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A Calorimetric Investigation of Superconductivity in α-Uranium*

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Although the occurrence of superconductivity in α-uranium is of particular interest in connection with the role of the 5f states, the relevant experimental evidence is contradictory. Magnetic susceptibility and resistance measurements[1-4] have shown the presence of superconductivity with transition temperatures T_c ranging from 0.2°K to above 1°K, and have also shown an unusually large increase in T_c with pressure.[5] On the other hand, calorimetric measurements on one sample[6] to 0.15°K and on two others[7] to 0.65°K have not shown any indication of a superconducting transition. To gain more information about the superconductivity of α-uranium we have made further heat capacity measurements at zero pressure and we have also measured the heat capacity at a pressure of 10 kbar.

At zero pressure, four different samples were investigated. Magnetic measurements were made on three of the samples and showed the presence of broad superconducting transitions in the region of 0.3 to 1.2°K. For each sample the heat capacity was measured in zero field between 0.3°K and 6°K. For two samples the measurements were extended to 0.1°K and for one of these, measurements were made between 0.1 and 1°K in magnetic fields up to 5000 Oe. In addition, 2000-Oe field measurements between 0.3 and 1°K were made on one of the samples that was investigated only above 0.3°K. No sample was the subject of a complete set of measurements, but all the measurements were consistent in showing similar behavior for the different samples. In particular, the heat capacities had qualitatively the same temperature dependence and were unaffected by the applied magnetic fields. Figure 1 shows the measurements below 1.4°K on one sample for which the magnetic measurements showed a broad superconducting transition extending up to 1.2°K. The T^{-2} hyperfine term associated with the U^{235} content was estimated from the lowest-temperature points, which were dominated by this contribution, and has been subtracted from the data in the figure. This accounts for the large scatter in the points below 0.2°K. The other sample measured to 0.1°K had a greatly reduced U^{235} content and showed more clearly that C/T is still increasing with decreasing T at 0.1°K. Above 0.7°K the heat capacity shows the usual temperature dependence of a normal metal with the coefficient of the electronic term $\gamma = 10.3$ mJ/mole deg^2, but below 0.7°K the heat capacity is anomalously high. This anomaly cannot be associated with the superconducting transition observed magnetically because (a) the same anomaly is found in samples with different magnetically determined transitions, (b) it is unaffected by magnetic fields, and (c) the observed entropy (above 0.1°K) is inconsistent with a superconducting transition. Since none of our measurements show a heat capacity anomaly of the type associated with a bulk superconducting transition, we conclude that T_c for α-uranium is less than 0.1°K and that the magnetically observed transitions are not associated with bulk superconductivity.

The origin of the observed heat capacity anomaly is puzzling. It does not have the T^{-2} temperature dependence expected for nuclear spin ordering, and it is furthermore independent of the U^{235} content (after the appropriate T^{-2} term is subtracted). Since there is some possibility of 5f states' being populated, it is natural to think of ordering of electron spins, but one would then expect the anomaly to be shifted upward in temperature by a 5000-Oe magnetic field, and no such effect was observed.

A part of the sample for which the zero-pressure heat capacity is shown in Fig. 1 was subjected to a pressure of 10 kbar in a specially constructed high-pressure cell and its heat ca- was remeasured. The corrections for the heat capacity of the cell were large, but reasonable accuracy was obtained by using a germanium thermometer that retained its calibration between the measurements on the filled and empty cell. The results are shown in Fig. 2, where the dashed curve represents the zero-pressure data. There are three striking effects of the pressure: (a) there is a bulk superconducting transition at 2°K, which is in good agreement with magnetic measurements on the same sample, showing that 10 kbar increases T_c by a factor of at least 20, (b) γ is increased by 18%, and (c) the heat capacity anomaly observed at zero pressure is eliminated (or at least reduced).

The BCS expression[8] for T_c is

$$T_c \approx 0.85\,\theta_D \exp[-1/N(0)V],$$

where N(0) is the normal-state density of states (proportional to γ), V measures the strength of the interaction that produces superconductivity, and θ_D is the Debye temperature. To explain an increase in T_c from 0.1 to 2°K, this expression would require a 65% increase in N(0)V. (θ_D is expected to change by no more than 2% and therefore makes a negligible contribution to the change of T_c.) Thus the enhancement of T_c cannot be ascribed to the change in N(0) alone, and a substantial increase in V is implied. Geballe _et al_[4] have recently suggested that such an enhancement of the superconducting interaction by pressure and the 43°K volume minimum in α-uranium might both be associated with a populating of 5f states below 43°K. This model is supported by analogies with the lanthanide metals: the 4f electrons are known to suppress superconductivity,[9] and the application of pressure to cerium is known to shift electrons out of 4f states.[10] The model also suggests other analogies between the effect of pressure on α-uranium and certain properties of the lanthanides. Heat capacity data[11] for the lanthanides indicate that transfer of electrons out of 4f states increases γ, as interpretation of our data in terms of the model would require for the 5f electrons in α-uranium. Furthermore, the heat capacity anomalies[12,13] in cerium associated with ordering of the 4f electrons disappear on application of pressure.[14] On the other hand, cerium does not become superconducting above 0.3°K at 10 kbar,[14] or above 1.2°K at 24 kbar.[15]

We are indebted to a number of our colleagues, in particular to T. H. Geballe, B. T. Matthias, and W. E. Gardner, for stimulating and informative discussions, and to C. E. Olsen for making available several of the samples.

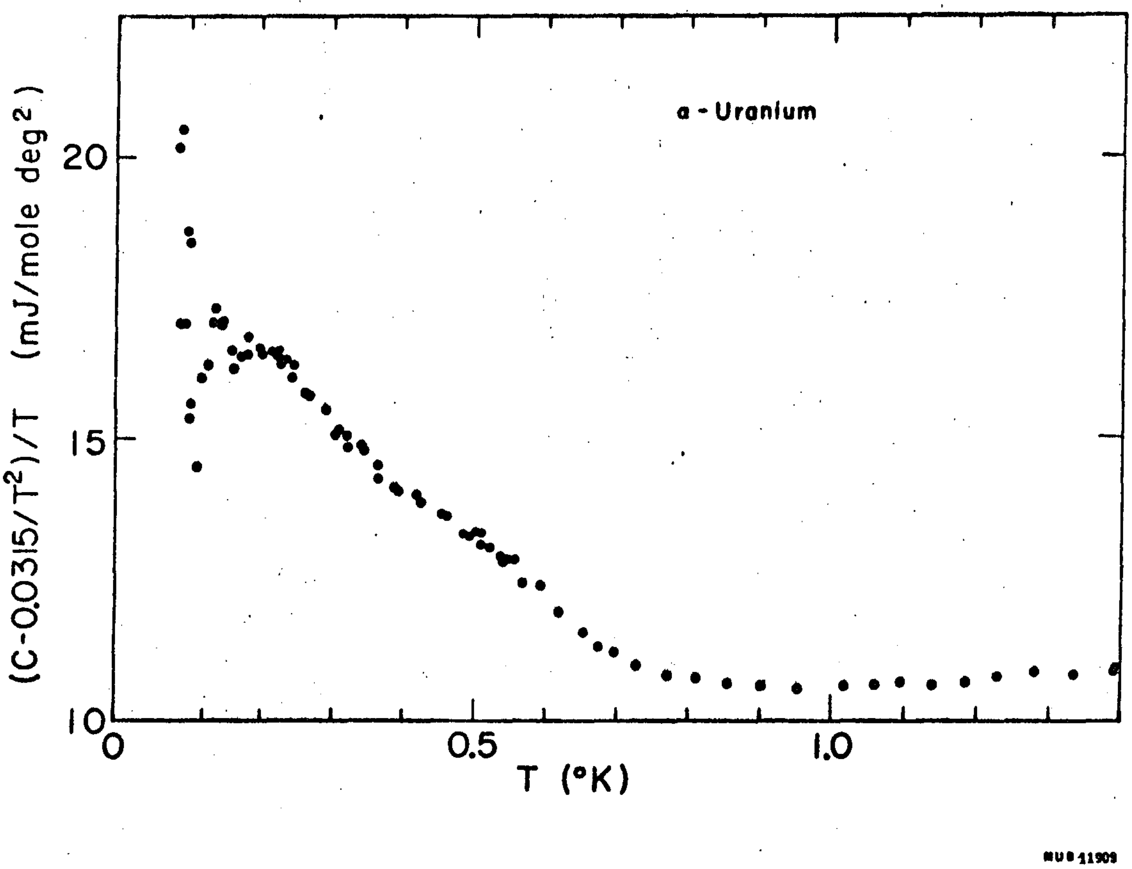

Fig. 1. The heat capacity of α-uranium at zero pressure. The experimental data have been corrected for the hyperfine contribution by subtraction of 0.0315 T^{-2} m/Jmole deg.

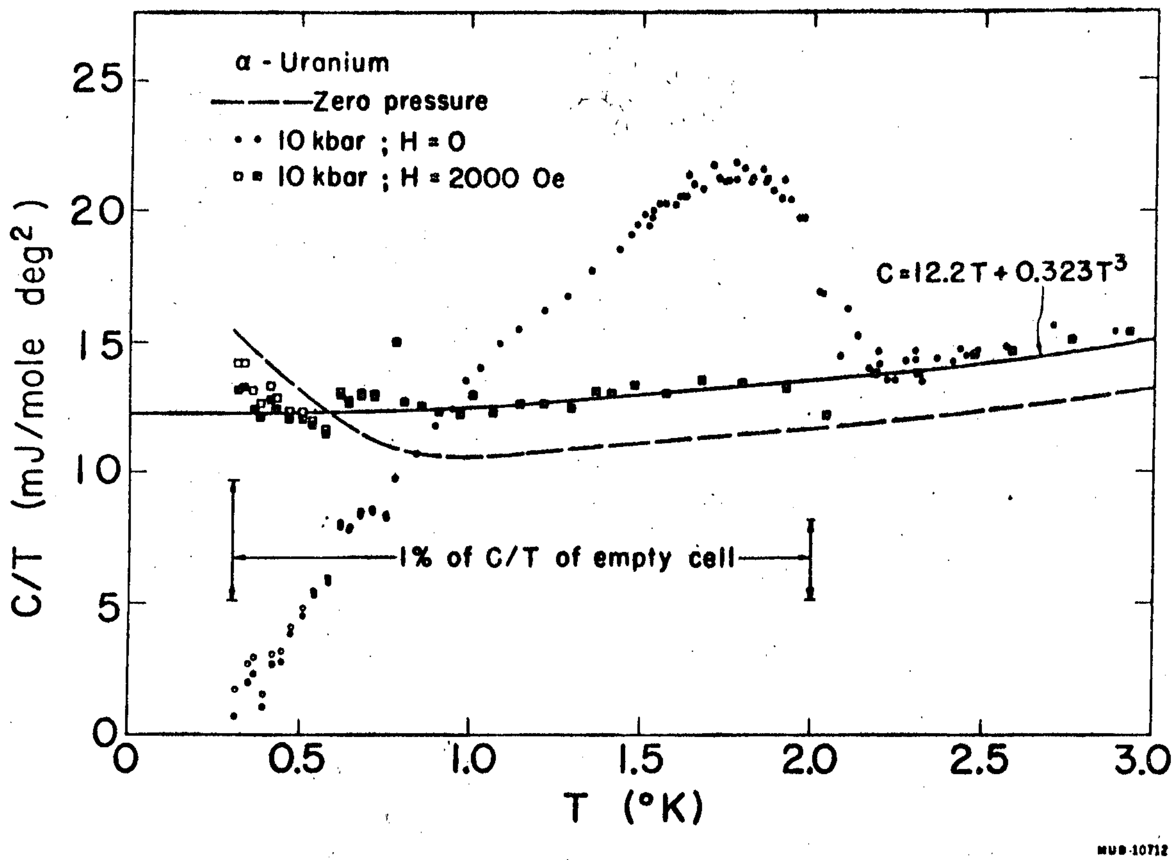

Fig. 2. The heat capacity of α-uranium at zero pressure and at 10 kbar. Points represented by solid symbols and the dashed curve have been corrected for the hyperfine heat capacity by subtraction of a T^{-2} term. The open symbols represent the total sample heat capacity. For $T > 1^{\circ}K$ the dashed curve corresponds to $C = 10.3\ T = 0.323\ T^3$.

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