Reports

Superconductivity of Beta-Uranium

The β-phase of uranium, stabilized by small amounts of other metals, has been found to undergo the superconducting transition at temperatures close to 0.8°K. This result casts severe doubt on previously reported results concerning the superconductivity of α-uranium, the phase stable at room temperatures.

In its pure form β-uranium is stable only at elevated temperatures between 661°C and 769°C. We stabilized the β-form at room temperature by the addition of 1.75 atomic percent of chromium and 1.75 atomic percent of platinum. After cooling from the γ-phase, the samples were annealed for approximately 24 hours at 700°C in the β-phase region and then quenched into ice water (*1*). The expected β-phase structures were confirmed by x-ray diffraction analysis. The experiments were carried out with different lots of uranium whose purity was always better than 99.9 percent and sometimes better than 99.99 percent. No significant differences were found between the different lots, provided that the same conditions were always maintained.

Measurements of specific heat of our stabilized β-phase ingots are shown in Fig. 1. There is no doubt that β-uranium is a well-behaved superconductor. The small additions necessary to stabilize the phase may have changed the transition temperature slightly. The T_c of the Pt-stabilized phase was 0.85°K, and it was independent of concentration between 1 and 3 percent. That of the Cr-stabilized phase was 0.75°K. Similarly, the electronic specific-heat coefficient, γ, was significantly higher in the Pt-stabilized phase than in the Cr-stabilized one, probably due to the higher valence electron per atom concentration in the Pt-stabilized phase. The fact that T_c is independent of concentration in the range between 1 and 3 percent indicates that we may have exceeded the solubility limit already. The present literature (*1*) is not unequivocal on this point. While we, therefore, cannot extrapolate in a straightforward way to the T_c of pure β-uranium, we think that it cannot be far from 0.8°K. The size of the anomaly, $(C_{es}/\gamma T)_{T_c}$, is 2.36 for the Pt-stabilized phase and 2.52 for the Cr-stabilized phase in reasonable agreement with the theory of Bardeen, Cooper, and Schrieffer (*2*). Measurements of the *ac* susceptibility on the same bulk material gave transitions about 10 millidegrees in width occurring over the same range as determined calorimetrically. The width of the calorimetric transitions, about 30 millidegrees, is an indication of how nearly ideal the superconducting behavior of the β-uranium is.

The superconductivity of α-uranium has been investigated frequently (*3*). The transition temperatures reported ranged from 0.7°K to quite a bit above 1.0°K, with different investigators reporting different values. All agreed, however, on the excess width of the transition region which was on the order of 0.5°. Recent specific heat measurements (*4*) failed to show any anomaly in the region between 0.15° and 0.75°K, and the authors state: "We conclude that our U^{238} sample was not superconducting. This is not surprising in view of the variety of results which have been reported for uranium." Their result combined with the anomalously broad magnetic transitions might be considered an intrinsic property of α-

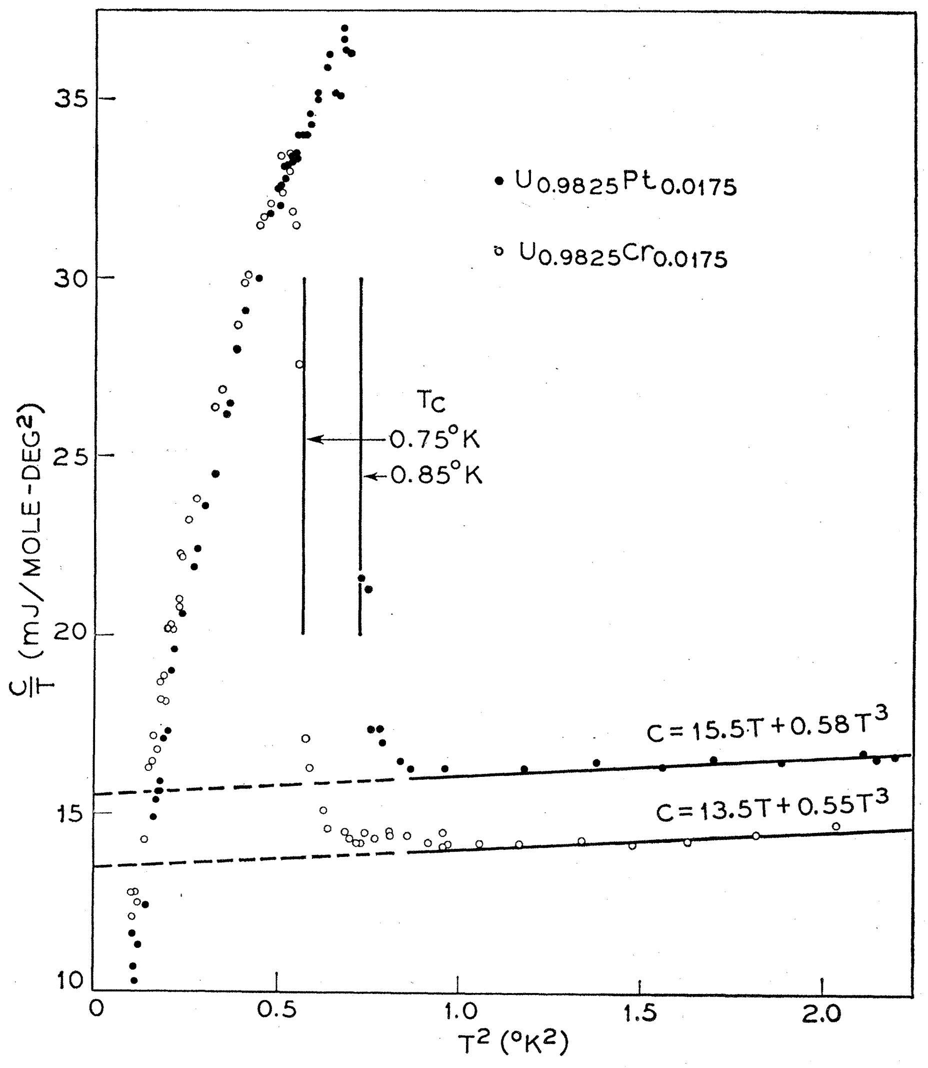

Fig. 1. The heat capacities of $U_{0.9825}$ $Pt_{0.0175}$ and $U_{0.9825}$ $Cr_{0.0175}$ between 0.3 and 1.5°K showing the superconducting transitions. The normal-state intercept gives the values of γ, the electronic heat capacity coefficient. The equations for the normal-state heat capacities were fitted to data taken between 1° and 6°K.

uranium, a superconductor in which 5*f* electrons might play a role (*5*).

In the light of the present results on β-uranium, we would like to offer an entirely different explanation. Namely, that the reported superconducting behavior of the α-phase of uranium at and above 0.7°K may be due only to superconducting filaments of retained stabilized α'-, β-, and γ-phases, or perhaps even filaments of superconducting compounds. Either the γ-phase or the superconducting compounds could account for the transition region above 0.8°K. This transition region can easily be destroyed by mechanical means, such as filing, pulverizing, or rolling. By such means we succeeded in reducing the superconductivity of all uranium samples to the transition temperatures near 0.8°K. The reproducible coincidence between transition temperatures near 0.8°K found for the β-stabilized phases and those found for the α-uranium phases points to the existence of an additional network of what might be β-stabilized filaments of a much finer mesh. We believe that both networks of filaments, which might be retained β- and γ-phases, are situated in the grain boundaries. They are stabilized by impurities insoluble in the α-phase and, therefore, precipitated in just those grain boundaries. Preliminary results of electron microscopic investigations by Arrhenius and collaborators (*6*) show two different domain patterns which could well correspond to the two networks we postulate. The *fine* mesh network is on such a scale that it cannot be destroyed by mechanical means. It has been shown in detail for the LaRh system (*7*) how an extremely fine and well-distributed network of filaments can give rise to complete diamagnetic shielding even though the total concentration was only on the order of a few percent.

The similarity in superconducting behavior recently reported for α-uranium and protactinium (*8*) suggests that aside from the tetragonal form of protactinium, stable at room temperature, there may be other crystallographic modifications which, again, could be stabilized in the grain boundaries. Most elements in which the possibility of 5*f* electrons exists also show different crystallographic modifications. Why should protactinium be an exception since the 5*f* series starts with protactinium (*9*)?

The phase stable at temperatures above those of the β-phase is γ-uranium. Specific heat data on γ-uranium stabilized with 13.7 atomic percent of molybdenum have already been shown to have the expected anomaly with sharp transitions near 2°K (*10*). We have also found that U_6Fe, the uranium compound with the highest known transition temperature, 3.8°K, equally displays the expected caloric features of a normal superconductor. The failure to observe a superconducting heat anomaly (*4*) above 0.15°K for α-uranium, together with the broad transition can be simply explained by the absence of superconductivity of the α-uranium above 0.15°K as was postulated by Dempesy *et al.* for their sample, or by the presence of some state involving the coexistence of magnetic order and superconductivity (*11*). Further heat capacity measurements will be necessary to decide if and where α-uranium becomes superconducting.

Finally, we would like to point out that an anomalous superconducting behavior will frequently be caused by an anomalous metallurgical situation. While previous metallurgical investigations have not clearly shown evidence for the presence of other phases in α-uranium we believe that the present results give strong evidence to the contrary.

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12. We acknowledge the assistance of J. P. Maita and L. D. Longinotti and thank Mrs. V. B. Compton for the x-ray diffraction analysis and many discussions and A. M. Clogston for one crucial discussion. Work at La Jolla supported in part by the U.S. Air Force Office of Scientific Research.

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Direct Evidence for the Cathodic Depolarization Theory of Bacterial Corrosion

Abstract. *Cathodic depolarization of mild steel by* Desulfovibrio desulfuricans *was demonstrated with benzyl viologen used as an electron acceptor. Direct measurement of the cathodic depolarization current indicated a maximum current density of 1 microampere per square centimeter. Aluminum alloys were also cathodically depolarized by the organism.*

In 1934, von Wolzogen Kühr and van der Vlugt proposed a theory for the anaerobic corrosion of iron by bacteria (*1*). In brief, the theory states that bacteria, primarily those of the genus *Desulfovibrio*, remove hydrogen that accumulates on the surface of iron as a result of their hydrogenase activity and reduce sulfate, yielding hydrogen sulfide. The electrons removed as a result of hydrogen utilization permit more iron to be dissolved or corroded at the anode. The hydrogen sulfide and the hydroxyl ions combine with the ferrous ions to form secondary reaction products at the anode.

Over the years evidence for and against this theory has accumulated. Much of this earlier evidence has been reviewed by Starkey (*2*). More recently, Raifsnider (*3*) and Scott (*4*) have presented observations that are not in agreement with this classical theory. Booth and his associates (*5*), using polarization techniques and weight loss measurements versus hydrogenase activity, have presented evidence for the theory. These methods, although involving standard techniques, are nevertheless indirect approaches and may be subject to various interpretations. The key step in the theory is the removal of hydrogen or electrons at the cathode and the subsequent dissolution of iron at the anode. If the *Desulfovibrio* cells are