New Phase Diagram for (U,Th)Be_{13}: A Muon-Spin-Resonance and H_{c1} Study

R. H. Heffner, J. L. Smith, and J. O. Willis
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

P. Birrer, C. Baines, F. N. Gygax, B. Hitti, E. Lippelt, H. R. Ott, and A. Schenck
Eidgenössische Technische Hochschule, Zurich, c/o Paul Scherrer Institute, CH 5232 Villigen, Switzerland

E. A. Knetsch and J. A. Mydosh
Kamerlingh Onnes Laboratorium der Rijksuniversiteit Leiden, 2300 RA Leiden, The Netherlands

D. E. MacLaughlin
University of California, Riverside, California 92521-0413
(Received 18 May 1990)

Zero-field muon-spin-resonance and lower-critical-field data are presented for a wide range of Th concentrations in $U_{1-x}Th_xBe_{13}$, spanning the region where both a superconducting and a second, lower-temperature phase transition are observed. Overall T-x phase boundaries are assigned and discussed according to the nature of the lower phase transition. Arguments for associating the lower phase with a possible magnetic (time-reversal-violating) superconducting state are given.

PACS numbers: 74.70.Tx, 74.30.Gn, 76.60.Jx, 76.75.+i

The origin and fascinating properties of the heavy-electron (HE) state in materials containing $4f$ and $5f$ elements remain topics of considerable current interest.[1] Of particular importance is the fact that many such materials possess multiple phase transitions, either superconducting or magnetic in nature. For example, the superconductors $CeCu_2Si_2$, URu_2Si_2, and UPt_3 all undergo magnetic phase transitions[2-4] to states with very small magnetic moments ($\simeq 10^{-2}\mu_B$ per U or Ce atom). There exists another class of HE compounds in which a few-percent substitution of impurity atoms also induces magnetic correlations. Examples[5,6] are (U,Th)Pt_3 and U(Pt,Pd)$_3$, and the unusual case[7] of $U_{1-x}Th_xBe_{13}$. In the latter system thorium substitution produces a nonmonotonic depression of the superconducting transition temperature T_{c1}, accompanied by a second phase transition at $T_{c2} < T_{c1}$ for $0.019 \leq x \leq 0.043$. Theoretical interpretations of this second phase have invoked a coexisting spin-density-wave state,[8] small local moments on the uranium[9] or thorium[10] sites, and a transition to a second superconducting state possessing orbital[11] or spin[12] magnetic moments. Until now, no experiments have been able to unambiguously distinguish between these different possibilities.[13] Hence the characterization of this system is important for understanding the HE state and the interplay between magnetism and superconductivity in these materials. If the second phase is characterized by a magnetic superconducting order parameter it would be the first observation of a magnetic signature associated with such a state in a metal.

We present both zero-field muon-spin-resonance (μSR) and lower-critical-field (H_{c1}) studies in $U_{1-x}Th_xBe_{13}$ across a broad range of Th concentrations (x=0.000, 0.0066, 0.0100, 0.0193, 0.0245, 0.0355, and 0.0600). We address the following questions: (1) Does pure UBe_{13} exhibit multiple, low-field phase transitions, as suggested by earlier critical-field measurements?[14] (2) How widespread is the magnetic behavior previously observed[13] below T_{c2} for x=0.035? (3) What is the likely explanation for the second phase below T_{c2}?

The μSR experiments were carried out at the Paul Scherrer Institute, Villigen, Switzerland, using the surface muon beam at the low-temperature facility. The experimental setup and data analysis are detailed in Ref. 13. Excellent fits to the zero-field time differential spectra were obtained using the Kubo-Toyabe relaxation function,

$$G_{KT}(t) = \tfrac{1}{3} + \tfrac{2}{3}(1-\sigma_{KT}^2 t^2)\exp(-\tfrac{1}{2}\sigma_{KT}^2 t^2),$$

appropriate for inhomogeneous broadening. Here $\sigma_{KT} = \gamma_\mu (\Delta H)_{rms}$, where γ_μ is the muon gyromagnetic ratio ($8.51\times10^4\ s^{-1}Oe^{-1}$) and $(\Delta H)_{rms}$ is the root-mean-square distribution of local magnetic fields at the muon site.

The $H_{c1}(T)$ measurements were carried out at the Kamerlingh Onnes Laboratory using a flux-gate magnetometer and a ^{3}He cryostat. Polycrystalline arc-melted samples were prepared from the same batches as for the μSR measurements and were cut in the shape of long thin cylinders so that demagnetization corrections were unnecessary. All samples exhibited >90% superconducting shielding and sharp transitions in χ_{ac} measurements, indicating good sample quality. In all the samples almost no Meissner effect was observed, indicative of polycrystallinity and strong pinning. The H_{c1} was obtained both as the first deviation (2%) from linearity of the initial shielding curve following zero-field cooling and by using a different procedure based on the Bean critical-state model.[15] The critical temperatures are given in Table I.

The temperature dependence of σ_{KT} is shown in Fig. 1. The values of the high-temperature ($T \geq 0.5$ K) re-

TABLE I. Collected parameters and transition temperatures of $U_{1-x}Th_xBe_{13}$. The notation is explained in the text.

Th (%)	T_{c1} (K) χ_{ac}	T_{c1} (K) $M(H)$	T_{c2} (K) $M(H)$	$H^L_{c1}(0)$ (mT)	$H^H_{c1}(0)$ (mT)
0.00	0.86	0.86	...	...	4.32
0.66	0.67	0.67	...	...	3.27
1.01	0.65	0.65	...	...	2.64
1.93	0.48	0.48	0.44	3.79	2.28
2.45	0.58	0.59	0.41	4.91	2.89
3.55	0.55	0.55	0.39	5.59	3.53

laxation rates $\sigma_n(T)$ are determined by the dipolar field distribution produced by the ^{9}Be nuclei. The small differences from sample to sample (at most 6%) are likely due to small variations in the equilibrium μ^+ lattice site for different thorium concentrations and systematic errors in data analysis. No change in linewidth was observed at T_{c1} in any sample. Also, no change in $\sigma_{KT}(T)$ with temperature is observed for $x=0.000$, 0.0100, or 0.0600, indicating a complete absence of magnetic correlations with moments $\gtrsim 10^{-3}\mu_B/(\text{U atom})$ down to $T \simeq 0.050$ K. The most striking feature of the data is the continuous increase in $\sigma_{KT}(T)$ below T_{c2} for $x=0.0193$, 0.0245, and 0.0355, indicating the onset of weak magnetic correlations of electronic origin. The electronic (σ_e) and nuclear (σ_n) contributions to σ_{KT} below T_{c2} are uncorrelated and so their respective linewidths add in quadrature: $\sigma_e^2(T)+\sigma_n^2(T)=\sigma_{KT}^2(T)$. As reported earlier[13] the temperature dependence of the derived magnetic order parameter $[\propto \sigma_e(T)]$ is consistent with a second-order, mean-field phase transition, and the effective electronic moment is of order $(10^{-3}\text{-}10^{-2})\mu_B/$(U atom). The extrapolated zero-temperature linewidths $\sigma_e(0)$ for $x=0.0193$, 0.0245, and 0.0355 are, respectively, 0.123 ± 0.005, 0.136 ± 0.004, and 0.161 ± 0.005 μs^{-1}, an increase of about 31% between $x=0.0193$ and 0.0355. This is significantly larger than the variations in the linewidths for $T > T_{c2}$, indicating that changes in dipolar coupling due to varying μ^+ sites alone are not sufficient to account for the increased relaxation rate. Thus the electronic moment increases with x in this range. This trend is discussed below in connection with the values of $H_{c1}(0)$.

The values of $H_{c1}(T)$ are plotted against T^2 in Fig. 2 for the representative cases $x=0.0000$ and 0.0355, to compare with the empirical relation $H_{c1} \propto 1-t^2$, where $t \equiv T/T_{c1}$. Values for the slope $|dH_{c1}/dt^2| \equiv H_{c1}(0)$ are given in Table I. $H^L_{c1}(0)$ and $H^H_{c1}(0)$ refer to the low-temperature and high-temperature slopes, respectively. Furthermore, $H_{c1}(0) \propto n_s(0)/m^*$ at $T=0$, where n_s is the superfluid density and m^* is the effective quasiparticle mass.[16]

For UBe_{13}, $H_{c1(T)}$ follows a single, quadratic temperature dependence over the entire temperature range measured (Fig. 2). A similar quadratic temperature dependence is found for $x=0.0066$ and 0.0100 (data not

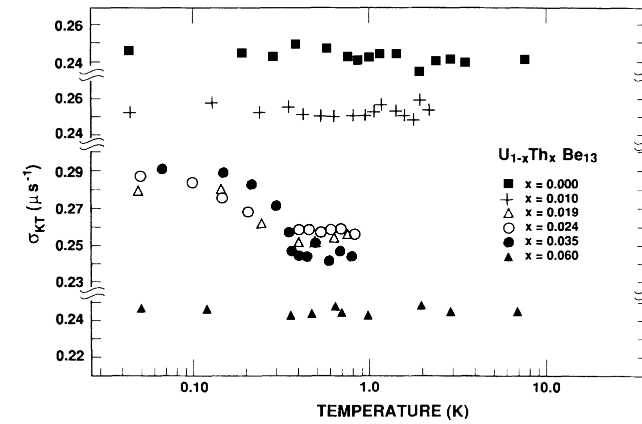

FIG. 1. Temperature dependence of the zero-field μSR rate $\sigma_{KT}(T)$ for various Th concentrations x in $U_{1-x}Th_xBe_{13}$.

shown) but with reduced values of T_{c1} and $H_{c1}(0)$ compared to UBe_{13}. Increasing the thorium concentration to the region where two specific-heat peaks are seen, $x=0.0193$, 0.0245, and 0.0355, we find that all three samples have two different regions of quadratic temperature dependence, with the lower region possessing the greater slope $H^L_{c1}(0)$. We note that these last three $H_{c1}(T)$ results are in qualitative agreement with results from

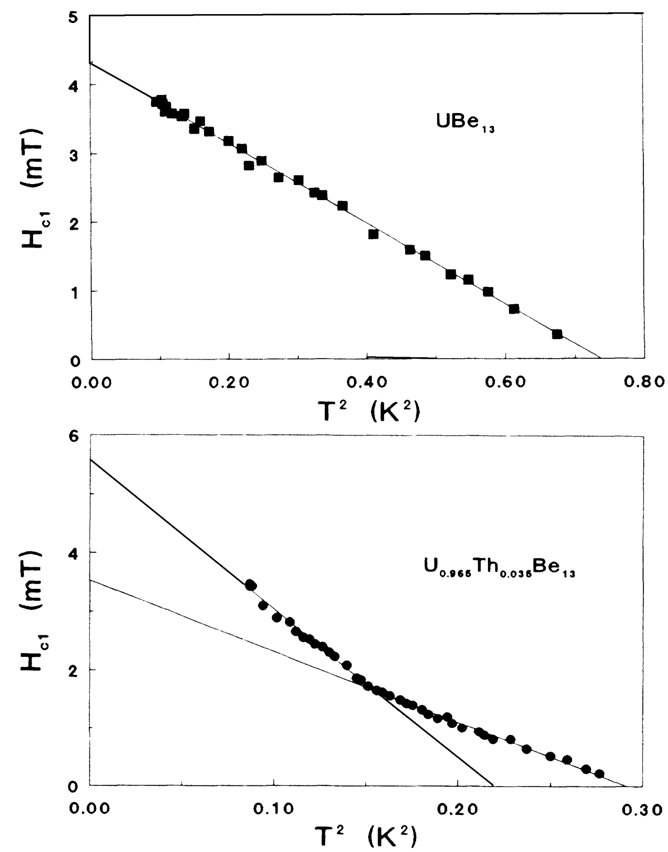

FIG. 2. $H_{c1}(T)$ plotted vs T^2 in $U_{1-x}Th_xBe_{13}$ for $x=0.0000$ (top) and $x=0.0355$ (bottom). The lines are guides to the eye.

Rauchschwalbe,[14] who studied a sample with $x=0.033$.

We now discuss our conclusions from these data, addressing first the nature of the overall T-x phase diagram. There is no evidence of a second phase transition at low fields below T_{c1} in pure UBe_{13} from either the μSR data or the $H_{c1}(T)$ data. This contradicts the data of Ref. 14, where a small deviation from the T^2 dependence in pure UBe_{13} below 0.56 K was claimed as evidence for a second phase, but supports previous specific-heat results.[17] The fact that we see an increase in the μSR linewidth below T_{c2} and two different quadratic temperature dependences in $H_{c1}(T)$ only for $x=0.0193$, 0.0245, and 0.0355, but not for $x=0.000$, 0.0100, or 0.0600, is a clear indication that there are magnetic correlations only in regions of the phase diagram where a second specific-heat peak has been observed ($0.019 \leq x \leq 0.043$).[17] The previous suggestion[14] that the superconducting transition at $T_{c1}=0.86$ K in UBe_{13} is to be associated with the lower transitions at T_{c2} for $0.019 \leq x \leq 0.043$ is also ruled out by our data, because the latter phase transitions exhibit magnetic correlations while the former does not. Within uncertainties in the Th concentration of about 0.005, the T-x phase diagram is constructed approximately as shown in Fig. 3, augmented by specific-heat data for other Th concentrations.[17] The dashed lines may not be absolutely vertical as drawn, but steep phase boundaries near $x=0.019$ and 0.043 are suggested by the present data and the specific-heat data in Ref. 17.

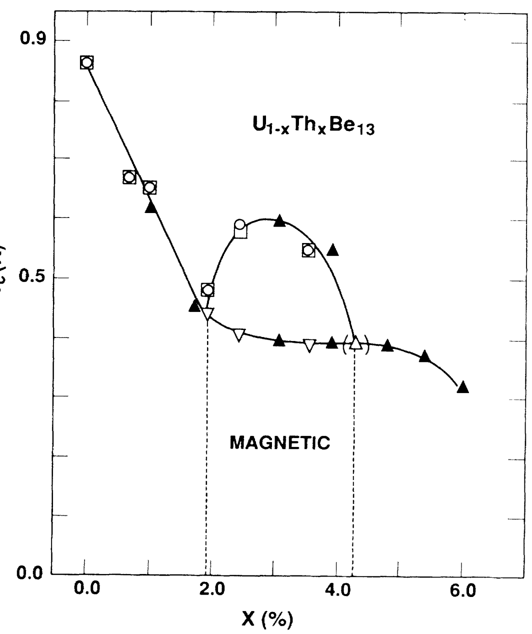

FIG. 3. Phase diagram for $U_{1-x}Th_xBe_{13}$. Open symbols are from this work. Squares, T_{c1} from χ_{ac}; circles, T_{c1} from magnetization $M(H)$; inverted triangles, T_{c2} from kink in $H_{c1}(T^2)$. The solid upright triangles are T_{c1} and T_{c2} from specific heat in Ref. 17. The symbol (△) at $x=0.043$ indicates a merging of T_{c1} and T_{c2}, as described in Ref. 17. $T_{c1}=0.39$ K for $x=0.0600$ was determined resistively.

We now discuss the nature of the phase below T_{c2}. The fact that within errors the transitions at T_{c2} begin and terminate on the line of superconducting phase transitions at T_{c1} means that the order parameters for the two phases must be strongly coupled. This could denote a purely antiferromagnetic (AFM) phase coexisting with and coupled to superconductivity (hypothesis I), or a single complex superconducting order parameter with different symmetry-group representations and a magnetic (time-reversal-violating) ground state (hypothesis II). Ultrasonic-attenuation data[18] are consistent with hypothesis I. We note that local moments on the Th sites[10] would give rise to a dipolar linewidth $\sigma_e(0)$ proportional to x,[19] which is not seen (Table II). The fact that the magnetism appears abruptly at $x=0.019$, and not continuously with $x<0.019$, is further evidence against local Th moments; this is consistent with either hypothesis. Hypothesis II is supported by the fact that $T_{c2}<T_{c1}$: That is, the Fermi surface is largely consumed by the superconducting transition at T_{c1}. Thus the large observed[7] specific-heat jump ΔC_p at T_{c2} (comparable to that at T_{c1}) would be very surprising for a purely AFM phase, and would require an exceptional enhancement of the density of states near the zeros of the superconducting gap to account for the large ΔC_p. Hence the connectedness of the phase diagram and the large specific jump at $T_{c2}<T_{c1}$ to an AFM ground state are properties unlike those observed in other small-moment heavy-electron *magnets*. Rather this feature of $(U,Th)Be_{13}$ is similar to the two *superconducting* specific-heat anomalies in UPt_3, and is also consistent with hypothesis II.

We note that both $H_{c1}^L(0)$ and $\sigma_e(0)$ increase with x for $0.019 \leq x \leq 0.043$. The increase of $H_{c1}^L(0)$ (Table I) with x must be due to an increase in $n_s(0)$ or a decrease in m^*. As argued previously[13] an AFM transition at T_{c2} would be expected to decrease m^* because magnetic order tends to suppress the f-moment spin fluctuations, which contribute greatly to m^*. Unfortunately, it is not possible to predict how much m^* should change with x below T_{c2} without a detailed and believable microscopic theory. If $n_s(0)$ increases with x the correlation between $H_{c1}^L(0)$ and $\sigma_e(0)$ could be explained under hypothesis II, because some models[20-22] for time-reversal-violating superconducting states predict orbital currents generated by inhomogeneities of the order parameter produced by electron scattering from nonmagnetic impurities. This

TABLE II. The x dependence of σ_e and $[H_{c1}^L]^{1/2}$ at $T=0$ in $U_{1-x}Th_xBe_{13}$.

x (%)	$x/1.93$	$\sigma_e(x)/\sigma_e(1.93)$	$[H_{c1}^L(x)/H_{c1}^L(1.93)]^{1/2}$
1.93	1.00	1.00	1.00
2.45	1.27	1.11 ± 0.06	1.14 ± 0.07
3.55	1.84	1.31 ± 0.07	1.21 ± 0.07

can yield currents proportional to $n_s(0)$, and a dipolar field $\mathbf{B}_L$ which scales as $n_s(0)$. If $\mathbf{B}_L$ were random in direction and magnitude, then $\sigma_e(0)$ should grow as $\sqrt{n_s}$, as expected from Gaussian statistics. Note that $\sigma_e(0)$ scales as $[H_{c1}^L(0)]^{1/2}$ (Table II), which yields $\sigma_e(0) \propto \sqrt{n_s}$, if m^* is relatively constant as expected for a superconducting transition. The required randomness could be realized when averaging over varying μ^+ sites (produced by the disorder associated with Th doping) and over magnetic superconducting domains characterized by different directions of $\mathbf{B}_L$. We note that even incomplete randomness would cause a sublinear dependence of $\mathbf{B}_L$ on $n_s(0)$.

In conclusion, we have presented unambiguous evidence for new phase boundaries in $U_{1-x}Th_xBe_{13}$ which separate magnetic from nonmagnetic regimes near $x = 0.019$ and 0.043. Our data show no evidence for multiple phase transitions below 8 K in pure UBe_{13} and rule out the suggestion in Ref. 14 of a crossed phase diagram in $U_{1-x}Th_xBe_{13}$. Recent magnetostriction experiments[23] suggesting AFM order in pure UBe_{13} at $T_N \sim 8.8$ K should be investigated further using μSR. Our data demonstrate that the magnetism and superconductivity below 1 K in (U,Th)Be_{13} are closely coupled and suggest a possible magnetic superconducting phase below T_{c2}. Sigrist and Rice[12] have interpreted such a phase as arising from a crossing of different representations of a complex superconducting order parameter, the lower phase between $0.019 < x < 0.043$ violating time-reversal symmetry. (See also the discussions in Ref. 24.) They do not address in detail the possible correlations between $n_s(0)$ and $\sigma_e(0)$ with x, however. Because we cannot reject the possibility that the phase below T_{c2} is a purely magnetic phase which coexists with superconductivity (hypothesis I), further theoretical studies which address these arguments and the data presented here are required.

We acknowledge helpful discussions with K. Bedell, B. Coles, M. Rice, and J. D. Thompson. This work was supported in part under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, and the National Science Foundation Grant No. DMR-8413730, and the University of California, Riverside, Academic Senate Committee on Research. Work at the Paul Scherrer Institute was supported by the Swiss National Science Foundation and the Schweizerische Schulrat.

[1]See, Proceedings of the International Conference on the Physics of Highly Correlated Electron Systems, Santa Fe, New Mexico, 1989 [Physica (Amsterdam) (to be published)].

[2]Y. J. Uemura *et al.*, Physica (Amsterdam) **153-155C**, 455 (1988).

[3]T. T. M. Palstra *et al.*, Phys. Rev. Lett. **55**, 2727 (1985).

[4]R. H. Heffner *et al.*, Phys. Rev. B **39**, 11 345 (1989); G. Aeppli *et al.*, Phys. Rev. Lett. **60**, 615 (1988).

[5]A. P. Ramirez *et al.*, Phys. Rev. Lett. **57**, 1072 (1986).

[6]A. de Visser *et al.*, J. Magn. Magn. Mater. **54-57**, 375 (1986).

[7]H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, Phys. Rev. B **31**, 1651 (1985).

[8]M. Kato and K. Machida, J. Phys. Soc. Jpn. **56**, 2136 (1987); K. Machida and M. Kato, Phys. Rev. Lett. **58**, 1986 (1988).

[9]See, for example, Z. Fisk *et al.*, Science **239**, 33 (1988).

[10]V. V. Moshchalkov, Pis'ma Zh. Eksp. Teor. Fiz. **45**, 181 (1987) [JETP Lett. **45**, 224 (1987)].

[11]G. E. Volovick and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **88**, 1412 (1985) [Sov. Phys. JETP **61**, 842 (1985)].

[12]M. Sigrist and T. M. Rice, Phys. Rev. B **39**, 2200 (1989).

[13]R. H. Heffner *et al.*, Phys. Rev. B **40**, 806 (1989).

[14]U. Rauchschwalbe, Physica (Amsterdam) **147B**, 1 (1987), and references therein.

[15]M. Naito *et al.*, Phys. Rev. B **41**, 4823 (1990).

[16]Michael Tinkam, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[17]H. R. Ott, Physica (Amsterdam) **162-164C**, 1669 (1989).

[18]B. Batlogg *et al.*, Phys. Rev. Lett. **55**, 1319 (1985).

[19]R. E. Walstedt and L. R. Walker, Phys. Rev. B **9**, 4857 (1974).

[20]G. E. Volovik and V. P. Mineev, Zh. Eksp. Teor. Fiz. **81**, 989 (1981) [Sov. Phys. JETP **54**, 524 (1981)].

[21]C. H. Choi and Paul Muzikar, Phys. Rev. B **39**, 9664 (1989); Mario Palumbo and Paul Muzikar, Phys. Rev. B **42**, 2681 (1990).

[22]Manfred Sigrist and Kazuo Ueda, Institute of Materials Science, University of Tsukuba, report, 1990 (to be published); M. Rice (private communication).

[23]R. N. Kleiman *et al.*, Phys. Rev. Lett. **64**, 1975 (1990).

[24]I. A. Luk'yanchuk and V. P. Mineev, Zh. Eksp. Teor. Fiz. **95**, 709 (1989) [Sov. Phys. JETP **68**, 402 (1989)].