IMAGING MAGNETIC NANOCLUSTERS AT THE ATOMIC SCALE USING SYNCHROTRON X-RAY SCANNING TUNNELING MICROSCOPY.

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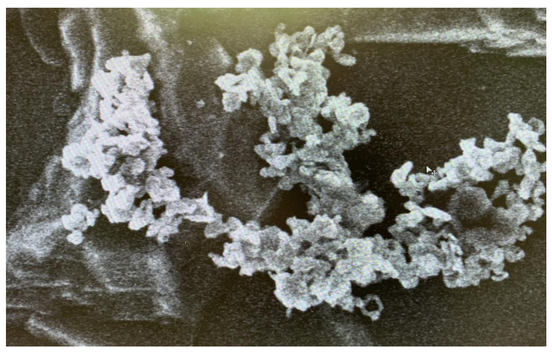
ABSTRACT

Synchrotron x-ray scanning tunneling microscopy (SX-STM) is a technique recently developed at Argonne National Laboratory that uses the chemical imaging capabilities of x-ray absorption spectroscopy with the spatial resolution of scanning tunneling microscopy to achieve atomic-level spatial and chemical resolution images of a surface. This imaging technique is potentially very powerful because it allows researchers to simultaneously gain information regarding systems that would not otherwise be possible - for instance, simultaneously probing the chemical and magnetic properties of nanoclusters deposited on a metallic substrate.

The goal of this experiment is to use synchrotron x-ray scanning tunneling microscopy to determine chemical information and magnetic information of Ni-Co nanoclusters. Using traditional x-ray absorption spectroscopy , only aggregate information averaged over multiple nanoclusters is possible, because the x-ray beam illuminates multiple particles. It is hoped that by using SX-STM, we can gain information regarding the chemical properties of individual nickel nanoclusters. Additionally, by using left and right circularly polarized x-rays, it is hoped that the magnetic properties of these nanoclusters can be probed to determine what effect the small length scale of these metallic nanoclusters has on the magnetic properties with the goal to design novel materials for future applications.

MOTIVATION

- The purpose of this experiment is to us the unique imaging techniques with chemical and magnetic specificity at the nanoscale to attempt to characterize the properties of Ni-Co nanostructures being investigated for their possible use in next-generation batteries. A SEM micrograph of these nanoclusters is shown below.



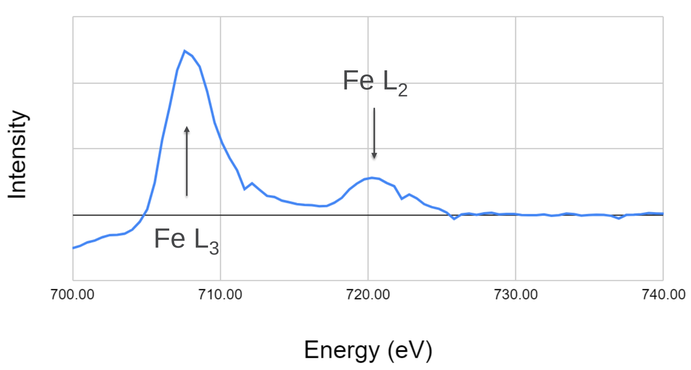
METHODS

- Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM), combines the elemental sensitivity of X-ray microscopy and the spatial resolution of scanning tunneling microscopy. With SX-XTM, it is possible to find the physical structure, chemical makeup, and magnetic properties of a sample in a single scan, which was a goal since STM was realized in the 1980s.
- This experiment solely used the x-ray spectroscopy capabilities of the beamline to attempt to determine the presence and chemical state of Co and Ni in nanoclusters being investigated for possible use in next-generation batteries.

DATA – BEAMLINE CALIBRATION

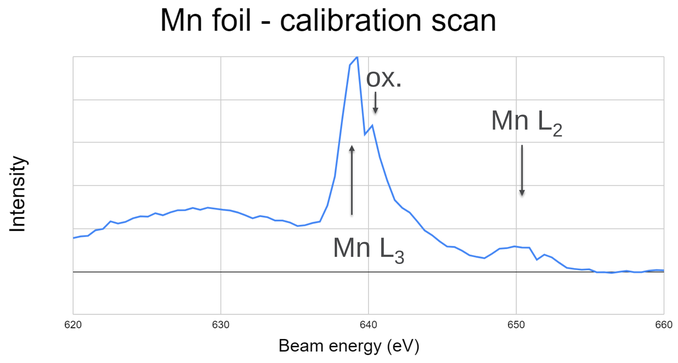
- The first step of our experiment was to use pure Fe and Mn standard foils to determine the energy calibration of our x-ray spectroscopy measurements.
- The expected values for the Fe L_3 peak is 706.8 eV and the expected value for the Mn L_3 peak is 638.7 eV. The measured peak for the L_3 peak for Fe in our experiment is 707.6 eV, and the measured L_3 peak for Mn in our experiment is 636.7 eV, as shown in the figures below.

Fe foil - calibration scan



- Our data shows that the experimental energy peaks were approximately 1 eV away from the expected energy peak, so the calibration was off by approximately ±1 eV.

Mn foil - calibration scan

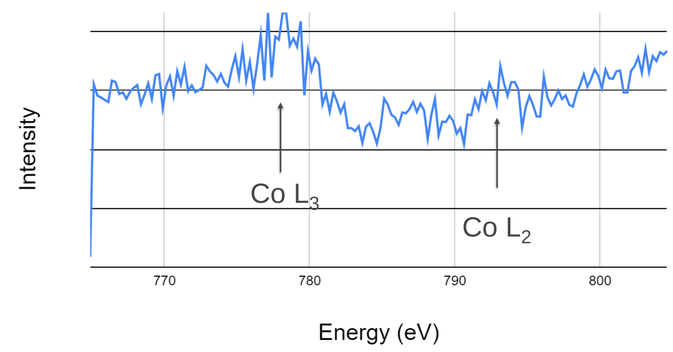


- A shoulder can be observed in the Mn foil at 640.2 eV. We attribute this feature to the presence of an oxide layer in the surface of the Mn foil. The Fe sample does not have a significant oxidation shoulder.

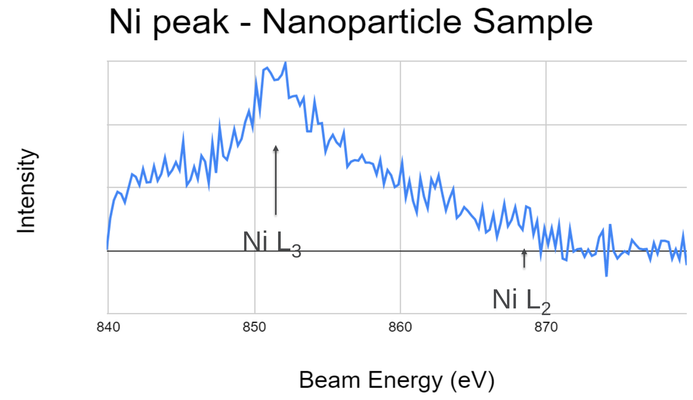
DATA – NANOPARTICLE CLUSTER MEASUREMENTS

- Localized spectra from a single nanoparticle are shown below. In our experiment, we were looking for the presence of Co and Ni in our samples.
- The expected values for the Co L_3 peak is 778.1 eV and the expected value for the Ni L_3 peak is 852.7 eV.
- Both scans indicate the presence of Co and Ni in our nanoparticle samples.

Co peak - Nanoparticle Sample



Ni peak - Nanoparticle Sample



- The selected particle clearly contains both cobalt and iron.
- Because there are very small amounts of nickel and cobalt present in an isolated particle, the data exhibit more noise than the standard spectra.
- The signal/noise ratio could be improved by increasing the dwell time or improve the stability of the tip detector used in SX-STM.
- There is no evidence of the presence of ether nickel oxide or cobalt oxide, although the noise level in the data prohibits a more definitive statement.

CONCLUSIONS

- As a result of these measurements, we can make the following observations.
  - SX-STM allows to study a single particle although the x-ray beam illuminates many.
  - The isolated nanocluster sample shows the presence of both Co and Ni.
  - There is no evidence of either cobalt oxide or nickel oxide in the sample.
  - The data from the nanocluster sample is noisy due to the small amount of material present in the sample and the relatively short time of the scans used to probe for the presence of these metals.

NEXT STEPS

- We suggest the following next steps:
  - In order to make more accurate observations regarding the chemical state of Co and Ni in the nanoparticle samples, longer time scale x-ray spectroscopy measurements should be performed.
  - The stability of the tip detector should be optimized to reduce noise.
  - The unique capabilities of the SX-STM beamline at the APS should be utilized to assay the magnetic properties of these nanoclusters.

REFERENCES

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- Rose, V., Shirato, N., Bartlein, M., Deriy, A., Ajayi, T., Rosenmann, D., Hla, S.-W., Fisher, M., Reininger, R. *XTIP – the world's first beamline dedicated to the synchrotron X-ray scanning tunneling microscopy technique,* J. Synchrotron Rad. **27**, 836-843 (2020).

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