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The Heat Capacity of α-Uranium at a Pressure of 10 kbar, between 0.3 and 6°K*

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We have measured the heat capacity of α-uranium at a pressure of 10 kbar between 0.3 and 6°K both in zero magnetic field and in 2000 Oe. A heat capacity anomaly typical of a bulk superconducting transition was observed at 2°K; the anomaly coincided with a superconducting transition observed magnetically on the same sample. Since zero-pressure heat capacity measurements to temperatures as low as 0.1°K have consistently failed to detect a bulk superconducting transition[1-3], these measurements constitute the first observation of bulk superconductivity in α-uranium and

show that 10 kbar increases T_c by a factor of at least 20--an even more striking effect than that suggested by magnetic measurements.[4] It seems possible that α-uranium may even be the first example of a metal that becomes superconducting only under pressure without undergoing a crystallographic transition. The application of 10 kbar pressure also increased the normal-state density of states by 18% and eliminated a low-temperature (<0.7°K) heat capacity anomaly that was observed at zero pressure.

Superconducting transitions in α-uranium at zero pressure have been observed[5-8] either magnetically or resistively, with values of T_c ranging from 0.2°K to above 1°K, but there is no indication of an anomaly of the type associated with a superconducting transition in heat capacity measurements on one sample[1] to 0.15°K or in measurements on two other samples[2] to 0.65°K. More recent heat capacity measurements on two samples to 0.1°K and on two other samples to 0.3°K also failed to show evidence of bulk superconductivity, although three of the samples had been studied magnetically and in each case these measurements showed superconducting transitions within the range of the calorimetric measurements.[3] Thus, the heat capacity measurements show that at zero pressure α-uranium is not a bulk superconductor above 0.1°K, and that all previously observed transitions were the consequence of multiply connected superconducting filaments. Since the superconductivity of α-uranium is of particular interest in connection with the role of the 5f states, these measurements were undertaken to determine whether or not the transition observed

magnetically at high pressure[4] is a bulk transition, and to look for any associated change in the normal-state density of states.

The sample was contained in a small Be-Cu piston and cylinder arrangement in which a pressure applied in a press at room temperature could be retained when the assembly was cooled to low temperatures. The pressure at the low temperature was determined from the magnetically measured T_c by use of the known pressure dependence.[4] Although the heat capacity of the cell was 20 to 40 times the normal-state heat capacity of the sample, reasonable accuracy was obtained by measuring the heat capacities of the filled and empty cell to a precision of a few tenths of 1%, using a germanium thermometer that retained its calibration between the two measurements.

Figure 1 shows the results of the high-pressure measurements for temperatures below 3°K, and, for comparison, a dashed curve which represents the zero-pressure heat capacity of a larger sample from which the high-pressure sample was cut. The open symbols represent the total sample heat capacity; the solid symbols and the dashed curve have been corrected for the hyperfine heat capacity of the U^{235} by subtraction of a T^{-2} term that was derived from lower-temperature measurements at zero pressure.[3] The zero-pressure heat capacity is independent of magnetic field to at least 5000 Oe, and the anomaly below 1°K was also observed in three other samples.[3] Above 1°K the dashed curve is represented by $C = 10.3\ T + 0.323\ T^3$ mJ/mole deg, and, therefore, the coefficient of the

electronic heat capacity is $\gamma = 10.3$ mJ/mole deg^2. At 10 kbar, the zero-field measurements show an anomaly typical of a superconducting transition at $T_c \approx 2°K$, in good agreement with the magnetically determined T_c. The 2000-Oe 10-kbar measurements show no anomaly at any temperature in the range of measurement and give $\gamma = 12.2$ mJ/mole deg.^{2} The accuracy with which the T^3 term can be determined is insufficient to permit any conclusion about its pressure dependence, but the 18% change in γ, which is proportional to the normal-state density of states N(0), is well outside the experimental error. Thus, the application of a pressure of 10 kbar to α-uranium raises T_c from below 0.1°K to 2°K, increases N(0) by 18%, and eliminates the low-temperature zero-pressure anomaly in the heat capacity.

The BCS expression[9] for T_c is

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

where V measures the strength of the phonon-mediated electron-electron interaction and θ_D is the Debye temperature. To explain an increase of T_c from 0.1 to 2°K this relation 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 marked increase in V is implied.

Geballe et al.[8] have recently suggested that the pressure enhancement of the superconducting interaction and the anomalous physical properties of α-uranium at 43°K might both be

related to a populating of localized 5f states below 43°K. They suggest that the electrons in these 5f states inhibit superconductivity, just as 4f electrons in lanthanum do,[10] but that application of pressure raises the 5f states above the Fermi surface. Such a pressure dependence of the 5f states would be similar to that of the 4f states in cerium.[11] We may employ this model and analogies with the lanthanide metals to explain the effect of pressure on γ and on the zero-pressure low-temperature heat capacity anomaly. The heat capacity anomalies in cerium[12,13] associated with the ordering of 4f electrons also disappear[14] on application of 10 kbar. Furthermore, the available γ values[15] for the lanthanide metals suggest that N(0) increases with increasing number of electrons in the 6s5d conduction band, but that the localized 4f states do not contribute to N(0). Thus, if the zero-pressure anomaly in α-uranium is associated with the ordering of 5f electrons, its disappearance at 10 kbar and the accompanying increase in γ could both be understood if the 5f and 7s6d states behaved in the same way as the 4f and 6s5d states in the lanthanides. (Since the 5f states in the actinides are generally believed to be less highly localized than the 4f states in the lanthanides, these analogies, although suggestive, should be applied with a certain amount of caution.) Although there is no evidence of a temperature-dependent magnetic susceptibility for α-uranium below 43°K,[16] the number of electrons involved may be very small (that part of the entropy of the zero-pressure anomaly actually observed above 0.1°K amounts to only 3×10^{-4} R)

or, alternatively, the ordering may be antiferromagnetic with an anomaly in χ which is small compared with the relatively large Pauli paramagnetism.[17]

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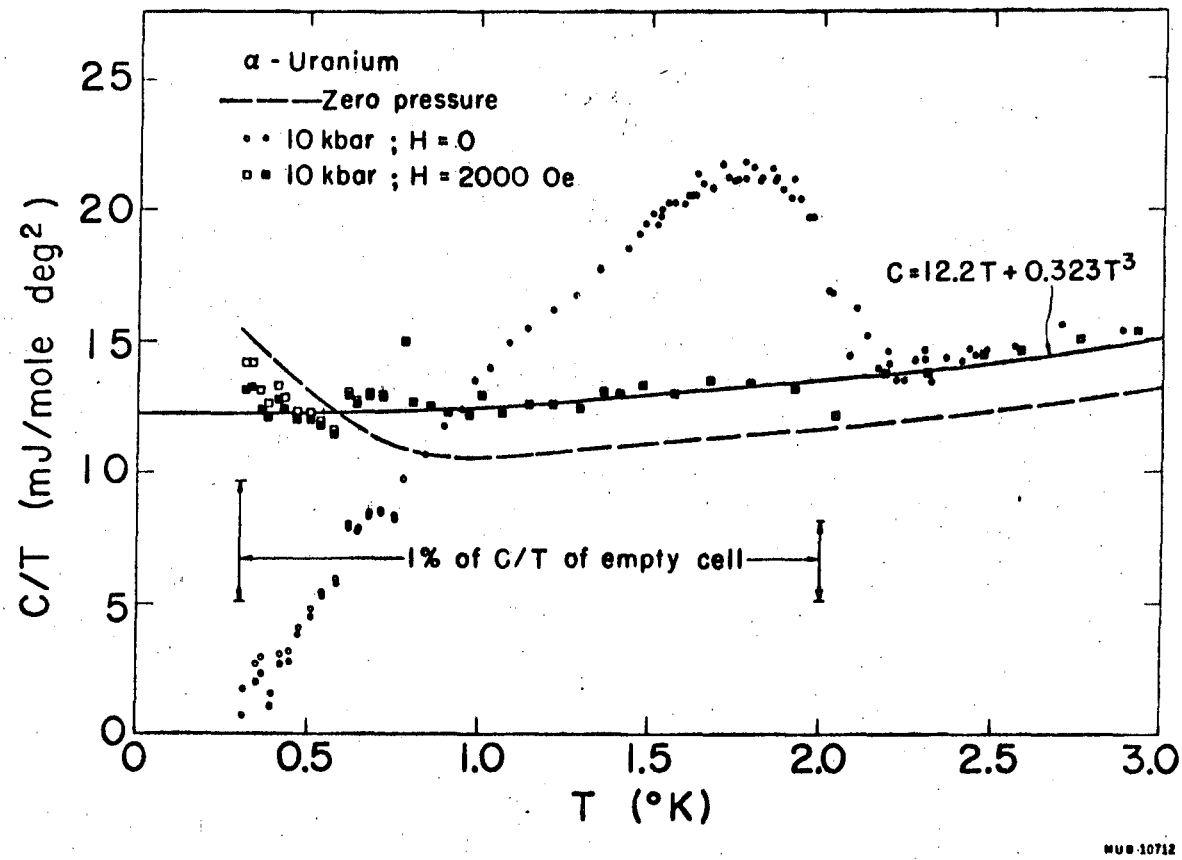

Fig. 1. The heat capacity of α-uranium at zero pressure and at 10 kbar. Points represented by solid symbols and the dashed curve have been corrected for the hyperfine heat capacity by subtraction of a T^{-2} term. The open symbols represent the total sample heat capacity. For $T \gtrsim 1$ °K the dashed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