Electrowinning DU from a KCl/LiCl Eutectic and Temperature-Dependent Resistance Characterization

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Abstract

This project’s goal is to grow single crystals of depleted uranium by means of electrorefining within a KCl/LiCl salt bath at vacuum pressure. At vacuum, we used a molten KCl/LiCl eutectic containing DU and applied a voltage across two stainless steel electrodes. Uranium was electrowon and single crystal x-ray diffraction performed. The temperature dependence of the resistance was also measured, and from this CDW transitions identified.

Introduction

Depleted uranium (DU) is uranium which contains less of the isotope U-235 than natural uranium (0.71% U-235) and is mostly made up of the isotope U-238. DU has uses in military and civilian applications, primarily making use of its high density for counterweights and armor-piercing munitions. There is still much to be learned about DU’s Fermi surface. The Fermi surface of a material is important in understanding the thermal, electrical, magnetic, and optical properties of that material. Recent experiments at NHMFL seeking knowledge of the Fermi surface of uranium suggest that high purity uranium with a good lattice configuration of the crystal.

Explanation

The electrorefining process of uranium in a chloride-salt system is done through electrowin and an intermediate UCl3 state. This electrometallurgical process was designed to electrowin plutonium during the Manhattan project, and was refined for uranium starting in the 1980’s [4]. Uranium is placed into a crucible with molten KCl and LiCl and with an applied voltage across two electrodes, uranium is deposited on the cathode.

X-ray Diffraction and x-ray crystallography is a method around 100 years old that can give information about the lattice structure of a crystal. X-rays are directed at a crystal and diffracted by atoms in the crystal lattice. Capturing the diffracted x-rays from many different incident angles gives an idea of the lattice configuration of the crystal.

Uranium undergoes a structural phase transition into alpha-uranium near 660°C. Alpha-uranium goes through three charge-density wave (CDW) phase transitions at low temperatures [1]. By measuring the resistance of a uranium crystal as it goes through this low temperature range (20 K to 50 K), we can observe the CDW transitions as peaks in the graph of dR/dT.

Results and Discussion

We used a quartz tube with inserts on top for electrodes and a K-type thermocouple. On the bottom there was a path for the vacuum pump and argon. A stainless steel crucible was used to house the salts, stainless steel electrodes and thermometer. Our eutectic was 44.3 mol% KCl – 55.7 mol% LiCl with a melting point of approximately 353 K [2]. Salts used were J.T. Baker granular LiCl (> 99.0%) and G-Biosciences KCl (>90.0%). The DU was vacuum induction melted U238. We used an RF induction heater to heat the crucible, which heated the elements inside. The eutectic was maintained at 450±5°C and a voltage of 1.00±0.01 V applied for 24 hours. At the end of the growth, the system was purged with Argon and transferred to an argon glovebox for evaluation and extraction of crystals. Crystals were etched with HNO3, then X-ray crystallography and resistance measurements were performed.

There was a growth deposit on the cathode. It was tree-like as expected, but quite condensed. The DU anode was eroded considerably. There was a large quantity of DU crystals in the crucible. These were not attached to either of the electrodes, but collected in the crucible.

Results and Discussion cont.

XRD was performed by Amanda Chown on four of the single crystals using an Oxford- Diffraction Xcalibur2 CCD system. The reflections of five peaks were indexed and FWHM calculated. A percentage was calculated describing the fit of the indexations to known uranium lattice configurations.

Conclusion

This experiment successfully grew uranium crystals by means of electrorefining from a molten eutectic. The deposit of crystals in the crucible was much greater than expected, and likely due to a combination of the voltage and the time duration of the applied voltage being greater than necessary. It would be good to repeat this experiment with varying voltages and time durations to determine how these affect the electrorefining process and resulting crystals.

XRD and resistance vs. temperature analysis suggest that the grown uranium crystals are of high purity. Future experiments will be done with these crystals to study the Fermi surface of uranium.

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References