UBe_{13}: An Unconventional Actinide Superconductor

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(Received 14 March 1983)

Electrical-resistivity, magnetic-susceptibility, and specific-heat data reveal that UBe_{13} is superconducting below 0.85 K. Highly anomalous low-temperature electronic properties in both the normal and superconducting states result in an enormous electronic specific-heat coefficient $\gamma = 1.1$ J/mole K^2 and a corresponding magnetic susceptibility $\chi = 1.5 \times 10^{-2}$ emu/mole. The superconducting state appears to be extremely stable with an initial slope of the temperature derivative of the critical field $(\partial H_{c2}/\partial T)_{T_c} = -257$ kOe/K.

PACS numbers: 74.10.+v, 65.40.Em, 72.15.Qm

In materials research there has recently been some excitement about electrically conducting materials which undergo superconducting transitions at low temperatures but exhibit rather unconventional properties in both their normal and superconducting states, respectively. Among others we mention in particular those substances where an intimate interplay of superconductivity and magnetism is observed, namely Chevrel phases containing rare-earth ions,[1] $RERh_4B_4$ compounds (RE denotes rare earth),[1] $CeCu_2Si_2$,[2] Y_4Co_3,[3] and most recently also organic conductors.[4] In the first two cases, a wealth of experimental data is available and it appears that theoretical understanding of the observed phenomena is fairly advanced. This is not so in the case of the other three examples, mainly because either $CeCu_2Si_2$, Y_4Co_3, or (tetramethyltetraselenafulvalene)$^+X^-$ salts are so far the only examples of substances showing their kind of particular properties.

If we especially consider $CeCu_2Si_2$, we recall that this material appears to change its properties from those of an intermetallic compound containing trivalent Ce ions with one localized $4f$ electron at high temperatures[5] to those of a system which may be described as a Fermi liquid having enormous effective mass at E_F and undergoing a transition to a superconducting state[3] with a comparatively large critical field.[6] In this Letter we should like to present experimental evidence that similar or even more spectacular properties are observed in UBe_{13}, an intermetallic compound containing actinide ions with $5f$ electrons.

Magnetic properties of polycrystalline UBe_{13} have been studied before.[7,8] Because of the large U–U distance of 5.13 Å in this compound[9] it was assumed that the U ions adopt a tetravalent configuration with two rather well localized $5f$ electrons. Curie-Weiss behavior of the temperature dependence of the magnetic susceptibility $\chi(T)$ above 100 K seemed to confirm this assumption but the expected Van Vleck–type temperature-independent susceptibility at low temperatures was not observed.[7,8] Instead a search for eventual magnetic ordering below 1 K, motivated by an increasing specific heat with decreasing temperature just above 1.5 K, led to the observation of strong diamagnetic signals below 1 K. However, intrinsic bulk superconductivity of UBe_{13} was discarded and the observation was ascribed to precipitated U filaments in the polycrystalline samples.[8] From our experimental data presented below we infer that UBe_{13} is a genuine but exotic superconductor.

It was found only recently that single crystals of $CeCu_2Si_2$ are not superconducting down to about 0.05 K,[10] but that external pressure of moderate strength induces superconductivity as observed in polycrystalline samples at zero pressure.[10] To avoid similar problems we synthesized UBe_{13} in both polycrystalline and single-crystalline form. Here we give only the details of data obtained with unannealed single crystals. They were grown from pre-arc-melted UBe_{13} embedded in Al flux which was slowly cooled from about 1400 °C. In this way we obtained ingots of approximately 2 g containing several bulk single crystals. On such crystals we measured the specific heat c_p between 0.06 and 10 K, the electrical resistivity ρ between 0.5 K and room temperature, the magnetic susceptibility χ between 0.03 and 250 K, and we also studied the influence of external magnetic fields on the low-temperature susceptibility. All magnetic measurements were made using single crystals that were cut from the same ingot.

In Fig. 1 we show both the low-frequency ac susceptibility χ_{ac} and the specific heat c_p in zero magnetic field below 1.2 K. It may be seen that in both measurements the transition occurs over an extended but identical temperature interval of about 0.2 K. The strong diamagnetic signal of χ_{ac} alone gives no definite evidence for bulk superconductivity in UBe_{13}; however, the additional observation of a specific-heat anomaly is already rather convincing evidence for it. The continuing decrease of c_p with steady slope upon decreasing temperature even at 0.065 K proves that the anomaly around 0.8 K cannot be related to magnetic ordering because in that case we would expect an indication of nuclear specific heat due to the hyperfine splitting of the nuclear levels of ^{235}U nuclei contained in the sample. Such contributions have recently been observed in other, magnetically ordering U compounds.[11] An alternative possibility, the occurrence of a structural phase transition at 0.8 K, can also be discarded, simply because $c_p(T)$ would be too small to account for such a transition. From our experimental $c_p(T)$ values we calculate an entropy change of about 1 J/mole K between 0 and 1 K. This is in excellent agreement with what we obtain if we assume that, without the transition, $c_p(T)$ would decrease linearly with decreasing temperature below 0.9 K, thus giving additional confirmation that the transition occurs within an electronic system with greatly enhanced density of states and, according to our experimental data, with a γ term of 1.1 J/mole K^2.

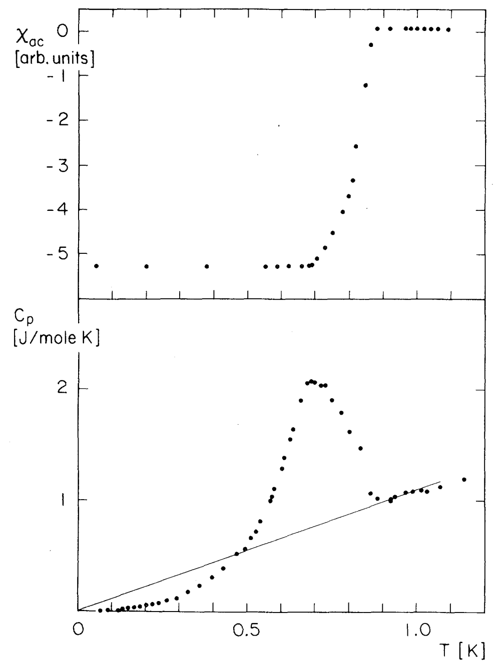

FIG. 1. Temperature dependence of the low-frequency ac magnetic susceptibility and the specific heat of UBe_{13} single crystals below 1.2 K in zero magnetic field (H_{ac} < 0.3 Oe).

From our results of the temperature dependence of the inverse magnetic susceptibility $\chi^{-1} = H/M$ above 1.5 K, we obtain good agreement with the previously published data of Ref. 8 which cover the temperature range from 1.5 to 60 K. The slope of $\chi^{-1}(T)$ in this temperature range is consistent with an effective moment $p_{eff} = 3.55\mu_B$ per U ion, as was also claimed in Ref. 8, almost the free-ion value for U^{4+} ions. The high-temperature behavior, however, indicates that this interpretation of $\chi^{-1}(T)$ is probably incorrect. Our data of $\chi^{-1}(T)$ above 150 K infer that the effective moment is only about $2.6\mu_B$ per U ion and we deduce a paramagnetic Curie temperature $\theta_p = -53$ K. This result is somewhat different from the conclusions in Ref. 7. A rather striking behavior is found for the magnetic-field dependence of the magnetization $M(H)$ at 4.2 K. It indicates that the low-temperature susceptibility is hardly affected at all up to 100 kOe, pointing to strong antiferromagnetic correlations. Just above the superconducting transition, χ reaches a maximum value of 1.5×10^{-2} emu/mole. We also checked the influence of external magnetic fields on χ_{ac} below 1 K. With increasing field, the diamagnetic transition is shifted to lower temperatures, as expected. Assuming that UBe_{13} is a type-II superconductor, we evaluate an initial slope of the temperature dependence of the upper critical field $(\partial H_{c2}/\partial T)_{T_c} = -257$ kOe/K, to our knowledge the highest value of this quantity ever measured up to now.

In Fig. 2 we show the temperature dependence of the electrical resistivity ρ between 0.5 and 290 K, which is clearly anomalous for an intermetallic compound. Below room temperature, ρ rises steadily with decreasing temperature, finally reaching a flat maximum of 228 $\mu\Omega$ cm around 10 K. Below 10 K, ρ rises once more, again reaching a maximum of 234 $\mu\Omega$ cm at 2.35 K. The developing decrease of ρ with still decreasing temperature is then intercepted by the

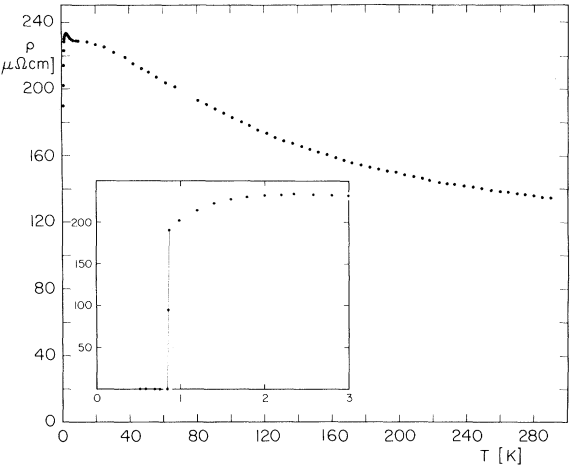

FIG. 2. Temperature dependence of the electrical resistivity of single-crystalline UBe_{13}. Inset: The low-temperature part on an extended temperature scale.

superconducting transition at 0.86 K. As may be seen from the inset in Fig. 2, the resistive transition to the superconducting state is much more narrow in temperature than the transitions shown in Fig. 1. These features are probably due to residual inhomogeneities in the not yet optimized samples.

For the room-temperature lattice constant of the UBe_{13} single crystals used in the present investigation we obtained 10.2607 Å, resulting in a nearest U–U distance of 5.130 Å in this compound. According to Hill's earlier arguments[12] it may therefore be expected that the $5f$ electrons of the U^{4+} ions are fairly well localized and with any conventional view, certainly no occurrence of superconductivity in such a system is anticipated. On the contrary, the common enhanced increase of c_p/T and χ (not shown explicitly here), as well as of ρ, with decreasing temperature below 10 K rather indicate precursor effects to a possible magnetic phase transition.

This pronounced temperature dependence of all these properties just above T_c makes a clear-cut interpretation of the experimental data somewhat difficult. Nevertheless it is interesting to quote some values for physically important parameters which we calculate from our experimental data. If, as indicated above, the specific heat up to about 1 K is interpreted as being of electronic origin we can calculate the corresponding magnetic susceptibility of that electronic system using

$$\chi = 2\mu_B{}^2 N(E_F) = 3\mu_B{}^2\gamma/\pi^2 k_B{}^2, \tag{1}$$

where $N(E_F)$ is the density of electronic states per spin direction at the Fermi energy E_F, μ_B is the Bohr magneton, and k_B is Boltzmann's constant. If we insert the above-quoted value for $\gamma = 1.1$ J/mole K^2 into Eq. (1), we obtain $\chi = 1.51 \times 10^{-2}$ emu/mole, in extremely good agreement with our experimental value of χ at about 1 K, again confirming the claim above, that we are dealing with an electronic system that can be described as a Fermi liquid.

The maximum resistivity is thought to be due to incoherent scattering of conduction electrons at the U ions and may, according to Friedel,[13] be described by

$$\rho_{\max} = (2l+1)c(2h/e^2 k_F z), \tag{2}$$

where $l = 3$ for f electrons, $c = \frac{1}{14}$ is the concentration of scattering centers, Z is the number of conduction electrons per atom, and $k_F = (3\pi^2 Z/\Omega)^{1/3}$ with Ω as the mean volume per atom. From it we can calculate Z and subsequently k_F through

$$Z = [2(2l+1)hc/e^2\rho_{\max}]^{3/4}[\Omega/3\pi^2]^{1/4}. \tag{3}$$

From the experimental value of $\rho_{\max}$ we obtain $Z = 0.81$ per atom and $k_F = 1.36 \times 10^8$ cm^{-1}. Within the Fermi-liquid model we then deduce an effective mass of the fermions of $m^* = 192 m_e$. The still rather high electrical resistivity at T_c indicates that superconducting parameters of the present material should be calculated in the dirty limit. According to Hake,[14] $(\partial H_{c2}/\partial T)_{T_c}$ is then given by

$$(\partial H_{c2}/\partial T)_{T_c} = -4.48 \times 10^4 \rho\gamma, \tag{4}$$

where γ is given in cgs units and ρ in Ω cm. Inserting our experimental values for γ and $(\partial H_{c2}/\partial T)_{T_c}$ we obtain $\rho = 42$ $\mu\Omega$ cm, the expected value of the residual resistivity for $T \to 0$. Once ongoing additional experiments give more information on other superconducting parameters of UBe_{13} we shall discuss them by comparing them with the presently available normal-state properties.

In conclusion we feel that the experimental data presented and described above show convincingly that, as was anticipated, $CeCu_2Si_2$ is not a singularity of nature.[15] It seems again quite clear that the presence of f electrons is essential for the occurrence of superconductivity in UBe_{13}, since no traces of superconductivity were found in $LaBe_{13}$, $LuBe_{13}$, and $ThBe_{13}$ down to 0.45 K.[8] Since UBe_{13} shows all the interesting features not only in polycrystalline but also in its single-crystalline form at zero pressure,[16] this material is very well suited to investigation of the microscopic origin of the spectacular and still puzzling low-temperature properties, i.e., the nature of both the normal and the superconducting states of such systems, resembling a Fermi liquid of particles with extremely large effective mass.

We thank Dr. W. Odoni and K. Mattenberger for assistance in part of the experiments. This work was done partially under the auspices of the U. S. Department of Energy, and also benefitted from financial support of the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung.

Note added.—Recent measurements of the specific heat and the critical field of superconducting U_6Fe (Ref. 17) were interpreted as being another manifestation of superconductivity in a strongly interacting electron gas.[18]

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