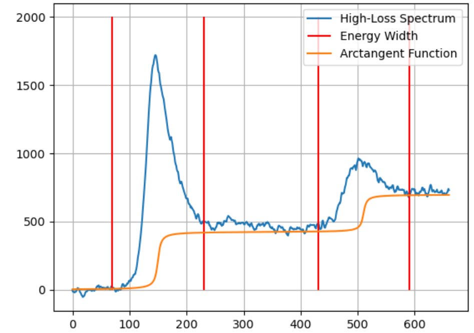
**Past FY:**

- Improved EELS acquisition procedures for high energy losses (especially for actinides)
- Automated the preprocessing – aligning spectra with zero loss peak, background correction, plural scattering removal, spikes removal, etc.
- Automated $L_3/L_2$ ratio measurements to reduce manual errors
- Denoised spectra at individual pixel using principal component analysis (PCA) for mapping purposes

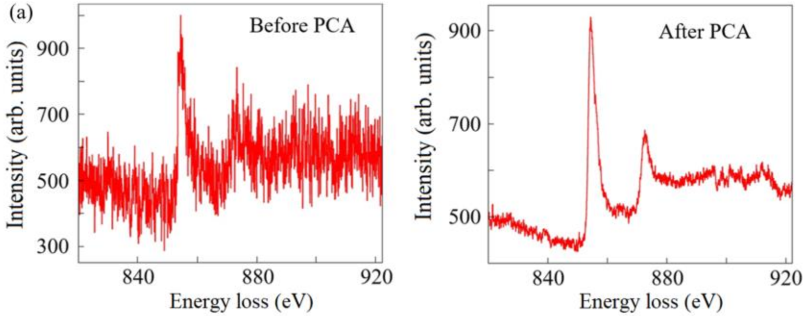
**Background correction**

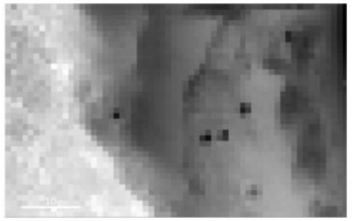


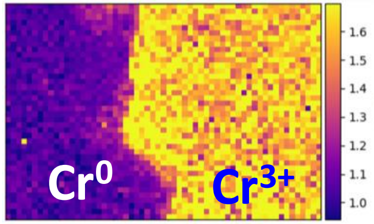
**$L_3/L_2$ ratio analysis and mapping**




**PCA denoising of EELS**





# Overview of NSUF instrument scientist (NSUF-IS) work

**FY 2024**

**Problem statement:**

1) Every analysis needs standard reference spectra. Can we make a repository of EELS core loss edges and use it for future analysis?

Current collection of standard reference spectra at INL:
Transition metal compounds: $Fe_2O_3$, $Fe_3O_4$, $FeCr_2O_4$, $FeCl_3$, $FeCl_2$, $NiCl_2$, $Cr_2O_3$, $CrCl_2$, $CrCl_3$
Lanthanides: $CeO_2$, CeN, $CeCl_3$, $EuCl_2$, $EuCl_3$
Actinides: $UCl_3$, $UCl_4$, $UCl_5$, $UO_2$, $UO_2(O_2)$, $UO_3$, $U_3O_8$, UN, $U_2N_3$, Pu borides
Mixed compounds: $UCl_3$+10wt%$UCl_4$, $UCl_3$+50wt%$UCl_4$

2) Use deep learning based EELS analysis – more accurate, instrument calibration invariant, no need for preprocessing

**Online databases**

EELS Data Base
Inner & Outer Shell Excitation Spectrum Repository

The Materials Project

- All the historic data at INL, data from the online repositories, and literature data may not be enough for deep learning
- Where will the vast amount training/test data come from?

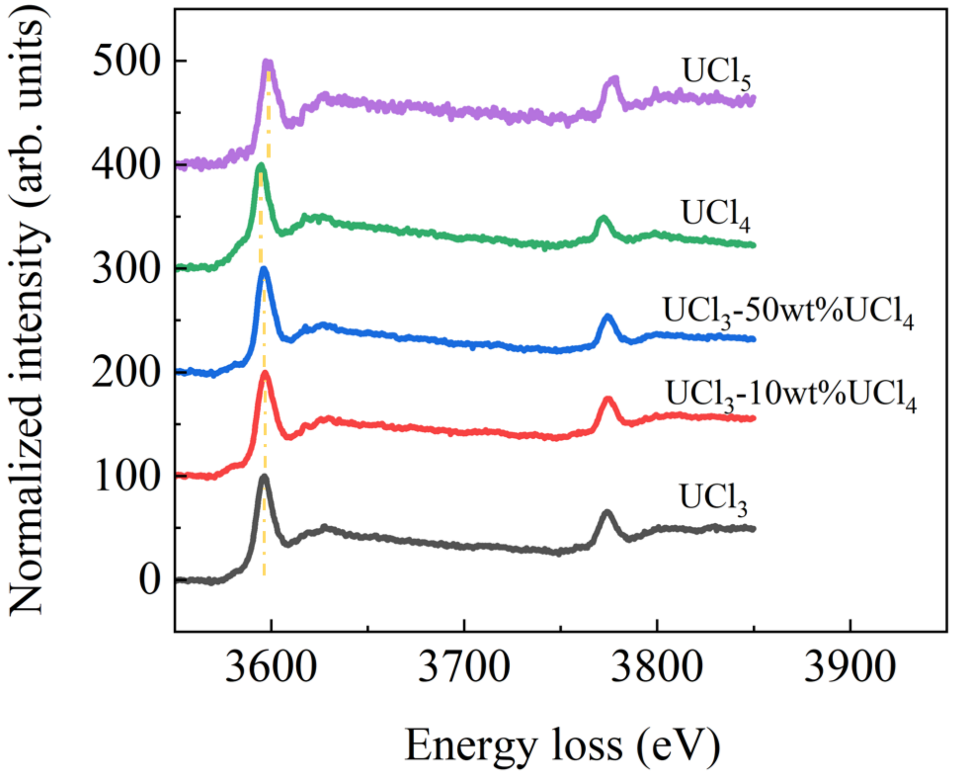
# Difficulties for samples with mixed valence states

- Technically it is possible to decompose EELS spectra into linear combination of reference spectra of each valence state

e.g., sample containing Mn ions with $Mn^{2+}$, $Mn^{3+}$, $Mn^{4+}$ - but this decomposition is affected by sample thickness (plural scattering), calibration

- In case of uranium – calibrating energy axis is not possible as M edges lie > 2000 eV (U $M_{5,4}$ ~3550)

- TerraPower provided us with $UCl_3$, $UCl_4$, $UCl_5$, $UCl_3$-10wt%$UCl_4$ and $UCl_3$-50wt%$UCl_4$ for EELS analysis

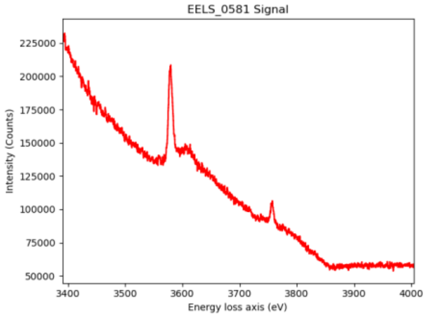



Only $UCl_5$ showed peak shift. It was very difficult to decompose $UCl_3$ and $UCl_4$ by linear combination fitting

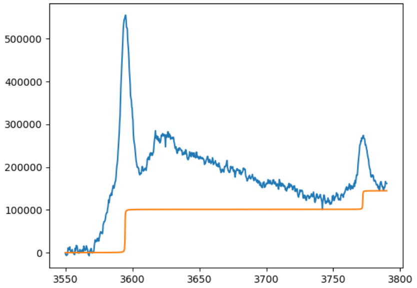
# Example: $UCl_3$ and $UCl_4$ mixed salts

**Automated $M_5/M_4$ intensity ratio measurements**

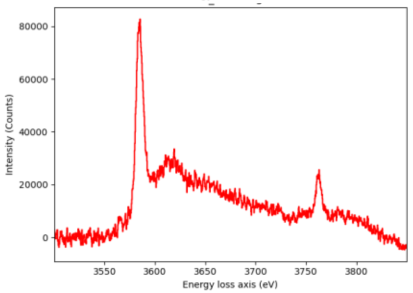
Raw U-$M_{5,4}$ spectrum



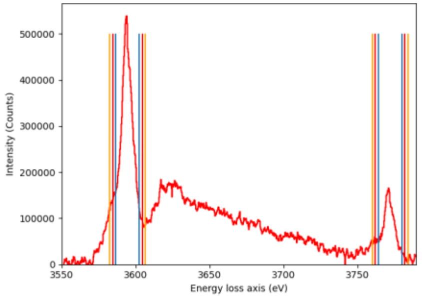

Continuum background correction (arctan function)



Power law background correction

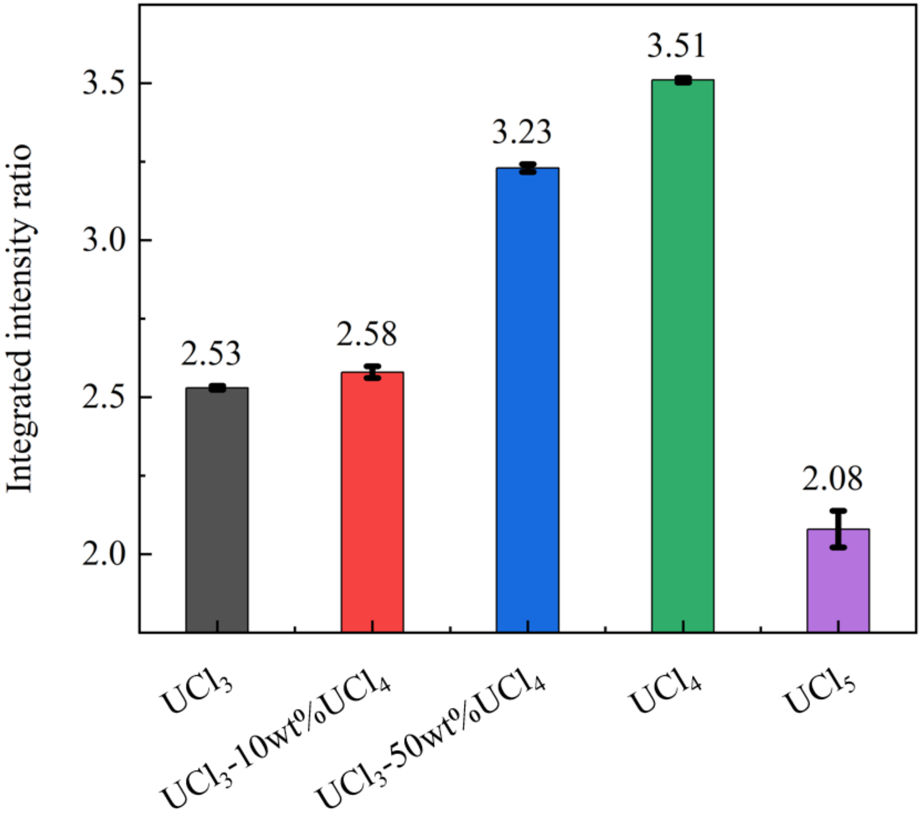



Intensity ratio measurements at different integral widths



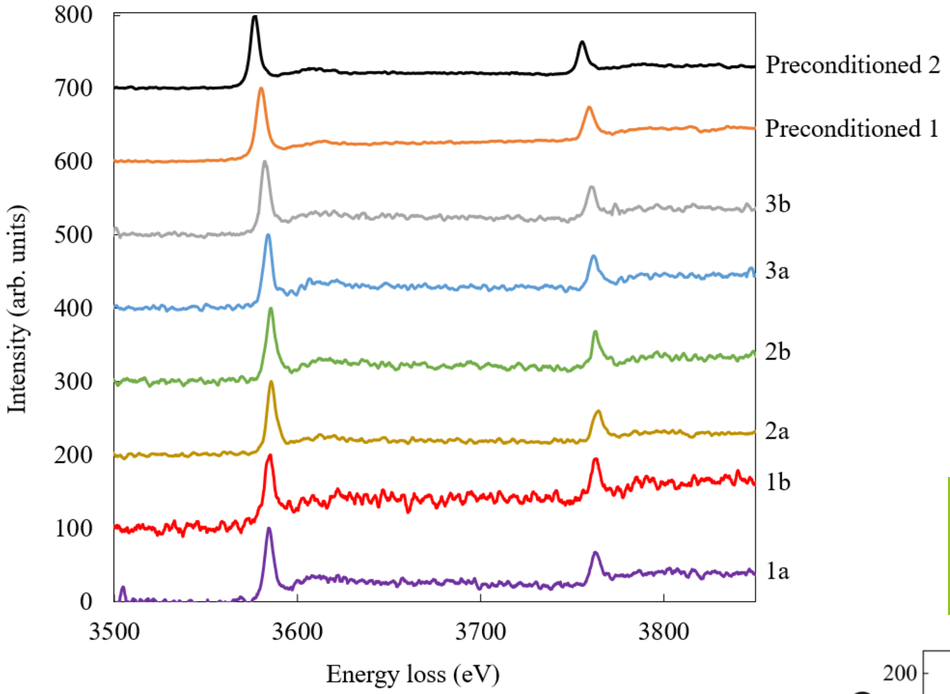

Here standard reference spectra – $UCl_3$, $UCl_4$ were collected around the same time. Energy axis calibration was addressed by acquiring zero loss peak right after U-$M_{5,4}$ edges. $M_{5,4}$ intensity ratio was carefully measured by following same protocols

$M_5/M_4$ integrated intensity ratios

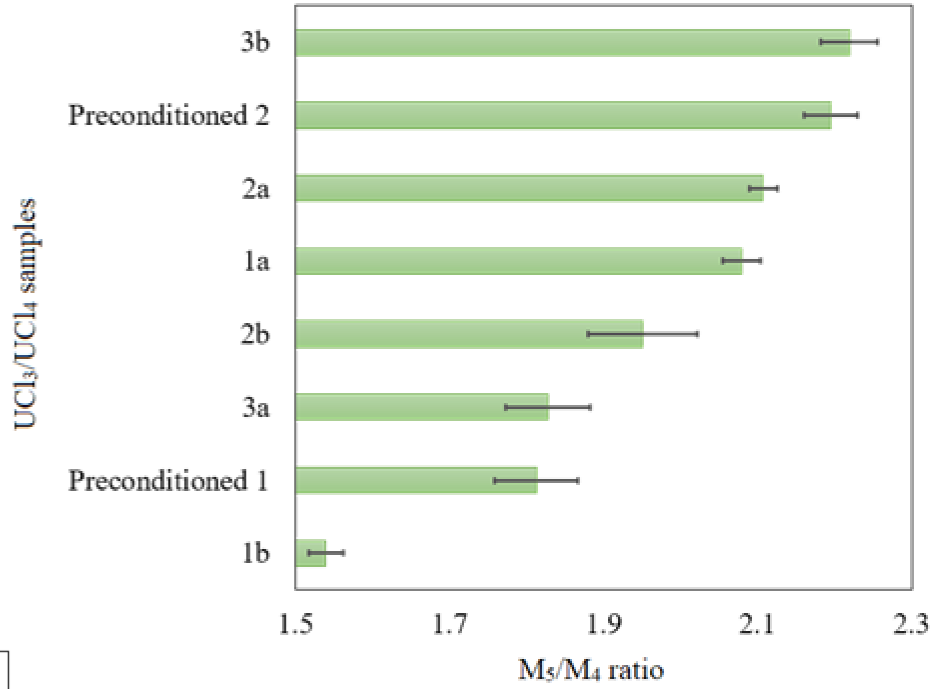


# Example: $UCl_3$ and $UCl_4$ mixed salts (unknown composition)

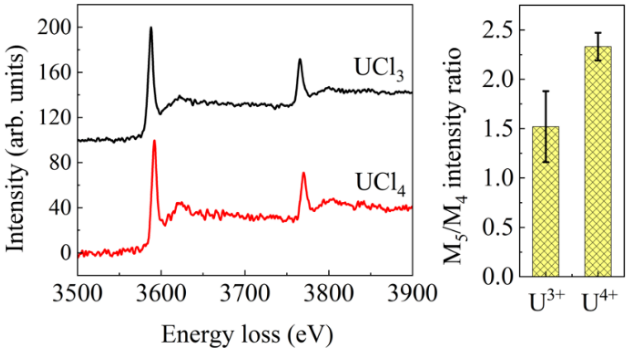
EELS of $UCl_3$-$UCl_4$ mixtures




$M_5/M_4$ ratios of $UCl_3$-$UCl_4$ mixtures




$UCl_3$ and $UCl_4$ standards from ORNL



# How do we get training and test data for deep learning based analysis? – Data Augmentation

Digitally mimicking what TEM does to data – this will allow us to create database of millions of labeled EELS spectra

Following features can be different in EELS spectra:

(1) Energy axis calibration, i.e., energy shifts
Titan TEM energy resolution ~ 0.85 eV
Spectra TEM energy resolution ~ 0.3 eV

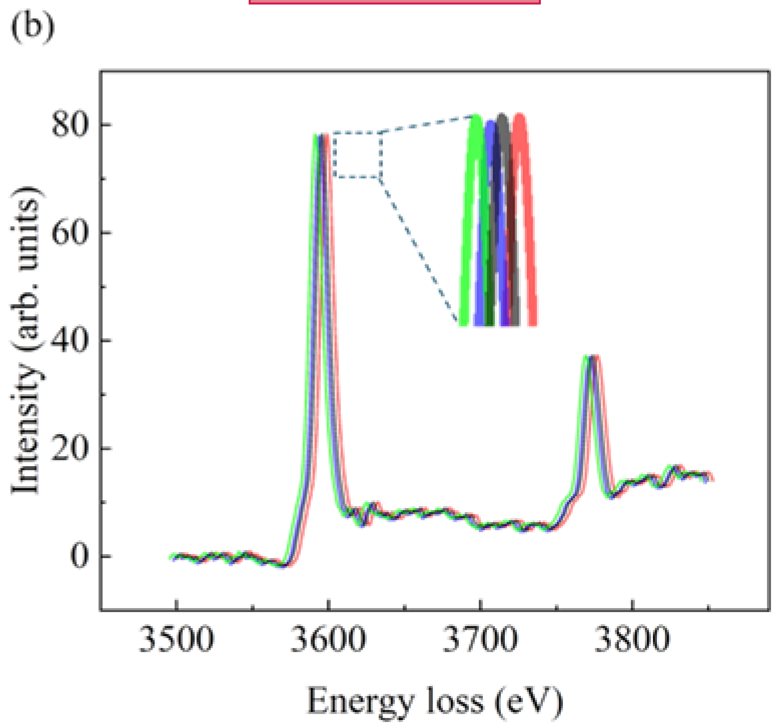
(2) Signal to noise ratios (SNR) can be different

(3) Signal broadening effect

(4) Plural scattering effect (due to changes in sample thickness)

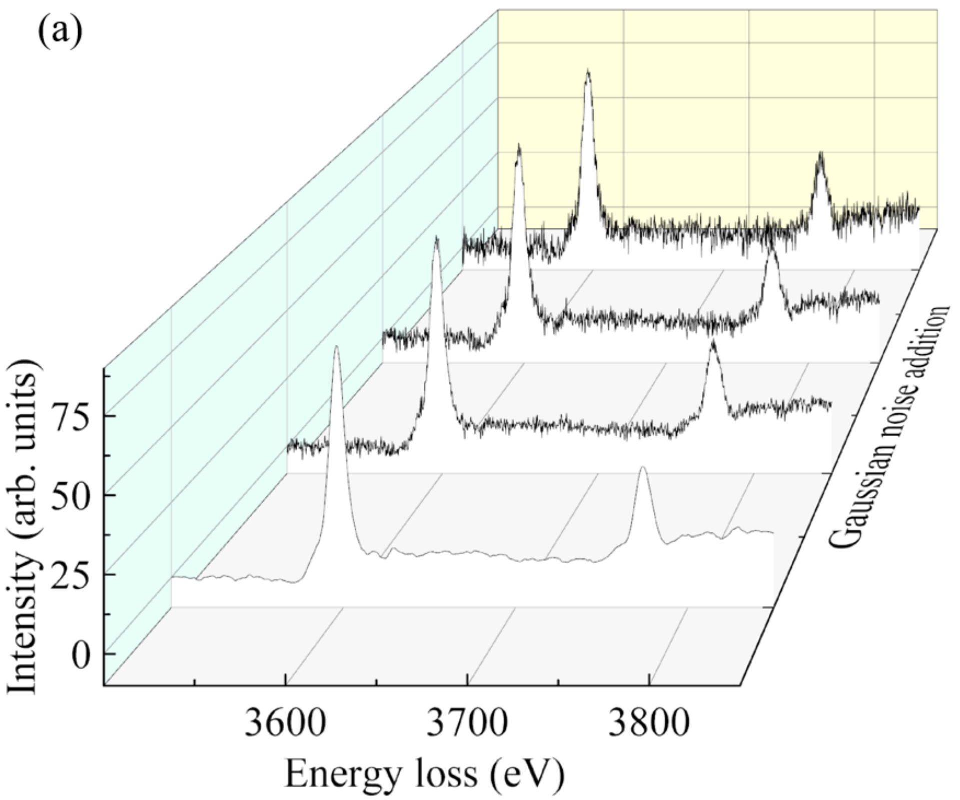
We can add these features digitally to limited available experimental data

Energy shifts



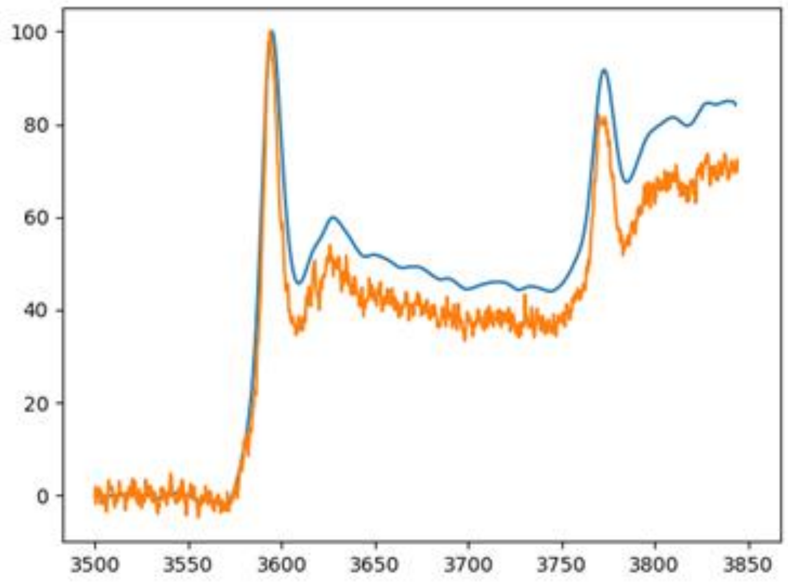
# Data augmentation example: U-$M_{5,4}$ edges in $UCl_3$

Addition of gaussian noise



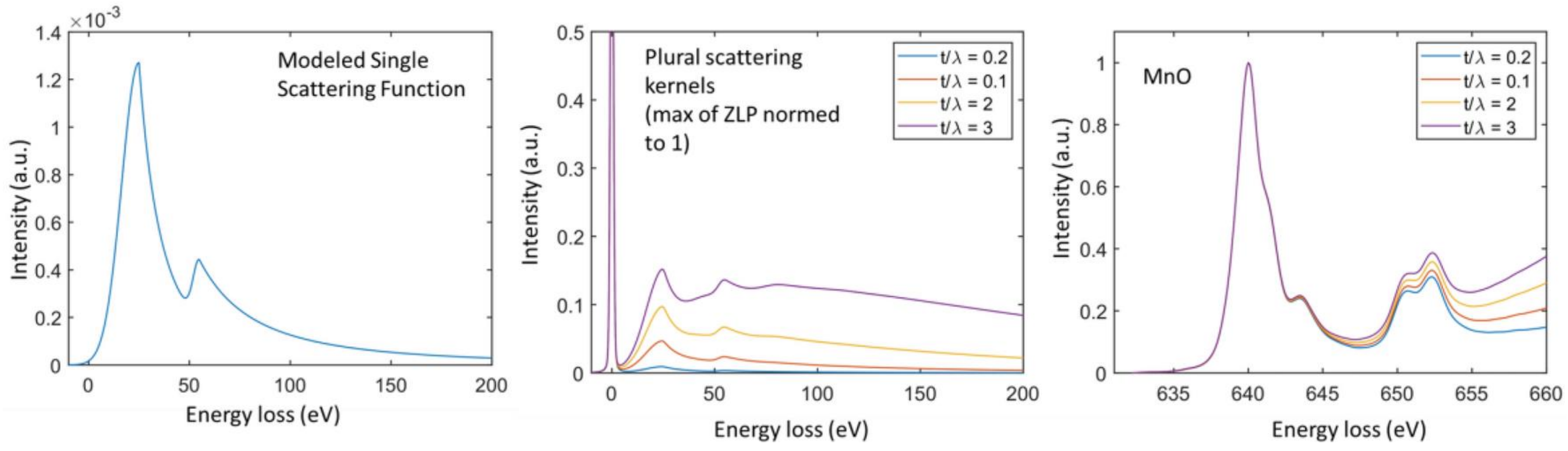

Addition of signal broadening

This involved convolution of the signal with gaussian point spread function (due to beam spread). Will also add Lorentzian point spread function (due to detector) in the future



# Data augmentation example: U-$M_{5,4}$ edges in $UCl_3$

Addition of plural scattering

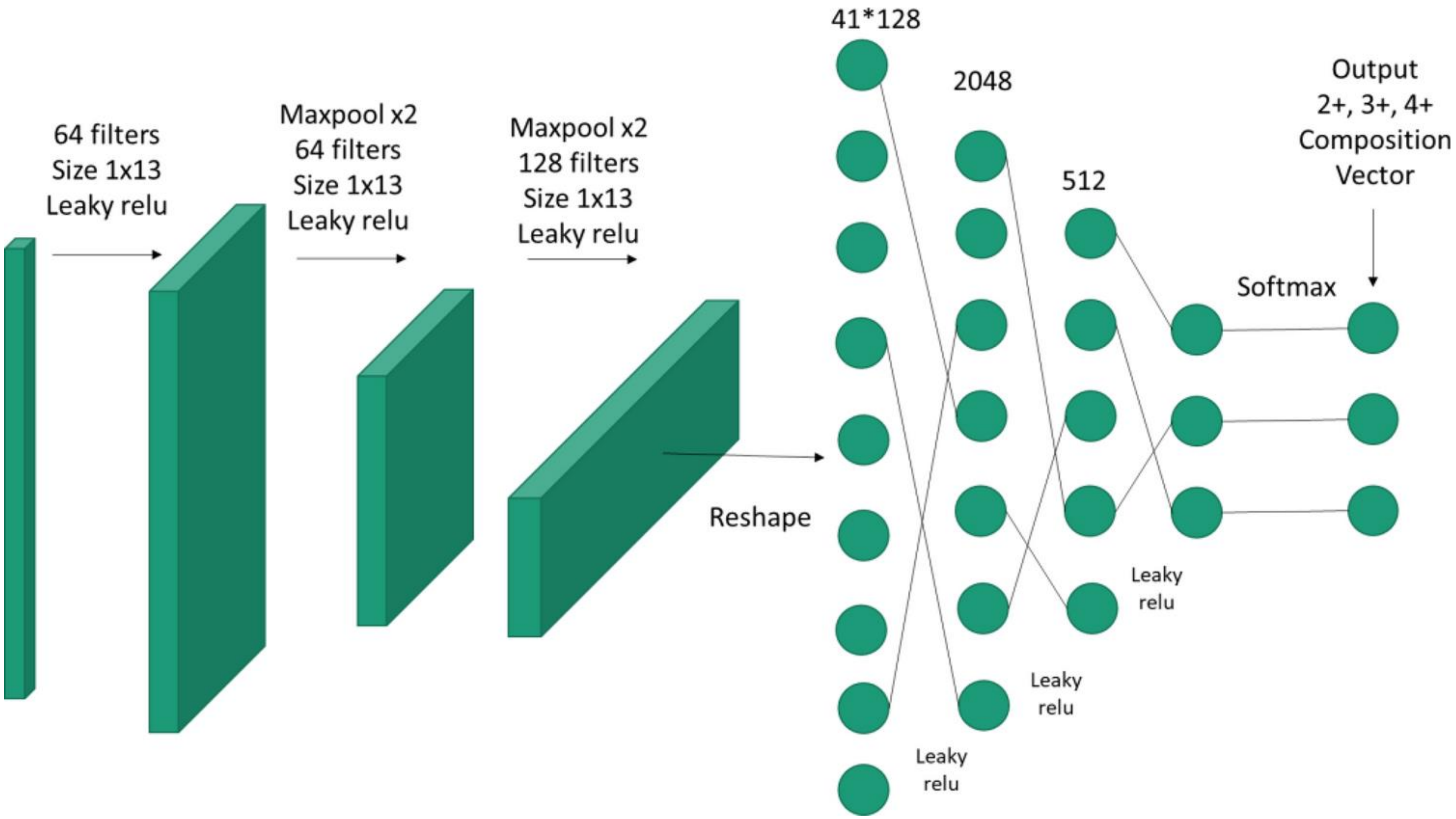



Ji et al., Scientific Reports, 2023

Synthesizing EELS for mixed valence states

This will be done by adding normalized standard reference spectra ($UCl_3$ and $UCl_4$) in different compositions, e.g., $UCl_3$-1wt%$UCl_4$, $UCl_3$-2wt%$UCl_4$, $UCl_3$-3wt%$UCl_4$ and so on

# Next step: Implement deep learning model




Training and test data: Augmented standard reference ($UCl_3$, $UCl_4$, $UCl_5$) and mixed valence state data (augmented and experimentally obtained)

Output will be composition of different valence states of uranium (3+, 4+, 5+)

It will be tested on unknown mixtures of $UCl_3$ and $UCl_4$

First such work for EELS of uranium compounds

# Acknowledgments:

Major support from NSUF Instrument Scientist funding

Dr. Fei Xu – for help with deep learning model development

Purified $UCl_3$ and $UCl_4$ samples came from Prof. Sheng Dai's group at ORNL (funded by MSEE EFRC)

Purified $UCl_3$, $UCl_4$, $UCl_5$ and known mixed chlorides $UCl_3$-10wt%$UCl_4$, $UCl_3$-50%$UCl_4$ were provided by Sayandev Chatterjee's group at TerraPower (EELS characterization funded by NSUF IS)

Unknown compositions of $UCl_3$ and $UCl_4$ mixtures came from Prof. Haiyan Zhao's group at University of Idaho (funded by NSUF RTE project)

Idaho National Laboratory

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