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

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^{9}Be NMR and relaxation have been used to probe heavy-fermion superconductivity in $U_{1-x}Th_xBe_{13}$, $x = 0$ 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 $\lesssim 1$ 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}He, and conventional singlet pairing in a "Kondo lattice" have both been proposed.[3–5] Low-temperature specific-heat data in the HFS UBe$_{13}$ have been interpreted as evidence for triplet superconductivity,[5] and recent ultrasonic attenuation measurements[6] in HFS 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}Be nuclear magnetic resonance (NMR) and spin-lattice relaxation experiments[7] in the normal and superconducting states of the HFS alloy system[2] $U_{1-x}Th_xBe_{13}$, $x = 0$ 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

$$1/T_1 \propto \int dE\, f(E)[1-f(E)] \times [N_s^2(E) + M^2(E)], \qquad (1)$$

where $f(E)$ is the Fermi occupation function for a quasiparticle state of energy E, and $N_s(E)$ 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 Th concentration x between 0.01 and 0.06 exhibit[10] an anomaly in the specific heat C_p at a temperature T_{c2} below the temperature T_{c1} at which the alloy first becomes superconducting. Transitions from one kind of superconducting pairing to another, analogous to the A-B transition in ^{3}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 $U_{1-x}Th_xBe_{13}$ 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 10^3 was observed near T_{c2} ($\simeq 0.4$ K in zero field). All NMR measurements were made in applied magnetic fields H_0 near 15.6 kOe, i.e., in the superconducting mixed state ($H_{c1} << H_0 << H_{c2}$) for temperatures below T_c and T_{c1}.

Figure 1 gives the temperature dependence of $1/T_1$ for both Th concentrations. Just above $T_c(x=0)$ the data follow the linear (Korringa) temperature dependence expected in a normal Fermi liquid well below the degeneracy temperature T_F. At higher temperatures ($T \gtrsim 2$ K), $1/T_1(T)$ varies less rapidly than linearly, which would also be expected in the vicinity of T_F (~ 10 K for UBe_{13}). The increased normal-state $1/T_1$ 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.

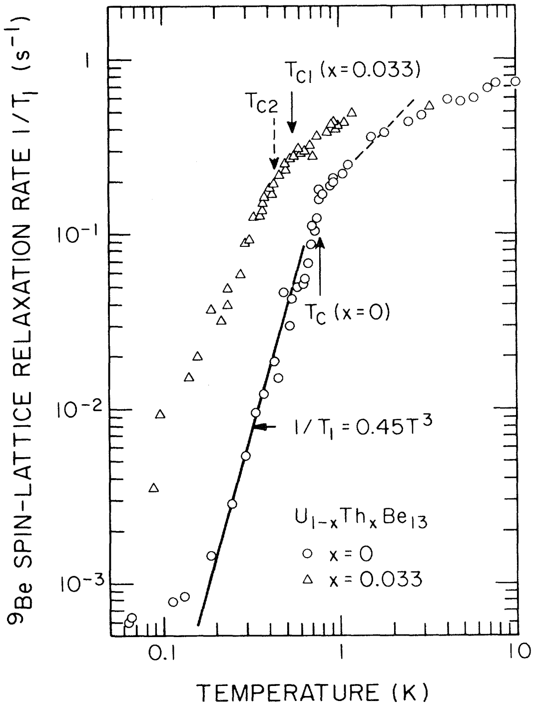

FIG. 1. Temperature dependence of the ^{9}Be nuclear spin-lattice relaxation rate $1/T_1$ in $U_{1-x}Th_xBe_{13}$, $x = 0$ and 0.033. Solid line: fit of a T^3 power law to low-temperature data above ~ 0.2 K. Dashed line: normal-state (Korringa) law $1/T_1 \propto T$. Solid arrows: superconducting transition temperatures $T_c(x=0)$ and $T_{c1}(x=0.033)$ in a field of 15.5 kOe. Dashed arrow: temperature T_{c2} of the zero-field specific-heat anomaly for $x = 0.033$ (Ref. 10).

In the superconducting state the data are consistent with a T^3 temperature dependence for 0.2 $\mathrm{K} \lesssim T << T_c$ (or T_{c2}) 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 cores[9] or incompletely compensated U local moments) or extrinsic (relaxation by paramagnetic impurities, etc.).

The power-law behavior of $1/T_1$ indicates that an appreciable density of quasiparticle states must exist for low energies. In particular, a T^3 law is obtained from Eq. (1) if $N_s(E)$ [and $M(E)$] vary *linearly* with E as $E \to 0$ 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 $L \geq 1$, $S = 0$ or 1 pairing, gap anisotropy can yield zeros of the gap parameter $\Delta(\theta,\phi)$, 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 anisotropy[3] and ultrasonic attenuation[6] in UPt_3, gives $\Delta = 0$ along the line $\theta = \pi/2$. Moreover, lines (but not points) of gap zeros yield $N_s(E), M(E) \propto E$ as $E \to 0$, and thus account for the observed T^3 behavior of $1/T_1$.

It should be noted that the very high normal-state resistivity[2] of UBe_{13} 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 $1/T_1$ 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 $1/T_1$ just below T_c and the specific-heat discontinuity ΔC_p at T_c.[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.[9] 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 ~ 0.2 K and T_c agree well with a calculation using Eq. (1) and the polar-state model.[6,8] 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.

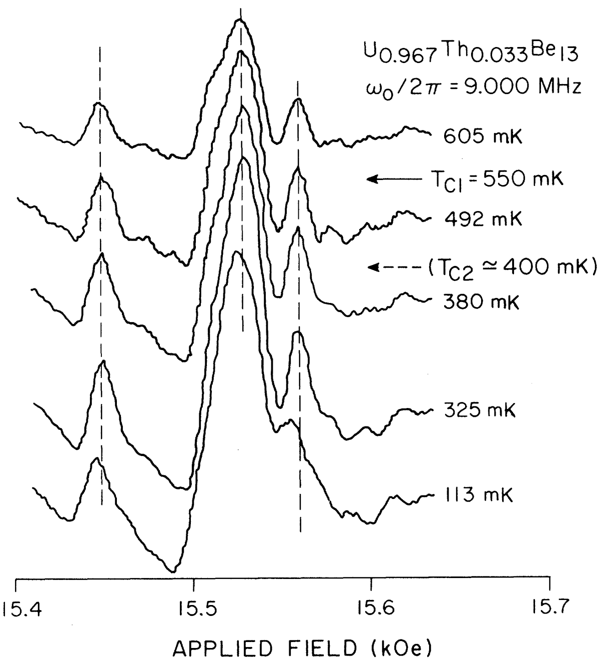

FIG. 2. Representative ^{9}Be field-swept spectra in the normal and superconducting states of $U_{0.967}Th_{0.033}Be_{13}$. Broadening and an absolute shift are observed only at the lowest temperature (113 mK), which is well below both transition temperatures, $T_{c1}(H=15.5$ kOe) (solid arrow) and $T_{c2}(H=0)$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

A broadened (~ 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 λ_0. For Ginzburg-Landau parameter $\kappa >> 1$ the rms width $(\Delta h)_{\rm rms}$ of the field inhomogeneity is given by[12]

$$(\Delta h)_{\rm rms} = \Phi_0 / 4\pi^{3/2}\lambda_0^2, \quad (2)$$

where Φ_0 is the flux quantum. If we estimate $(\Delta h)_{\rm rms} \sim 10$ Oe we obtain $\lambda_0 \sim 2000$ Å from Eq. (2). Using a rough estimate[13] $\xi_0 \sim 100$ Å for the superconducting coherence length ξ_0 in UBe_{13}, we have $\kappa = \lambda_0/\xi_0 \sim 20$. This is close to values deduced[1,14] for the other HFS systems $CeCu_2Si_2$ 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 $(\Delta\omega_Q/\omega_Q)_{\rm max} \sim 0.05$ and $(\Delta a/a)_{\rm max} \sim 0.02$ for changes in the quadrupole splitting frequency ω_Q and the lattice parameter a, respectively. Here $(\Delta a/a)_{\rm max}$ was estimated with use of a point-charge model, which is known[15] 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[16] to alter ω_Q.

Local dipolar fields between electronic moments and nuclei can be easily calculated, and are of the order of 10^{13} Oe/μ_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. Similarities between nuclear relaxation in UBe_{13} and ultrasonic attenuation[6] 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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