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Charge density waves and superconductivity in alpha-uranium

Derrick VanGennep



Abstract:

We have measured the electrical resistivity and magnetoresistance of several α -uranium single crystals under pressure. The residual resistivity ratios (RRRs) of these samples ranged from 158 to 265 and the pressure dependence is discussed. Superconductivity was observed at temperatures varying from approximately 20 mK at ambient pressure to 3 K at 16 kBar and critical fields were observed up to 0.5 T at 16 kBar. Sharp features were seen at each of the three charge density wave (CDW) transitions starting near 40 K. The magnetic field and pressure dependences of the CDWs as well as superconductivity are presented and discussed.

Key words: resistivity, charge density wave, superconductivity

THE FLORIDA STATE UNIVERSITY
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CHARGE DENSITY WAVES AND SUPERCONDUCTIVITY IN
 α -URANIUM

By
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1. Introduction

Ever since the extreme potential of uranium as both a nuclear weapon and power source was realized, it has been of utmost importance to understand the fundamental physics behind this mysterious element. While most of the attention has been placed on the nuclear physics behind the element, the electronic interactions in uranium, as well as many other f-level systems, have also been shown to be unique and interesting. The electronic interactions in the f-level elements continue to baffle the scientific community. There are no theoretical models that reliably predict the behavior of the f-level electrons, and in many cases we are not even sure which orbitals are responsible for chemical bonding.¹

It is surprising that the basic physics behind many elements is not well understood. Figuring out the electronic interactions in uranium is an especially difficult task for many reasons. The orthorhombic unit cell of uranium consists of 20 atoms and is perhaps the most complex of all of the elements.² This makes uranium a very difficult metal to model theoretically.

The most important factor to understanding electronic structure is the Fermi surface. The study of the Fermi surface of uranium is complicated by the difficulty of growing large, clean, single crystals necessary to observe quantum oscillations in magnetization and magnetoresistance, which are the probes of fermiology. Uranium has a transition from the orthorhombic α phase, under ambient conditions, to the tetragonal β phase at 668 °C and a transition from the β phase to the body-centered-cubic γ phase at 775 °C.³ These transitions have made it difficult to grow high quality crystals in the past.⁴

Uranium is one of the only elemental metals in which charge density waves have been observed. The three charge density waves that occur under 45 K are thought to damage the crystal structure of α -uranium due to rapid lattice distortions that trigger the modulation of electron density within the metal.⁴ Having to traverse through these volume collapses further complicates the problem of observing quantum oscillations and identifying the Fermi surface of α -uranium. The charge density waves are a result of Peierl's distortions which are caused by nesting of the Fermi surface. After the first, second, and third charge density waves (going from highest to lowest transition temperatures) the phases are labeled α -1, α -2, and α -3 respectively.

Superconductivity in α -uranium has been seen at varying temperatures and pressures, having a maximum critical temperature, T_c , of 2.3 K at 11 kBar.² Superconductivity in uranium was first observed by Mott in 1942, but was not published until 1946 due to the complications of WWII.⁵ The question of whether or not superconductivity is intrinsic to α -uranium has yet to be answered, and a wide range of critical temperatures has been observed under ambient pressure. Also, unlike most elements, magnetic measurements have shown that uranium is a type II superconductor rather than type I.³ A type I superconductor has a critical magnetic field, H_c , which causes the material to become resistive. Type II superconductors have two critical fields, one which causes magnetic flux vortices to penetrate the material, but keeping the rest of the

material superconducting, and another field that causes the vortex density to become too large, making the entire material non-superconducting.

Advances in the understanding of the α phase of metallic uranium had come to a halt in the early 1990's due to the lack of high quality crystals.² However, in 1997, a group of scientists at Argonne National Laboratory made advances in the growth of uranium crystals by using a metallurgical growth technique to extract spent uranium from a nuclear reactor.⁶ The samples used in this report were taken from this batch of crystals which was grown in a bath of Li-Cl and K-Cl eutectic containing about 3% UCl by weight.⁶ Resistivity measurements of these samples were taken at high pressures, low temperatures, and high magnetic fields, and the results are shown and discussed.

2. Review of Techniques and Terminology

2.1 Superconductivity

Heike Kamerlingh Onnes found that the resistance of mercury suddenly vanished when cooled slightly below the boiling point of liquid helium in 1911.⁷ The resistance quickly dropped from more than 0.1 ohm to less than 10^{-5} ohms at 4.2 K (**Figure 1**). This state of zero resistance has been since referred to as “superconductivity.” Since 1911 there have been many thousands of superconductors that have been discovered.

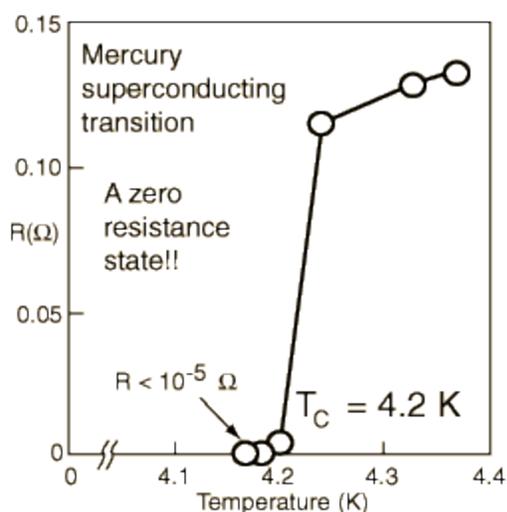


Figure 1.

After successfully liquefying helium in 1908, Onnes decided to study the resistance of mercury at low temperatures with mercury samples that were made very pure by distillation processes. This phenomenon of a zero resistance state has since been called superconductivity, and it occurs at a critical temperature, T_c .⁷

High temperature superconductors have recently been a topic of interest in condensed matter physics due to their numerous possible applications. Superconducting cables for both AC and DC have been developed, which gives the advantage of avoiding Joule heating and maximizes efficiency of energy transport. Most laboratory magnets use superconducting coils, as

well as many magnets involved in magnetic resonance tomography which help probe the inside of the body without actually having to cut one open. In the future, superconducting magnets will be responsible for the levitation of trains as well as the confinement of plasma in nuclear reactors. Having a fundamental understanding of superconductivity is necessary for many promising technological advances.

It would not be surprising to find that the resistance of a perfectly pure metal goes to zero when the temperature approaches absolute zero because all phonons are frozen out, but to find a zero resistance at a nonzero temperature goes against our intuition. BCS theory, formulated in 1957, proposed that there is an attractive interaction between electrons which comes from the exchange of phonons.⁸ These electrons that are held together through phonons form Cooper pairs. This means that the electrons are coupled together through their spin and momenta such that the correlated electrons have opposite spin and move in opposite directions. These effects from the “coherent Cooper pair soup” make it easy to see how this model is vastly different than the model of a gas of non-interacting electrons and makes the phenomenon of superconductivity much more plausible theoretically.

Meissner and Ochsenfeld found that when a sample undergoes a superconducting transition it will expel an applied magnetic field completely.⁹ This allows for a contactless measurement of a superconducting transition. The more conventional method of observing these transitions is to simply apply contacts over your sample, introduce a current, and measure the voltage drop over a certain section of the sample. The resistivity measurements made in this paper were done using a four probe method, which is explained in more detail in section 2.3.

2.2 Charge Density Waves

A charge density wave (CDW) occurs when there is a spatial modulation of electron density, which implies a modulation of charge density. This charge density wave is coupled to a mass density wave of the positively charged ions which make up the crystal lattice (see **Figure 2**). The three Peierls transitions that occur in uranium below 45 K cause an effectively simultaneous change in electronic configuration, which can be seen as a drastic change in the derivative of the resistivity v temperature plot. Thermal fluctuations that occur at nonzero temperatures allow for the heavy ions to shift to positions which create a more energetically stable environment for both the nuclei and electrons. The CDWs of α -uranium are said to be incommensurable, meaning that the ratio between the wave vector \mathbf{q} and the reciprocal lattice vector is an irrational number. The electron density is given by equation (1);

$$\rho = \rho_0 \cos(\mathbf{q} \cdot \mathbf{r} + \delta) \quad (1)$$

where ρ_0 is the initial charge density, and δ is a phase angle. The creation of a Coulomb gap in a half-filled band due to electronic interactions is shown in **Figure 2**.

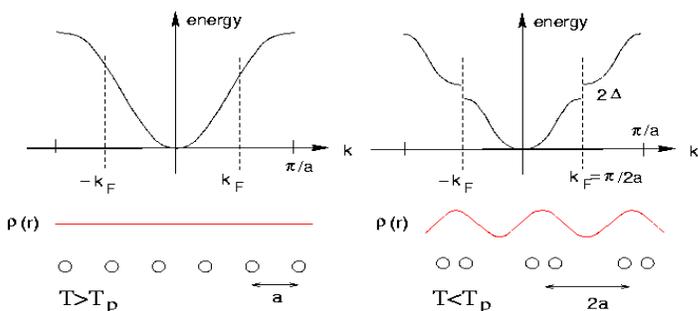


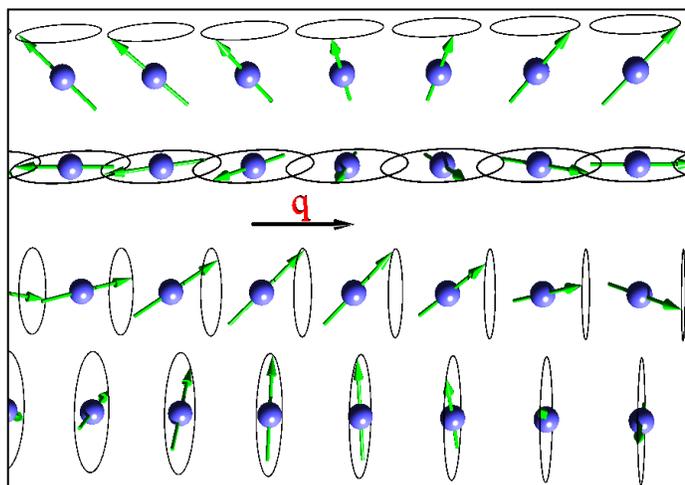
Figure 2.

A Coulomb gap is introduced when the electron-electron interactions are taken into consideration. As T passes by T_p , a modulation in the charge density occurs.¹⁰

The last CDW in uranium, which occurs near 23 K, behaves differently during cooling down and warming up the sample. Properties of this CDW seem to be dependent on whether the temperature is increasing, going from an α -3 phase to an α -2 phase, or decreasing and transitioning from the α -2 phase to the α -3 phase. It has been theorized that this third CDW may be accompanied by a spin density wave (SDW) because of its unique behavior.¹¹ A SDW is similar to a CDW but instead of the electron density modulating, it is the electron spin density that is changing (see **Figure 3**). This is not to be confused with a spin-Peierls transition which has a corresponding lattice distortion as well as the SDW.

Figure 3.

Shown are several spin-spiral states as function of the wave-vector \mathbf{q} pointing from left to right. The upper two spin-configurations show transversal spin-spiral states and the lower two spin-configurations show a longitudinal spin-spiral state.¹²



2.3 Four-Terminal Sensing

One of the most reliable methods for measuring resistivity is four-terminal sensing. Four-terminal sensing involves attaching four contacts to a sample. Two of these probes are used to supply a current through the sample, while the other two are used to measure the voltage drop across a section of the sample (see **Figure 4**). The advantage of doing a four-probe measurement rather than a two- or three-probe measurement is that the four probe measurement separates the voltage and current terminals, eliminating impedance contributions due to contact resistances and wiring. This is necessary to get a reliable resistance measurement of conductors because the

contact impedances are often of an order of magnitude larger than that of the sample itself. The same is true with the wiring since all of the resistance measurements in this study were taken inside of magnets, requiring wires running from the sample chamber of the magnet to the measurement devices 10 to 20 ft away. The resistivity of a material is given by equation (2);

$$\rho = R \frac{A}{L} \quad (2)$$

where R is the resistance drop across a portion of the material with a cross-sectional area A and length L. A small resistivity allows for one to observe small changes in resistivity resulting from charge density waves. This equation emphasizes the importance of having a long, thin sample when looking for the effects of charge density waves on the resistivity.

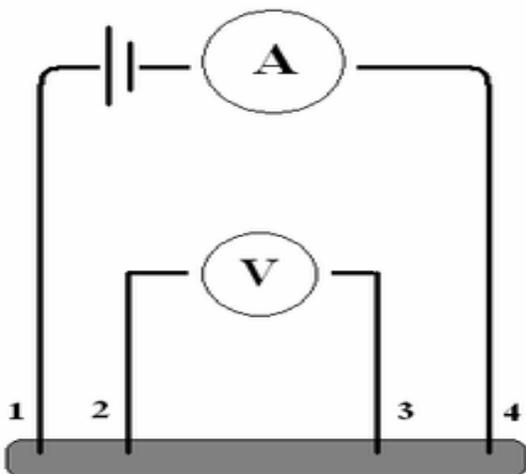


Figure 4.

Current is supplied to the sample (grey) via contacts 1 and 4. The voltage drop over the center section of the sample can then be measured very accurately because there is almost no current in the circuit loop that is used to measure the voltage.¹³

Uranium is a good electrical conductor which makes the task of minimizing contact resistances crucial to improving signal quality in resistance measurements. Although the four-terminal method removes the impedances from the contacts, electrically poor contacts having large resistances act as capacitors, charging and discharging frequently which increases noise in a resistance measurement. Uranium behaves as an excellent getter, having five possible oxidation states and accumulating an oxide layer rapidly. Phase relationships in the uranium-oxygen system are complex. The most common oxidation states are uranium (IV) and uranium (VI), consisting of uranium dioxide (UO_2) and uranium trioxide (UO_3), respectively, but triuranium octaoxide (U_3O_8) is also common.¹⁴

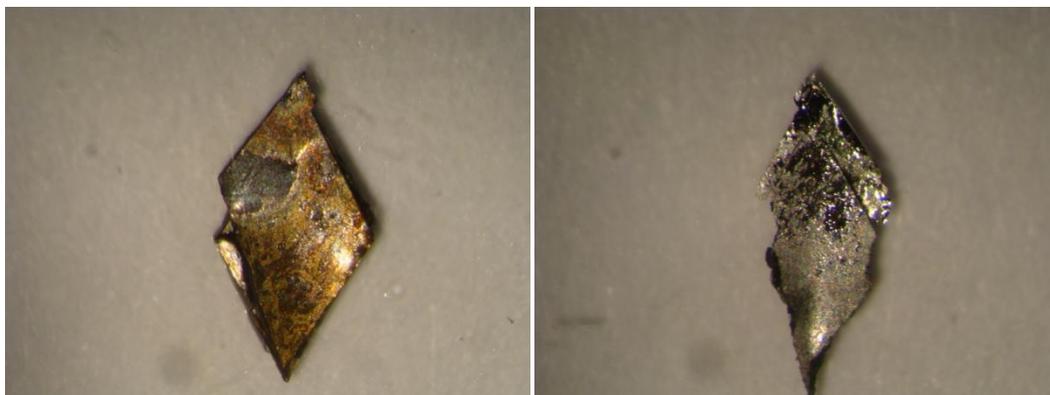
A non-conducting oxide layer that forms very quickly can cause problems in creating mechanically sound, ohmic contacts. The idea behind creating low resistance contacts in our studies was to remove the oxide layer as much as possible, then to sputter gold contacts onto the uranium with the hope of having a clean, gold-on-uranium contact and preventing any future oxidation.

Removing the oxide layer of uranium without damaging the outer layers of the crystal has proven to be a difficult task. Mechanical polishing introduces too much stress to the crystal, negatively affecting transport measurements, while chemical etching did not remove the oxide layers effectively due to the wide variety of oxidizers on the surface. Electrochemically polishing the uranium samples proved to be the most effective technique used thus far. This process

involves submerging the uranium in a mixture of phosphoric and sulfuric acid and introducing two electrodes containing a low voltage across them into the solution, one touching the uranium and one slightly off of the uranium. The electrode touching the uranium is used for electron transfer, and the one that does not touch the uranium is used as a surface for the electrochemical deposition to occur [Figure 5].

Figure 5.

Below left/right: Pictures before/after electropolishing uranium show a drastic improvement in cleanliness of the surface. This sample is approximately 2mm long from top to bottom.



After the electropolishing procedure is finished, the uranium is ready for a gold film to be deposited to create each of the four contacts necessary to conduct the four-terminal transport measurement. The electropolishing is done in a glovebag filled with an inert gas in order to minimize oxidation before the gold sputtering starts. The sample is then covered with a metallic mask, which leaves only four portions of the sample uncovered. These sections will be the electrical contacts once the gold is deposited (see Figure 6). Gold wires are attached to these contacts with silver paint. This sample geometry is new and was not used in the measurements shown below. Simple, needle-like bars of uranium were cut for those measurements.

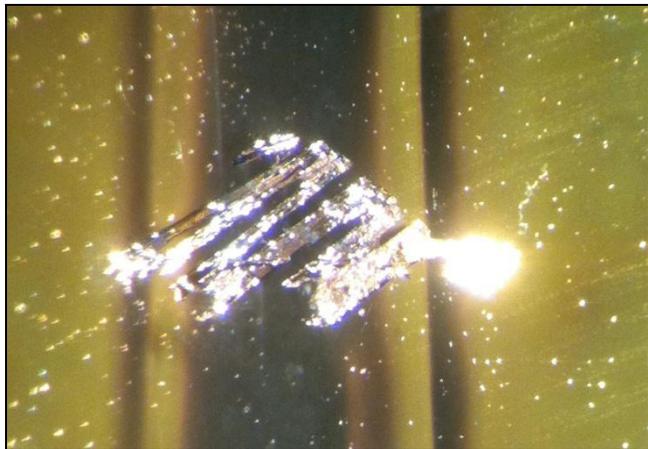


Figure 6.

This figure shows a uranium sample post-sputtering. The vertical yellow stripes are from a thin layer of gold (approx. 1800 Å thick), and the shadow is from the mask which was covering the sample during gold deposition, creating the separation between contacts needed for the four probe measurement. The sample here was cut using an electric discharge machine in order to create a “zig-zagging” path for the current to follow, increasing the voltage drop across the two middle terminals. The length of this sample is less than 1.5 mm from head to tail. Wires were affixed to the sample at each of areas covered in gold.

All of the samples in this study were annealed prior to the measurements. Annealing took place in a sealed quartz tube backfilled with argon gas. Tantalum foil was used as a “getter” to help reduce the oxidation of uranium. The samples were heated to 600 °C over 15 hours, soaked for 8 hours, and then cooled over 48 hours. This anneal was shown to be helpful in releasing stress throughout the sample through the observation of dHvA quantum oscillations measured on piezoresistive cantilevers.¹¹ The residual resistance ratio (RRR), given by equation (3), has also been known to increase after anneals.

$$RRR = R_{RT}/R_{LT} \quad (3)$$

Here, R_{RT} and R_{LT} are the resistances taken at room temperature and low temperature. The low temperature is defined as the lowest temperature at which the sample was still non-superconducting. The RRR of a sample is a good measure of sample purity, as well as of judging how metallic something acts. In general, metallic materials should have high RRR values. The resistance measurements shown below were carried out in two different systems. A Quantum Design PPMS with a 16 T superconducting magnet was used for resistance measurements down to 6 K. All low temperature measurements were taken in an Oxford top loading dilution refrigerator with an 18 T superconducting magnet. The high pressure measurements were taken with the samples inside piston cylinder cells (PCCs) designed by Stan Tozer (Florida State University). A photo of one of the pressure cell mounted on a probe for the dilution refrigerator is shown in **Figure 7**.

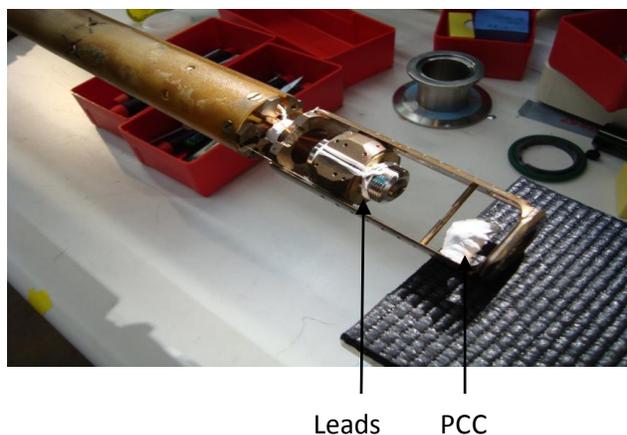


Figure 7.

A piston cylinder cell (PCC) is shown mounted on the end of a probe designed to facilitate a variety of measurements inside the Oxford top loading dilution refrigerator. Teflon tape (white) was used to help secure the cell and the electrical leads originating at the sample can be seen coming out of the cell.

3. Results

3.1 Superconductivity Under Pressure

For this particular sample, the RRR at ambient pressure was 265 and was 430 at 10.3 kBar. T_c at 10.3 kBar was near 2 K. The magnetoresistance curves, show sharp superconducting transitions at fields below 0.5 T (**Figure 8**).

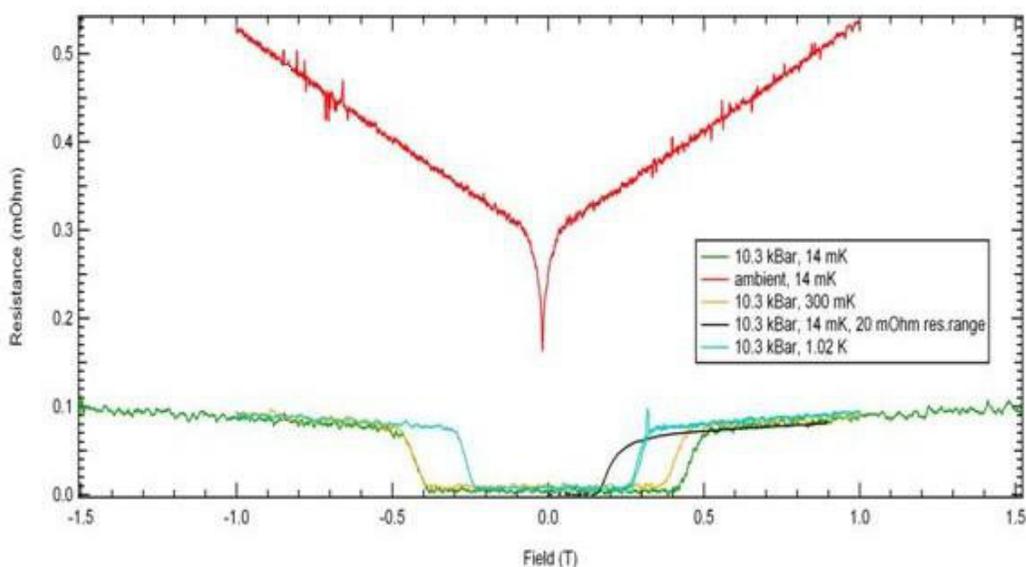


Figure 8.

The magneto resistance of α -uranium shows superconducting transitions at low temperatures and fields when pressure is applied to the sample. However, at ambient pressure the resistance does not completely go to zero.

Two charge density waves were observed at 23 K and 37 K at ambient pressure. The transition near 40 K was not easily identified within our resolution. Most likely, this resulted from a rapid cooldown in that temperature region which results from lowering the probe quickly into the dilution refrigerator.

Another sample was pressurized to ≈ 16 kBar and had a RRR of 210. No CDWs were seen during the cooldown, but the superconducting transition is clear and occurs near 3 K (Figure 9).

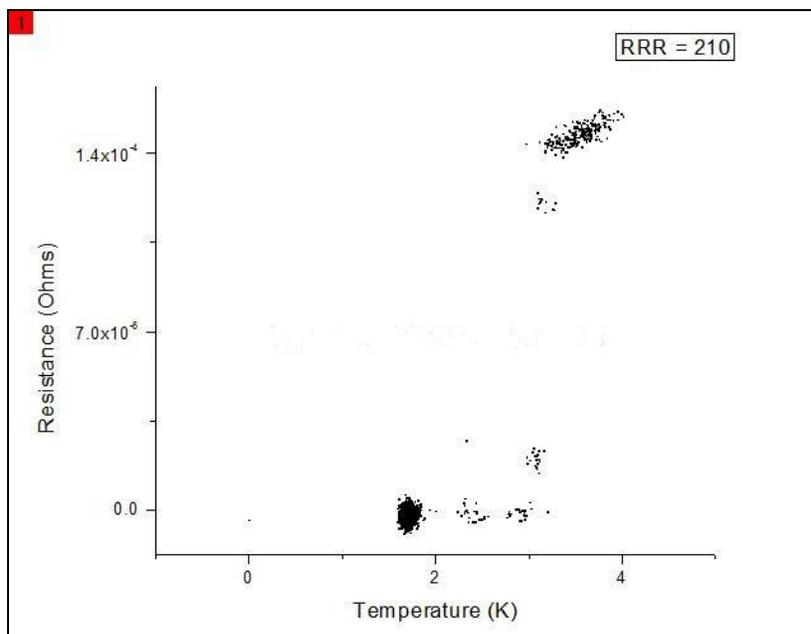


Figure 9.

Shown is a clear superconducting transition of α -uranium at 16 kBar occurring near 3 K. This was the highest T_c value recorded to date for uranium, and the value of the “true” temperature is discussed in the text.

3.2 Charge Density Waves Under Pressure

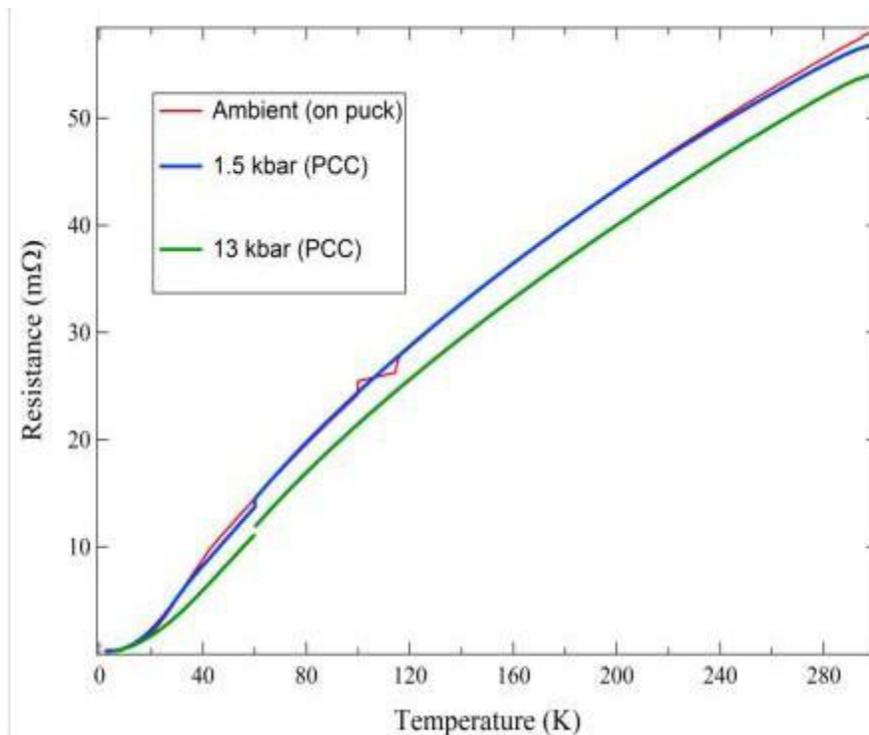
Table 1: The room temperature (RT) resistance, the resistance at 6 K, and the residual resistivity ratio of one single crystal of uranium at varying pressures.

RT resistance (m Ω):	6K resistance (m Ω):	RRR = R_{RT}/R_{LT}
Ambient 58.2	0.364	158.9
1.5 kBar (LT) 56.9	0.289	195.9
13 kBar (LT) 53.9	0.257	208.7

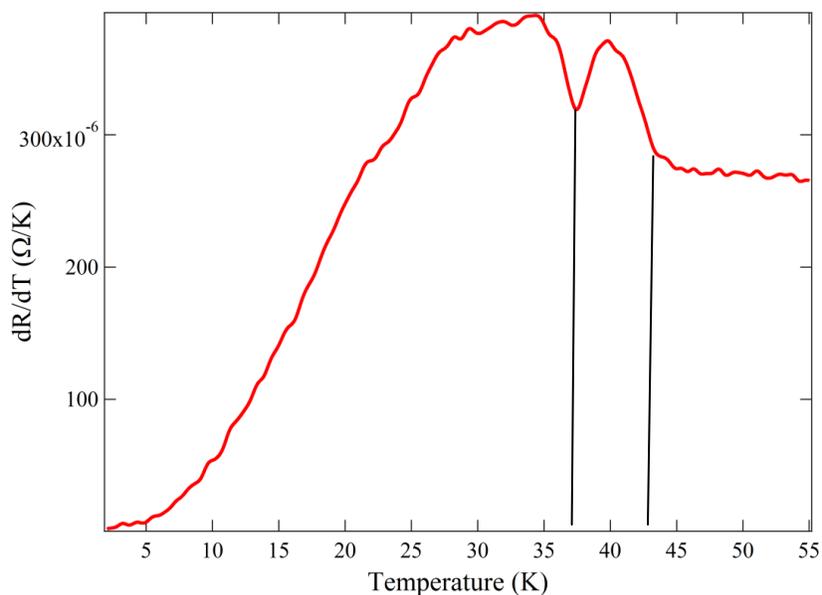
From this limited data set, the RRR value has been shown to increase with pressure, but the RRR seems to saturate at higher pressures. T_c and H_c also have significant increases with pressure; however, the effects due to charge density waves drastically decrease with pressure. The pressure dependence of the RRRs is shown in **Figure 10**.

Figure 10:

The resistance plotted vs temperature at three different pressures for this sample. Spikes and discontinuities in the curves are due to a change in cooling rate.



For this same sample, the charge density wave occurring at 37 K showed a sharp change in the plot of the derivative of resistivity v temperature (**Figure 11**). The onset of the increase in resistance occurring near 41 K marks the first charge density wave. The 23 K transition shows hysteresis and is more easily identified on the heating curve rather than a cooling curve.¹¹

**Figure 11:**

A cooling curve showing the ≈ 37 K transition, seen as a local minima in the dR/dT vs temperature plot at ambient pressure. The 43 K transition is also shown as the beginning of the increase in the derivative. Neither of these transitions was resolvable at any other pressures for this sample of α -uranium.

4. Discussion

The idea that superconductivity is not intrinsic to uranium and is instead caused by impurities and stress has been proposed, as well as the possibility that the charge density waves suppress superconductivity,^{2,3} but the data shown should support the argument that superconductivity is intrinsic to α -uranium. Charge density waves were seen in an annealed sample at ambient pressure, and a partial superconducting state was seen in **Figure 8**. The possibility that at low temperatures a pressure-tuned quantum critical point separates the normal phase from a superconducting phase still seems plausible if the samples above were subject to strain or excessive amounts of impurities, but this seems unlikely. The relatively large T_c at 3K is the highest observed value that we are aware of, topping the T_c peak from Lander *et al.* of 2 K which was also found near 16 kBar.² Two thermometers were used to measure the temperature during the superconducting transition, a diode as well as a RuO₂ thermometer, and the T_c values differed by almost 1 K. Also, the pressure cell itself is very thermally isolated, making it difficult to determine the true value of the sample during the transition. This, coupled with the fast cooling rate of the dilution refrigerator complicates the problem of plotting the superconducting dome on a temperature-pressure curve.

The apparent vanishing of the CDWs under pressure is not surprising given that fact that most materials that exhibit CDWs are highly sensitive to strain.^{4,11} The annealing process, along with improved ohmic contacts has made the CDWs more easily identifiable. The magnetic field dependence of the CDWs shown in the past, as well as the hysteresis seen in the α -3 transition, suggests that SDWs may coexist with the CDWs observed in α -uranium.³

5. Conclusion

We have observed superconducting transitions in α -uranium with a variety of critical temperatures varying from approximately 20 mK at ambient pressure to 3 K at 16 kBar. Critical fields for these samples have been observed up to 0.5 T at 20 mK and 16 kBar. With a limited data set, the RRR value of uranium increases with pressure indicating a lower scattering rate. At ambient pressure, the resistivity of the first sample described above does not go completely to zero, but the beginning of a superconducting transition is clear. Charge density wave transitions were clearly visible in this sample, so it is unlikely that charge density waves suppress superconductivity in uranium completely. The question of whether or not superconductivity is intrinsic to α -uranium remains unanswered. Repeating these measurements with higher quality single crystals seems to be the only way to yield a definite answer. The charge density wave

transitions were not identifiable within our resolution under any pressure above ambient. In order to find the α -1,2,3 domes these transitions should be studied under lower pressures and perhaps the new sample geometry, shown in **Figure 6**, will provide promising results in the future. There is still much that is unknown about the behavior of the f-level electrons, and more experimental data should aid modeling efforts in the future.

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