Nuclear Magnetic Resonance and Heavy-Fermion Superconductivity in \((U, \text{Th})\text{Be}_{13}\)

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\(^{9}\text{Be}\) NMR and relaxation have been used to probe heavy-fermion superconductivity in \(U_{1-x}\text{Th}_x\text{Be}_{13}\), \(x = 0\) and 0.033. The spin-lattice relaxation rate \(1/T_1\) varies approximately as \(T^{3}\) well below the transition temperature. This is consistent with a class of anisotropic pairing models for which the gap vanishes along lines on the Fermi surface. NMR spectra give no indication of magnetic, structural, or charge-density ordering at a second transition for \(x = 0.033\).

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A number of intermetallic compounds of cerium and uranium, the so-called “heavy-fermion superconductors” (HFS), exhibit extremely large conduction-band masses and superconductivity below transition temperatures \(\leq 1\) K. \(^{1,2}\) The nature of Cooper pairing in these compounds is of considerable importance. Generalized spin-triplet pairing, similar to that found in superfluid \(^3\text{He}\), and conventional singlet pairing in a “Kondo lattice” have both been proposed. \(^{3-5}\) Low-temperature specific-heat data in the HFS \(\text{UBe}_{13}\) have been interpreted as evidence for triplet superconductivity, \(^5\) and recent ultrasonic attenuation measurements \(^6\) in HFS \(\text{UPt}_3\) appear to agree well with a “polar-state” model for \(L = 1\) triplet pairing. It should be noted that the HFS discovered to date \(^1,2\) possess rather different normal- and superconducting-state properties, and it would be remarkable if they could all be explained within a single theoretical framework.

This Letter reports \(^{9}\text{Be}\) nuclear magnetic resonance (NMR) and spin-lattice relaxation experiments \(^7\) in the normal and superconducting states of the HFS alloy system \(^2\) \(U_{1-x}\text{Th}_x\text{Be}_{13}\), \(x = 0\) and 0.033. Such experiments are relevant to two aspects of the pairing.

First, the nuclear spin-lattice relaxation rate \(1/T_1\) probes the density of superconducting quasiparticle excitations. \(^8,9\) Relaxation by quasiparticles in the limit of small nuclear level splitting is described by the general relation

\[
1/T_1 \propto \int dE \frac{f(E)}{1 - f(E)} \left[ N(E) + M(E) \right],
\]

where \(f(E)\) is the Fermi occupation function for a quasiparticle state of energy \(E\), and \(N(E)\) and \(M(E)\) are the so-called “normal" and “anomalous" densities of quasiparticle states, respectively. \(^9\) These can be obtained from various theories of superconductivity.

Second, alloys with \(\text{Th}\) concentration \(x\) between 0.01 and 0.06 exhibit \(^10\) an anomaly in the specific heat \(C_p\) at a temperature \(T_{c1}\) below the temperature \(T_{c2}\) at which the alloy first becomes superconducting. Transitions from one kind of superconducting pairing to another, analogous to the \(A-B\) transition in \(^3\text{He}\), cannot occur for singlet pairing, which yields only one superconducting order parameter. Identification of \(T_{c2}\) as a second superconducting transition temperature would, therefore, be strong evidence for unconventional pairing. Other candidates for the anomaly are magnetic, \(^11\) structural, or
charge-density ordering, all of which should affect the NMR absorption spectrum.

Bulk (−5 mm) and crushed (−0.5 mm grain size) specimens of U₁₋ₓThₓBe₁₃ were studied. Sample preparation and experimental techniques will be described in a future paper. Superconducting transition temperatures were measured by means of an ac inductance technique. For x = 0.033 no change in ac susceptibility to within 1 part in 10⁴ was observed near Tc₂ (≈ 0.4 K in zero field). All NMR measurements were made in applied magnetic fields H₀ near 15.6 kOe, i.e., in the superconducting mixed state (Hc₁ ≪ H₀ ≪ Hc₂) for temperatures below Tc and Tc₁.

Figure 1 gives the temperature dependence of 1/T₁ for both Th concentrations. Just above Tc(x = 0) the data follow the linear (Korringa) temperature dependence expected in a normal Fermi liquid well below the degeneracy temperature TF. At higher temperatures (T ≳ 2 K), 1/T₁(T)

FIG. 1. Temperature dependence of the ⁹Be nuclear spin-lattice relaxation rate 1/T₁ in U₁₋ₓThₓBe₁₃, x = 0 and 0.033. Solid line: fit of a T³ power law to low-temperature data above ~0.2 K. Dashed line: normal-state (Korringa) law 1/T₁ ~ T. Solid arrows: superconducting transition temperatures Tc(x = 0) and Tc₁(x = 0.033) in a field of 15.5 kOe. Dashed arrow: temperature Tc₂ of the zero-field specific-heat anomaly for x = 0.033 (Ref. 10).

varies less rapidly than linearly, which would also be expected in the vicinity of Tc (≈ 10 K for UBe₁₃). The increased normal-state 1/T₁ for x = 0.033 (Fig. 1) tracks the increase of the normal-state specific heat,¹⁰ so that both effects appear to be due to an increase of the density of states with Th concentration.

In the superconducting state the data are consistent with a T³ temperature dependence for 0.2 K ≤ T ≪ Tc (or Tc₂) for both Th concentrations, as shown in Fig. 1 for x = 0. Deviations from this power law below 0.2 K are not well understood, but could be intrinsic (relaxation by vortex cores⁹ or incompletely compensated U local moments) or extrinsic (relaxation by paramagnetic impurities, etc.).

The power-law behavior of 1/T₁ indicates that an appreciable density of quasiparticle states must exist for low energies. In particular, a T³ law is obtained from Eq. (1) if N₁(E) and M(E) vary linearly with E as E → 0 at low temperatures. Note that for singlet pairing the excitation spectrum exhibits an energy gap, so that no low-lying states are present.

To our knowledge only two classes of models provide low-lying excitations in a straightforward manner: (1) extreme energy-gap anisotropy, and (2) pair breaking. We discuss these in turn.

(1) For L ≥ 1, S = 0 or 1 pairing, gap anisotropy can yield zeros of the gap parameter Δ(θ, φ), where θ and φ indicate directions on the Fermi surface. In particular, the polar-state model for L = 1 triplet pairing, invoked to explain critical-field anisotropy¹ and ultrasonic attenuation⁶ in UPt₃, gives Δ = 0 along the line θ = π/2. Moreover, lines (but not points) of gap zeros yield N₁(E), M(E) ~ E as E → 0, and thus account for the observed T³ behavior of 1/T₁.

It should be noted that the very high normal-state resistivity² of UBe₁₃ suggests rapid conduction-electron scattering, which could average out gap anisotropy. This appears to be a serious objection to models in which anisotropy plays a crucial role. It may be, however, that the scattering (which appears to be intrinsic) increases the resistivity but does not effectively average the gap anisotropy.

(2) An alternative explanation of the 1/T₁ data could be attempted in terms of pair breaking, perhaps due to incompletely compensated moments in a Kondo lattice,⁴ which would also reduce or eliminate the gap in the superconducting excitation spectrum. But a good fit to the data cannot be obtained with the standard Abrikosov-Gor'kov theory of pair breaking.⁹ Furthermore, a comparison can be made between 1/T₁ just below Tc and the specific-heat discontinuity ΔCₚ at Tc.² The latter is
quite large, which suggests that pair breaking at $T_c$ is weak. But in that case $1/T_1$ should increase strongly and go through a maximum just below $T_c$. This is not observed (Fig. 1). The marked decrease of $1/T_1$ just below $T_c$ could only be explained by strong pair breaking, which would nearly fill in the gap.

The specific heat and $1/T_1$ data therefore seem incompatible with pair breaking near $T_c$, and suggest instead an explanation based on gap anisotropy. In fact, the $1/T_1(x=0)$ data for all temperatures between $\sim 0.2$ K and $T_c$ agree well with a calculation using Eq. (1) and the polar-state model. But such a simple picture does not include spin-orbit and crystal-field effects, strong-coupling corrections, etc., and the agreement may be somewhat fortuitous.

We next consider NMR evidence related to the nature of the second transition for $x=0.033$. Examples of field-swept spectra for this spectrum are given in Fig. 2. Asymmetric spectra with well-resolved lines were observed, as expected from a small number of single crystals where quadrupole splittings (nuclear spin $I=\frac{3}{2}$ for $^{9}$Be) depend on crystal orientation.

![Diagram of Be field-swept spectra](image)

**FIG. 2.** Representative $^{9}$Be field-swept spectra in the normal and superconducting states of $U_{0.967}$Th$_{0.033}$Be$_{13}$. Broadening and an absolute shift are observed only at the lowest temperature (113 mK), which is well below both transition temperatures, $T_{c1}(H=15.5$ kOe) (solid arrow) and $T_{c2}(H=0)$ (dashed arrow).

A broadened ($\sim 10$ Oe) and shifted spectrum is found only for a temperature (113 mK) well below both $T_{c1}$ and $T_{c2}$. If we associate this broadening with field inhomogeneity in the vortex lattice, we can estimate the superconducting penetration depth $\lambda_0$. For Ginzburg-Landau parameter $\kappa \gg 1$ the rms width $(\Delta h)_{\text{rms}}$ of the field inhomogeneity is given by

$$\langle (\Delta h)^2 \rangle_{\text{rms}} = \Phi_0 / 4\pi^2 \lambda_0^2,$$

where $\Phi_0$ is the flux quantum. If we estimate $(\Delta h)_{\text{rms}} \sim 10$ Oe we obtain $\lambda_0 \sim 2000$ Å from Eq. (2). Using a rough estimate $\xi_0 \sim 100$ Å for the superconducting coherence length $\xi_0$ in UBe$_{13}$, we have $\kappa = \lambda_0 / \xi_0 \sim 20$. This is close to values deduced for the other HFS systems CeCu$_2$Si$_2$ and UPt$_3$. It is remarkable, however, that the broadening appears only well below both $T_{c1}$ and $T_{c2}$.

The absence of shifts in spectra taken above and below $T_{c2}$ (Fig. 2) is consistent with the absence of either structural or magnetic ordering at that temperature. The former would modify electric field gradients at $^{9}$Be sites and hence alter the $^{9}$Be quadrupole splitting, and the latter would shift and/or broaden the spectrum as a whole. Assuming that the flanking lines in the spectra of Fig. 2 are quadrupole satellites, we obtain upper bounds $(\Delta \omega_Q / \omega_Q)_{\text{max}} \sim 0.05$ and $(\Delta a/a)_{\text{max}} \sim 0.02$ for changes in the quadrupole splitting frequency $\omega_Q$ and the lattice parameter $a$, respectively. Here $(\Delta a/a)_{\text{max}}$ was estimated with use of a point-charge model, which is known to underestimate the sensitivity of electric field gradients in metals to lattice parameter. The data are also consistent with the absence of a charge-density wave, which would be expected to alter $\omega_Q$.

Local dipolar fields between electronic moments and nuclei can be easily calculated, and are of the order of $10^{13}$ Oe/$\mu_B$ in UBe$_{13}$ and many other $4f$ and $5f$ compounds. Our observed line broadening at 113 mK could be due in part to such dipolar fields. Under the worst-case assumption that the broadening is entirely of this origin, a very crude upper limit of $\sim 0.01 \mu_B$ is obtained for the moment per U atom. But the NMR spectra are consistent with the assumption that the broadening is entirely due to vortex-lattice field inhomogeneity.

Spin-lattice relaxation rates for $x=0.033$ are also given in Fig. 1. Small changes in slope on this log-log plot were observed at $T_{c1}$ and $T_{c2}$, but no prominent features were found at either transition.

We conclude that nuclear relaxation in UBe$_{13}$ is best explained by strong gap anisotropy, of the kind which can arise from unusual Cooper pairing. Simi-
larities between nuclear relaxation in UBe$_{13}$ and ultrasonic attenuation in UPt$_3$ are remarkable in view of the differences between other properties of these compounds. We have also found no evidence for a magnetic, structural, etc., transition at $T_{c2}$ in the $x=0.033$ sample. It is tempting to speculate that the transition is between two superconducting states. If this speculation is correct, it would make the argument for unconventional pairing extremely attractive.

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7Previously reported $1/T_1$ data for $x=0, T<T_c$ [W. G. Clark, Z. Fisk, K. Glover, M. D. Lan, D. E. MacLaughlin, J. L. Smith, and C. Tien, in Proceedings of the Seventeenth International Conference on Low-Temperature Physics, edited by U. Eckern, A. Schmid, W. Weber, and H. Wühl (North-Holland, Amsterdam, 1984), p. 227] were not reproduced in the present experiments. The data presented in this Letter have been confirmed for several specimens and over several experimental runs.

8Cu spin-lattice relaxation experiments have been reported in the HFS CeCu$_2$Si$_2$ by Y. Kitaoka, K. Ueda, T. Kohara, and K. Asayama, Solid State Commun. 51, 461 (1984).


10H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, to be published.


