Low-temperature properties of the heavy-fermion system UCd_{11}

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We present electrical-resistivity, magnetic-susceptibility, specific-heat, and thermal-expansion data for UCd_{11}. The low-temperature specific heat indicates that the electronic subsystem has a highly enhanced specific heat which is partially removed by a phase transition at 5.0 K.

Recent work on various U intermetallic compounds has demonstrated that the low-temperature properties of these materials are dominated by a very unusual behavior of the electronic subsystem.[1-3] Most probably, it originates from very strong electron-electron interactions, and, as the most obvious result, extremely large electronic specific heats are observed at low temperatures. The electronic nature of these specific heats has most convincingly been demonstrated by the observation of superconductivity in UBe_{13} and the corresponding anomaly of the specific heat at the phase transition.[1] UPt_3 is another, more recent example where superconductivity is formed out of an electronic state with a large density of states at E_F,[2] similar to what was first observed in $CeCu_2Si_2$.[4] In all these compounds the strong enhancement of the electronic specific heat occurs only below about 10 K, giving rise to a strongly-temperature-dependent C_e/T ratio below this temperature. A somewhat different behavior is observed in U_2Zn_{17}.[3] A very large specific heat varying linearly with temperature is already observed at 15 K. Here, the C_e/T ratio is temperature independent with decreasing temperature. The temperature dependence of C_p through and below the antiferromagnetic phase transition is governed by a sharp positive discontinuity at T_n, a finite and still rather large contribution to C_p varying linearly with temperature and, in addition, a considerable nonlattice T^3 contribution at the lowest temperatures. The data were interpreted as being due to an antiferromagnetic ordering within the strongly interacting electron system.[3]

These facts stimulated the search for other examples of low-temperature phase transitions in similar materials. UCd_{11} crystallizes in the cubic $BaHg_{11}$ structure with a lattice constant of 9.29 Å.[15] The nearest U-U neighbor distance is large (6.56 Å with 5.13 Å for UBe_{13} and 4.39 Å for U_2Zn_{17}). Therefore direct overlap of the $5f$-electron wave functions should be negligible. By simple analogy, we expected similar low-temperature features of the physical properties of UCd_{11} as were observed before in UBe_{13} and U_2Zn_{17}.

Magnetic-susceptibility measurements on UCd_{11} have been made before. Cafasso and co-workers[5] measured the magnetic susceptibility χ between 2 and 300 K. From six data points a Curie-Weiss behavior at high temperatures with an effective magnetic moment $p_{\text{eff}}=3.79\mu_B$ and a paramagnetic Curie temperature of -41.5 K, as well as a temperature-independent χ of 39.6×10^{-3} emu/mol below 4.2 K, were reported. Later, Misiuk and co-workers[6] repeated the measurements over an extended temperature range between 4.2 and 900 K. They more or less confirmed the results of Cafasso and co-workers, although with a somewhat larger low-temperature value of $\chi=45\times10^{-3}$ emu/mol. The temperature-independent χ at low temperatures was, in both cases, interpreted as being due to a singlet ground state of the crystal-field-split $J=4$ Hund's-rule ground state of a $5f^2$ configuration of the U ions. Our experimental data shown below demonstrate convincingly that UCd_{11} undergoes a phase transition at about 5 K.

Our experiments were performed variously on small single-crystalline cubes grown from excess molten Cd, as well as on polycrystalline material. The latter was obtained by reacting uranium tubings with cadmium vapor for 4 d at 320 °C in closed silica tubes and subsequent annealing of the pressed powder in a quartz tube at 440 °C for 10 d. A Guinier photograph confirmed the correct $BaHg_{11}$-type structure. An x-ray analysis of our single crystals revealed a lattice constant a_0 of 9.283(8) Å, close to what has been reported before.[5,6] Samples with good chemical composition could also be identified by the absence of superconducting transitions around 0.5 K which indicate precipitated excess Cd. In Fig. 1 we show the temperature dependence of the inverse magnetic susceptibility χ^{-1} between 1.5 and 300 K, measured on a polycrystalline sample with a sample-moving magnetometer. The high-temperature Curie-Weiss—type behavior may be characterized by an effective moment of $p_{\text{eff}}=3.45\mu_B$ and a paramagnetic Curie temperature $\Theta=-20$ K. Below about 80 K, deviations from this behavior are discernible, and around 5 K there is an abrupt change of slope, the susceptibility below this temperature being nearly constant, with a value of 38.4×10^{-3} emu/mol at 1.5 K, close to what has been reported by Cafasso and co-workers.[5] These results give no conclusive clue to the $5f$-electron configuration of the U ions. In view of the occurring phase transition, as will be shown below, the previously suggested Van Vleck—type behavior at low temperature, indicative of a $5f^2$ configuration of the U ions, can no longer be considered valid.

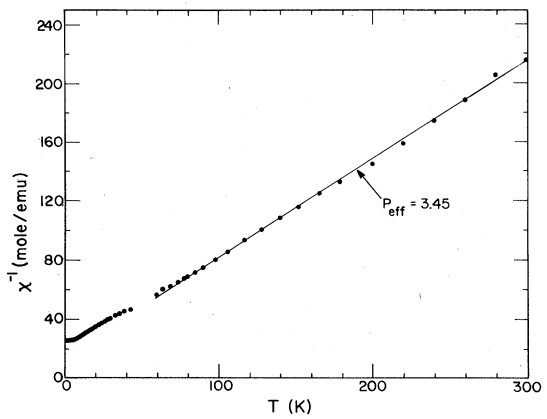

FIG. 1. Temperature dependence of the inverse magnetic susceptibility of polycrystalline UCd_{11} between 1.5 and 300 K.

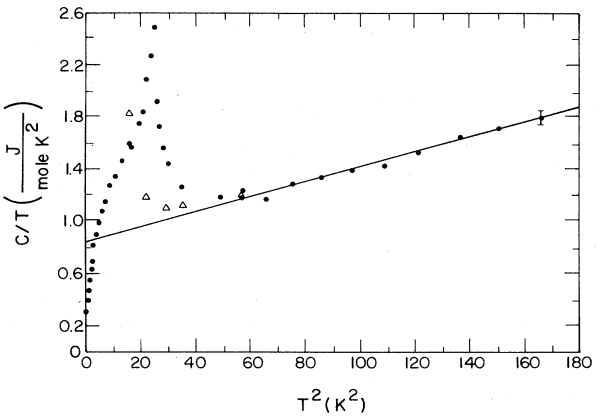

FIG. 3. C_p/T versus T^2 measured on single crystals of UCd_{11} between 0.4 and 13 K. Triangles denote data taken in an external 11-T magnetic field.

The temperature dependence of the electrical resistivity ρ between 1.3 and 300 K is shown in Fig. 2. The single crystal measured was not suitable for an accurate determination of the geometry factors and, hence, the absolute value of ρ. We estimate an approximate room-temperature value for ρ of about 100 $\mu\Omega$ cm. The observed temperature dependence of ρ is similar to that reported for USn_3,[7] except for a distinct break in the $\rho(T)$ curve (see inset of Fig. 2) near 5 K, corresponding to the temperature dependence of χ and therefore suggestive of some kind of phase transition.

Clear evidence for such a phase transition is obtained from our results of specific-heat and thermal-expansion measurements as shown in Figs. 3 and 4, respectively. In Fig. 3 we show the ratio C_p/T as a function of T^2 for temperatures between 0.4 and 13 K, measured on a collection of single-crystalline specimens weighing a total of 20 mg. The specific-heat anomaly associated with the phase transition peaks at 5.0 K. Above 8 K our data are consistent with a temperature dependence of C_p given by

$$C_p=\gamma T+\beta T^3\ ,$$

where $\gamma=840$ mJ/mol K^2 and $\beta=5.75$ mJ/mol K^4, resulting in a Debye temperature $\Theta_D=152$ K. Also shown in Fig. 3 are some data points taken in an external magnetic field of 11 T. Similar to U_2Zn_{17}, UCd_{11} has an anomalously large electronic specific heat in the paramagnetic state just above the phase transition, but this γ value is again drastically reduced below the phase transition to about 250 mJ/mol K^2, as may be evaluated from our experimental data below 1 K. Of course, this value is still considerably higher than those found in normal metals or transition-metal compounds. An external magnetic field of 11 T depresses the transition temperature to below 4 K. Similar to $C_p(T)$, the linear thermal-expansion coefficient α, measured on a suitably shaped polycrystalline sample, also displays a rather broad anomaly with a high-temperature tail ranging from 5 to about 8 K. The absolute magnitude of the α peak value is comparable to that observed in U_2Zn_{17}, and, again, is rather small when compared with anomalies at phase transitions of other U compounds at similar temperatures.[8] While it seems clear that UCd_{11} undergoes a phase transition at 5 K, it is less obvi-

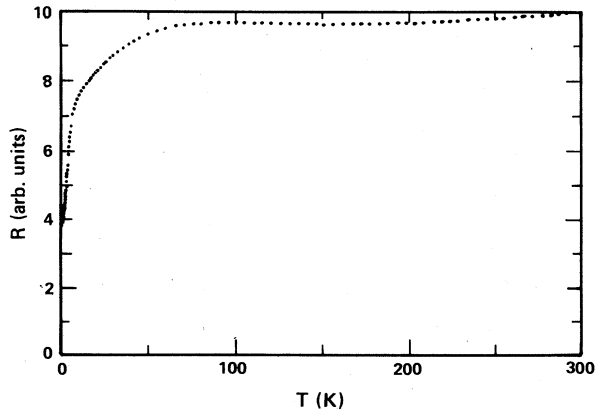

FIG. 2. Temperature dependence of the electrical resistivity of single-crystal UCd_{11} between 1.3 and 300 K.

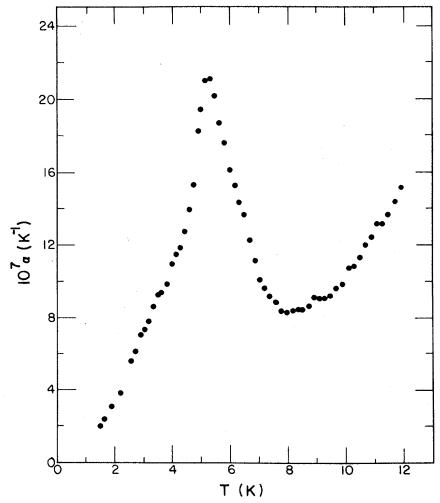

FIG. 4. Thermal expansion of polycrystalline UCd_{11}.

ous as to how it should be interpreted. The temperature dependence of χ around the transition, while not definitive, may be taken as an indication of antiferromagnetic ordering. This interpretation is also supported by the substantial loss of Fermi surface through the transition, as evidenced by the large reduction of γ, as mentioned above. Although these facts suggest an antiferromagnetic ordering among itinerant electrons with a large effective mass, we note that with decreasing temperature a net entropy loss is associated with the phase transition. The estimate of the entropy balance is again obscured by the large high-temperature tail of the specific heat, but an integration up to 8 K, where C/T reaches a constant value, reveals $\Delta S = 0.28R \ln 2$, where ΔS is the difference between $\int_0^{T=8\text{ K}} (C/T)dT$ and 8γ. This, of course, raises the question of whether additional degrees of freedom from localized electrons may, at least partly, be involved.

Since the $5f$-electron configuration of the U ions is not really known, one should not rule out a Jahn-Teller–type structural transition, which is most likely to occur if the U ions adopt a $5f^2$ configuration, and which is often observed in Pr compounds where the rare-earth ions adopt a $4f^2$ configuration.[9,10] However, the magnitude of the anomaly of the linear thermal-expansion coefficient is, as mentioned above, rather small, and therefore gives little support for such an interpretation.

Although both the specific-heat and the thermal-expansion results indicate a considerable high-temperature tail of the phase transition, a possible explanation for part of this behavior is suggested by a comparison with the low-temperature properties of UBe_{13},[11] UPt_3,[2] $CeAl_3$,[11] and $CeCu_2Si_2$.[4] In these compounds the ratio C_e/T increases rapidly with decreasing temperature below a certain temperature (~ 7 K for UPt_3). Such a behavior, if it occurs below about 8 K in UCd_{11}, could easily be hidden in the observed tail in C_p above 5 K for UCd_{11}. The $T=0$ K value for γ would then be larger than 840 mJ/mol K^2, and the net entropy valence of the transition might be zero or even negative, as in U_2Zn_{17}. Similarly, both in UBe_{13}[12] and $CeAl_3$,[13] increasing α values with decreasing temperatures have been observed in the same temperature range. Thus, at least part of the high-temperature tail in C of UCd_{11} might be accounted for by a behavior as just described, and is observed in compounds that are in many ways very similar to UCd_{11}. Since both positive and negative changes of C_p of 5–10 % in magnetic fields of 11 T have been observed before in UBe_{13} (Ref. 14) and UPt_3 (Ref. 15), the field data for UCd_{11} cannot conclusively decide for or against a possible variation of C_e/T with T below 8 K that would significantly alter ΔS. The amount of temperature dependence required to make $\Delta S = 0$ would give C_e/T (extrapolated to $T=0$) of 1.3 J/mol K^2, or only a 50% increase in γ from 8 K, whereas γ changes by over a factor of 7 in the same temperature range in UBe_{13}. It should be noted that the field data for UCd_{11} *do* rule out, down to 5 K, the same sort of rapid variation in C_e/T observed in UBe_{13}, $CeCu_2Si_2$, and $CeAl_3$, where C_e/T increases by $\sim 50\%$ between 8 and 5 K.

In conclusion, UCd_{11} is another compound whose electronic subsystem has a highly enhanced specific heat at low temperatures. Part of this specific heat is removed by a phase transition at 5.0 K whose origin and character remains to be clarified.

ACKNOWLEDGMENTS

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