Investigation of some beryllium compounds and superconductors with heavy fermions

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Several beryllium compounds are investigated. Some of these compounds exhibit superconductivity. The samples UBe_{13} were found to have $T_c \simeq 0.6$ K and $\partial H_{c2}/\partial T \approx 270$ kOe/K, in agreement with (5). Dissolution of isostructural $ZrBe_{13}$ and $CeBe_{13}$ in UBe_{13} sharply decreases T_c and $\partial H_{c2}/\partial T$.

The superconductivity of beryllium and of several compounds based on it has been studied extensively.[1–4] Interest in beryllium compounds has recently again increased in view of the peculiar properties of uranium beryllide UBe_{13}.[5] According to the data in Ref. 5, this compound has the parameters $T_c = 0.85$ K, $\partial H_{c2}/\partial T = 257$ kOe/K, $\gamma = 1.1$ J/mole K^2, and $m^* = 192 m_0$.

Our investigation of the beryllium compounds[1,4] showed that WBe_{13}, for example, becomes a superconductor at 4.1 K. It was of interest to make an additional study of beryllium compounds. We investigated the compounds $CeBe_{13}$, $ZrBe_{13}$, $HfBe_{13}$, as well as UBe_{13} at temperatures up to 0.02 K. Superconductivity was observed in some of the compounds. For the superconducting compounds, we studied the temperature dependence of the critical magnetic field, and for some systems we studied the magnetic-field and temperature dependence of the resistance. The samples were prepared by fusing the components in a high-frequency furnace in beryllium oxide crucibles, in some cases the fusion was performed in a small arc furnace with a tungsten electrode and a water-cooled copper hearth. To perform the measurements at superlow temperatures, we used the apparatus described in Ref. 6, in which erbium-yttrium-aluminum garnet was used for adiabatic demagnetization. To measure the critical magnetic fields

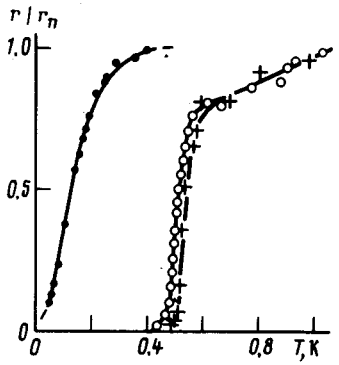

FIG. 1. Curves showing the behavior of the superconducting state. + — UBe_{13} with a field $H = 0$ ○ — UBe_{13} with a field $H = 11$ kOe and ● — $U_{0.85}Ce_{0.15}Be_{13}$ with a field $H = 0$.

TABLE I.[2)]

Composition	T_c, K	$\partial H_{c2}/\partial T$, kOe/K	ρ_n, 10^{-5} $\Omega\cdot$cm	γ_{exp} mJ/mole·K^2	γ_{av} mJ/mole·K^2	Structure
UBe_{13}	0.55	270	4.8	1100	7.97	$NaZn_{13}$
$ZrBe_{13}$	1.34	0.15	1.3	2.2	2.25	$NaZn_{13}$
$CeBe_{13}$	< 0.01	–	7	–	–	$NaZn_{13}$
$U_{0.9}Zr_{0.1}Be_{13}$	0.07	15	62	0.5	–	$NaZn_{13}$
$U_{0.85}Ce_{0.15}Be_{13}$	0.12	20	30	1.5	–	$NaZn_{13}$
$HfBe_{13}$	0.35	–	1.6	–	2.06	fcc
WBe_{13}	4.1	0.57	11	0.97	0.720	bct
Mo_6S_8Be	2.58	7	9	33	8.79	rhomb.

H_{c2} the sample and the thermometer were fastened at one end of a copper refrigeration line, while the other end which was glued to a cylindrical garnet rod. A magnetic field of 16 kOe was created with an electromagnet. After placing the specimen in the magnetic field, the garnet was lowered into a magnetic screen and fastened at the center of the magnet yoke. This device is similar to the device that we used previously, in which potassium chrome alum was used as the working body.[7] The pressure was created in Bridgeman anvils, also prepared from erbium-yttrium-aluminum garnet, whose demagnetization permitted decreasing the temperature of the compressed sample down to 0.1 K. Table I shows some of the results of the measurements. It is evident from the data presented that for most of the beryllium compounds and alloys the critical magnetic fields are low and only UBe_{13} has an anomalously high value, consistent with the results of Ref. 5. If the electronic heat capacity is estimated from the values of $\partial H_{c2}/\partial T$ and ρ_n, then the Sommerfeld coefficient γ turns out to be several mJ/mole K^2. As already noted, in contrast to most superconductors based on beryllium, UBe_{13} has an anomalously high value of γ equal to 1.1 J/mole K^2. For the UBe_{13} samples, the value of T_c measured at the center of the transition curve is $\approx$0.6 K.[1)] At a pressure of $\approx$14 kBar T_c increased by 0.07. [X-ray analysis of the lattice constant "a" permits assuming the presence of a peak in the dependence T_c (a).] Preliminary measurements of the Hall emf showed that UBe_{13} has a hole conductivity. At 4.2 K we have $n = 4\times10^{20}$ cm^{-3}. With increasing temperature from 2.5 to 100 K the Hall's constant dropped by a factor of approximately 12. In spite of the difference in T_c, the properties of the UBe_{13} samples investigated in this work were similar to the samples investigated in Ref. 5. For example, they had an analogous dependence $r(T)$. As the temperature was reduced from room temperature to 2°, the resistance of the sample increased twofold. In the region from 2° to 1.6, the resistance remained essentially constant, and then decreased linearly approximately by a factor of two down to

$T = T_c$. (In contrast to UBe_{13}, for samples of $ZrBe_{13}$ as the temperature was reduced, the resistance dropped by a factor of 10–20.) An investigation of the systems $U_{1-x}Zr_xBe_{13}$ and $U_{1-x}W_xBe_{13}$ has shown that while in the first case there is a good solubility of $ZrBe_{13}$ in UBe_{13}, which is indicated by the smooth change in the lattice constant with x, in the second case, the system is not a single-phase system. The samples $U_{1-x}W_xBe_{13}$ contain phases such as UBe_{13}, WBe_{22}, and WBe_2. The absence of solubility accounts for the fact that when there is a nonsuperconducting phase Be_2W in addition to UBe_{13} the T_c of the alloy is 0.57 K and $(\partial H_{c2}/\partial T)_{T\to T_c} = 144$ kOe/K. If, on the other hand, the alloy contains a superconducting phase WBe_{22}, for which $T_c = 4.15$ K, then T_c of the sample is ≈ 4 K, while $(\partial H_{c2}/\partial T)_{T\to T_c} = 343$ Oe/K. The superconductivity of the sample in this case seems to be determined by the presence of WBe_{22}.

In the case $U_{1-x}Zr_xBe_{13}$, T_c decreases sharply with x, and at $x = 0.1$ is ≈ 0.07 K, while $\partial H_{c2}/\partial T \approx 15$ kOe/K. For large values of x, for example, $x = 0.5$, T_c drops below 0.02 K, and then increases to 1.3 as $x \to 1$. The strong drop in T_c was also observed when $CeBe_{13}$, which dissolves in UBe_{13}, was introduced into UBe_{13}. In this case at $x = 0.15$ we have $T_c \approx 0.12$ K and $\partial H_{c2}/\partial T \approx 20$ kOe/K. Thus the dissolution of a small quantity of $ZrBe_{13}$ or $CeBe_{13}$ in UBe_{13}, which leads to a smooth change in the lattice parameters, causes a sharp decrease of T_c and of $\partial H_{c2}/\partial T$. The values of T_c presented in Table I correspond to the temperature at which $r(T) = 1/2r_n$.

The data on the electronic heat capacity presented above, obtained for beryllium compounds with transition and rare-earth metals, are not surprising, since in order of magnitude they correspond to the values of γ of many metallic systems. They do not differ too strongly from the average values calculated from γ_{Be} and γ for the second component. On the other hand, the exceptionally high values of γ obtained for UBe_{13} are unique. To explain such high values of γ, many investigators have used hypotheses such as the formation of a Fermi liquid of heavy fermions,[5] superconductivity caused by P pairing,[8] the properties of the Kondo lattice, etc.[9] It was hypothesized that the unusual properties of UBe_{13} are determined primarily by the U atoms and are related to the particular behavior of $5f$ electrons.[5] However, the series of uranium compounds such as U_6Fe, which transform into the superconducting state at $T_c = 3.8$ K,[10] although they have rather high critical magnetic fields (which are associated with the $5f$ electrons of uranium), differ considerably from UBe_{13}. Thus, for example for U_6Fe we have $\partial H_{c2}/\partial T = 34.2$ kOe/K and $\gamma = 155$ mJ/mole K^2, i.e., almost ten times less than for UBe_{13}. On the other hand, in some Shevreul phases $\partial H_{c2}/\partial T$ also have rather high values, for example, for $PbMo_6S_8 \approx 55$ kOe/K (in this case $m^* \approx 10m_0$).

In support of the fact that the $5f$ electrons are primarily responsible for the superconductivity of UBe_{13}, it is reported in Ref. 5 that compounds such as $LaBe_{13}$, $LuBe_{13}$, and $ThBe_{13}$ do not exhibit a transition to the superconducting state down to 0.45 K. As we can see from this letter, however, several beryllium compounds, which have a structure similar to UBe_{13}, are superconductors.

For the specific properties of the $5f$ electrons to be manifested the uranium atoms must presumably be in a "favorable" crystalline lattice. In such a lattice the $5f$ electrons of U are rather strongly localized. For uranium beryllides, such a lattice is apparently a lattice of the type $NaZn_{13}$. Compounds which crystallize in such a lattice,

like the Shevreul phases, can be categorized as cluster compounds,[11] which include several superconductors with unusual properties. We recall, however, that in the Shevreul phases the introduction of uranium leads to a drop in T_c and H_{c2}, while UMo_6S_8 is not a superconductor.[12,1)] It is possible that in the case of UBe_{13}, just as noted in Ref. 9 for $CeCu_2Si_2$, there is a resonant Abrikosov-Suhl state, which is very sensitive to a change in the parameters of the system. It should also not be ruled out that in the case of UBe_{13} a covalent instability can appear.[13,14] In this case H_{c2} can become infinite, while J_c approaches zero.[15] Our preliminary measurements of J_c do not seem to rule out this possibility.

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[1)]We have recently obtained samples with $T_c = 0.88$ K.

[2)]We have recently discovered superconductivity in $YbBe_{13}$, for which $T_c = 0.4$ K and $\partial H_{c2}/\partial T = 4.32$ kOe/K.

[3)]We have recently prepared a sample of $U_{1,2}Mo_{6,4}S_8$, which becomes a superconductor at $T = 0.25$ K and has $\partial H_{c2}/\partial T \simeq 7$ kOe/K. According to the x-ray data, Mo_2S_3 and uranium oxysulfide UOS were present in it in addition to the Shevreul phases.

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