Muon Knight Shift in the Heavy-Fermion Superconductors $U_{1-x}Th_xBe_{13}$, $x = 0$ and 0.033

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We report the first Knight-shift studies of the heavy-fermion superconducting state. In 5 kOe the Knight shift of muons in superconducting $U_{1-x}Th_xBe_{13}$ remains near the normal-state value for $x = 0.033$, but shows an unexpected strong decrease for $x = 0$. If the pairing is of odd parity, this decrease suggests that the anisotropic order parameter is pinned to the lattice. The qualitatively different behavior for $x = 0.033$ reflects either spin-orbit scattering by Th doping or a change of pairing symmetry.

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It has become increasingly evident that the so-called heavy-fermion (HF) compounds exhibit a new and unique ground state of condensed matter.[1] Extremely low characteristic temperatures $T_0 \sim 10$–100 K are obtained, for example, from the low-temperature linear specific heat $C \sim k_B T/T_0$ and magnetic susceptibility $\chi \sim \mu_B^2/k_B T_0$. If T_0 is interpreted as the Fermi temperature of a strongly interacting electron liquid, the effective mass $m_{\text{eff}} \sim 1/T_0$ is found to be hundreds of times the bare electron mass. The very existence of such a narrow band of itinerant electrons has proved difficult to understand.[2]

Superconductivity in the HF systems $CeCu_2Si_2$, UBe_{13}, and UPt_3, and their dilute alloys, has also attracted a great deal of attention. Superconductivity in these narrow-band metals is hard to explain with use of conventional theory.[2] In ordinary superconductors the energy gap is nearly isotropic, whereas considerable evidence suggests that in HF superconductors the gap vanishes at certain points on the Fermi surface.[3–5] In analogy with superfluid ^{3}He-A, where a strongly anisotropic gap is associated with triplet Cooper pairing, both the attractive electron-electron interaction and the resulting Cooper-pair condensate in HF superconductors are thought by some to differ markedly from the conventional (BCS) model of phonon-mediated singlet pairing.[2]

We report in this Letter positive-muon (μ^+) spin-rotation experiments[6] which yield the first systematic observation of the Knight shift in a HF superconductor. The muon Knight shift[7] is a measure of the local magnetic susceptibility of itinerant electrons, which is modified by superconductivity in a manner dependent on the kind of Cooper pairing.[8] In the conventional BCS model, if we neglect spin-orbit scattering, the spin susceptibility $\chi_s(T)$ in the superconducting state vanishes at $T = 0$. Spin-orbit scattering increases $\chi_s(0)$ toward the normal-state value χ_n, as the mean free path $l_{\text{s.o.}}$ for spin-flip scattering becomes less than the superconducting coherence length ξ_0.[9] In a ^{3}He-like model of odd-parity spin-triplet superconductivity, $\chi_s(0)$ is also of order χ_n, although its value can be reduced by Fermi-liquid corrections.[8] A full theory of $\chi_s(T)$ in a HF superconductor, incorporating spin-orbit and band-structure effects, is yet to be reported.

Our experiments were carried out at the Clinton P. Anderson Meson Physics Facility (LAMPF), Los Alamos National Laboratory, using a time-differential spectrometer[6] and a ^{3}He-^{4}He dilution refrigerator[10] to attain temperatures below 3 K. The samples were arc-melted polycrystalline ingots attached to the mixing chamber with a silver rod. Thermometry consisted of a modified Spear resistor in direct thermal contact with the sample. Superconducting transition temperatures $T_c(x=0) = 0.86$ K and $T_{c1}(x=0.033) = 0.60$ K were determined by ac susceptibility measurements. Knight-shift measurements were performed in an applied field $H_0 = 5$ kOe, the stability of which was monitored by use of an NMR probe. All measurements in the type-II superconducting mixed state were made after cooling in constant field. The measured shifts were corrected for a copper reference shift (60 ppm),[7] for nonlinearities in the data-acquisition electronics, and, in the normal state only, for Lorentz and demagnetization fields. The latter corrections were at most of order 10%. The uncertainty in the measured μ^+ precession frequency was 200–400 ppm.

A two-line Fourier-transform spectrum was observed for both specimens. One line was unshifted from the bare μ^+ frequency to within error, while the second line exhibited a negative, temperature-dependent frequency shift. It was determined in auxiliary experiments that the unshifted line was largely due to muon stops in the cryostat. Only the Knight shift K_μ of the shifted line is discussed here.

Figure 1 gives the dependence of K_μ on bulk susceptibility χ (measured in the same samples) in the normal state, with temperature an implicit variable. For $\chi \gtrsim 7\times10^{-3}$ emu mole^{-1} ($T \lesssim 100$ K) a linear $K_\mu(\chi)$ relation is obtained. This implies that the μ^+ shift samples the same electrons which produce the large temperature-dependent susceptibility component $\chi_f(T)$. From the slope of K_μ vs χ a value of $(-1.84\pm0.13$ kOe$)/\mu_B$ is obtained for the hyperfine field H_{hf}. The negative value of H_{hf} is probably due to negative interstitial spin polarization as seen in other metals, e.g., Pd and Pt.[11]

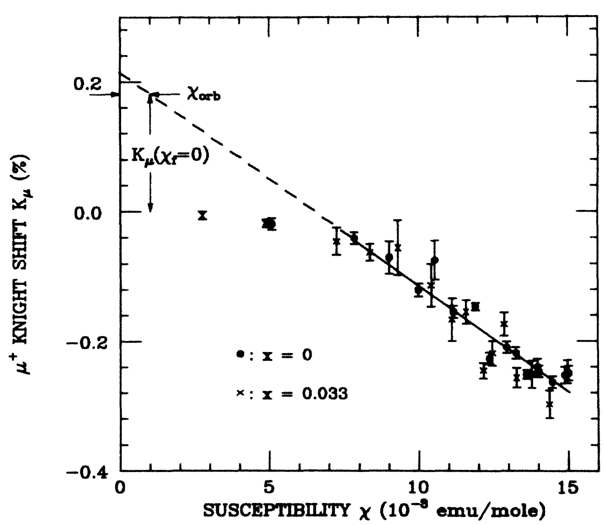

FIG. 1. Dependence of μ^+ Knight shift K_μ on bulk paramagnetic susceptibility χ in $U_{1-x}Th_xBe_{13}$, $x=0$ and 0.033; applied field $H_0=5$ kOe. Temperature is an implicit variable. The departure from linearity for $\chi \lesssim 7\times10^{-3}$ emu/mole^{-1} is attributed to motional averaging by muon diffusion between nonequivalent sites. The estimated orbital susceptibility $\chi_{orb} \simeq 1\times10^{-3}$ emu mole^{-1} is indicated. The procedure for estimating K_μ for f-spin susceptibility $\chi_f=0$ is described in the text.

The departure of $K_\mu(\chi)$ from linearity at high temperatures appears to reflect averaging of the μ^+ local field by thermally activated muon diffusion between nonequivalent sites,[7] as indicated by a reduction of the linewidth above about 150 K [Fig. 2(b)]. No such departure is observed in ^{9}Be NMR Knight-shift studies of UBe_{13} single crystals.[12] We estimate the value of K_μ for vanishing f-electron susceptibility $\chi_f(T)$ by first obtaining the temperature-independent orbital contribution $\chi_{orb} \simeq 1\times10^{-3}$ emu mole^{-1} from the intercept of a χ vs $1/T$ plot of the susceptibility. The low-temperature linear $K_\mu(\chi)$ variation is then extrapolated to $\chi=\chi_{orb}$ to obtain $K_\mu(\chi_f=0)=(0.18\pm0.03)$%, as indicated in Fig. 1.

Figure 2 gives the temperature dependence of K_μ and the μ^+ Gaussian linewidth σ between 0.3 and 300 K. Below T_c the specimens were in the type-II mixed state. Lorentz and demagnetizing corrections have not been made to these data, since the superconducting-state susceptibility has not been measured directly; however, as discussed below, these corrections appear to be relatively small.

A considerable decrease of the magnitude of K_μ is observed below T_c for $x=0$, but not for $x=0.033$. Before concluding that these properties are intrinsic to the materials, we estimate the effect of a reduction in the internal magnetic field due to screening super-

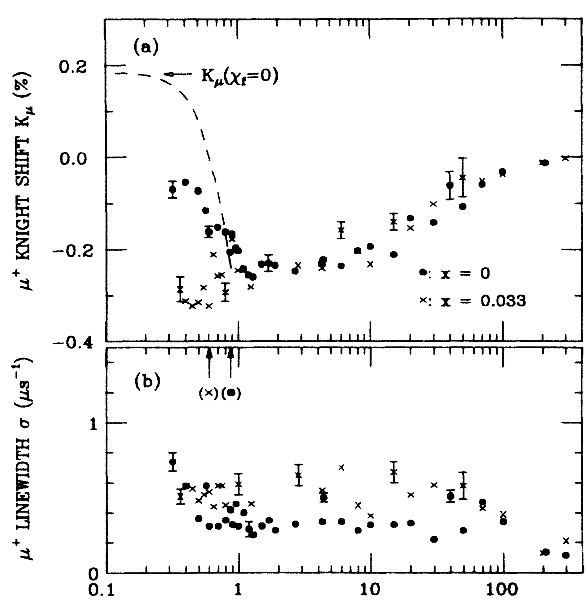

FIG. 2. (a) Temperature dependence of μ^+ Knight shift K_μ between 0.3 and 300 K in $U_{1-x}Th_xBe_{13}$, $x=0$ and 0.033; applied field $H_0=5$ kOe. The superconducting transition temperatures are indicated by arrows, labeled by the symbols in parentheses. The dashed curve gives the estimated Knight shift in a conventional superconductor with no spin-orbit scattering. (b) Temperature dependence of μ^+ Gaussian linewidth σ; conditions as in (a).

currents in the mixed state.

For pure UBe_{13} the screening magnetization $4\pi M$ should be small, because the estimated Ginzburg-Landau parameter κ is large ($\kappa \simeq 100$).[13] In conventional Ginzburg-Landau theory[14] one has $-4\pi M = (H_{c2}-H_0)/[(2\kappa^2-1)\beta+n]$, where κ is the Ginzburg-Landau parameter, $\beta \simeq 1.1$, H_{c2} is the upper critical field, and n is the demagnetization coefficient $\simeq 0.15$ for our samples. This leads to a small change in the observed Knight shift, estimated at $-4\pi \times M/H_0 \simeq 0.05\%$ at $T \simeq 0.3$ K. The effect is smaller at higher temperatures. Diamagnetic screening would decrease the μ^+ precession frequency, and hence cannot explain the increasingly positive shift observed below T_c in UBe_{13}. Any flux trapping that occurs during the constant-field cooling used in these experiments would reduce the diamagnetic perturbation of the internal field.

The constant, or slightly increasing, shift below T_c for $x=0.033$ might be attributed to diamagnetic screening if the diamagnetism in the doped sample were much larger than in pure UBe_{13}. Neither magnetization measurements nor a value of κ have been reported for $x=0.033$, however. Nevertheless, $\kappa(x=0.033)$ can be estimated, again within conventional theory ($\kappa \sim H_{c2}/\sqrt{\gamma} T_c$), by use of $\kappa(x=0)$, $H_{c2}(T)$, T_c, and the linear coefficient of specific heat γ. At $T=0.3$ K [Fig. 2(a)] the resultant magnetization is unchanged from the estimate for $x=0$, which implies that the observed differences in K_μ between $x=0$ and $x=0.033$ are not due to different diamagnetic responses.

The decrease of the magnitude of K_μ in superconducting pure UBe_{13} would be expected if the superconductivity were conventional (even-parity isotropic pairing). The calculated BCS temperature dependence of χ_s/χ_n for no spin-orbit scattering,[9] normalized to the observed $K_\mu(T_c)$ and estimated $K_\mu(\chi_f=0)$, is given by the dashed curve in Fig. 2(a). It can be seen that the observed decrease, to a value $\sim 50\%$ of the difference $K_\mu(T_c)-K_\mu(\chi_f=0)$ [Fig. 2(a)], is somewhat weaker than this curve.

NMR Knight-shift studies have established that spin-orbit scattering ($l_{s.o.} < \xi_0$) from particle surfaces and impurities is the chief cause of the nonvanishing $\chi_s(0)$ observed in most conventional superconductors.[9] As an example, $\chi_s/\chi_n \simeq 0.7$ and 0.8 for mercury and tin, respectively, for $T/T_c < 0.25$. Although the K_μ data for $x=0$ are compatible with isotropic singlet pairing (including some spin-orbit effects), conventional superconductivity is inconsistent with the considerable experimental evidence[1-5] for strong gap anisotropy in UBe_{13}.

Anisotropic odd-parity Cooper pairing yields $\chi_s(0)=\chi_n$, contrary to our Knight-shift data, if the order parameter is free to rotate in the field.[8] A reduction of $\chi_s(0)$ would occur if the order parameter were pinned to the lattice, but then random orientations in a polydomain sample should yield a significant increase in anisotropic broadening of the μ^+ linewidth σ. An increase of σ is indeed observed [Fig. 2(b)]. An isotropic odd-parity (Balian-Werthamer-type) state[8] also leads to $\chi_s(0) < \chi_n$, but again seems inconsistent with the other evidence for strong gap anisotropy.[1-5] Anisotropic even-parity pairing also gives $\chi_s(0)=0$ in a ^{3}He-like theory with zero spin-orbit interaction.[8] Our results are also consistent with such pairing for pure UBe_{13}, since spin-orbit scattering could increase $\chi_s(0)$. The roles of strong superconducting coupling (T_c is not very small compared to T_0) and Fermi-liquid effects are not well understood, however.

The most striking feature of these data is the difference in Knight-shift behavior for the two $(U,Th)Be_{13}$ alloys. A conventional explanation of this observation would invoke a decrease of $l_{s.o.}$ with Th doping, so that $l_{s.o.} << \xi_0$ for $x=0.033$. Alternatively, the difference in shift behavior could be taken as evidence that the superconducting states for the two alloys are qualitatively different. In this regard, we note that $x=0.033$ is in the Th concentration range for which a second phase transition below T_c is inferred from specific-heat data.[15] The latter interpretation would also suppport the view that the superconducting order parameter is not of the conventional isotropic BCS type, which gives rise to only one distinct superconducting phase.

We now briefly mention two other related measurements, ^{9}Be NMR[16] and spin-polarized neutron scattering.[17] In an applied field of 15 kOe the ^{9}Be NMR shift in UBe_{13} changes less than 0.01% below T_c.[16] (μ^+ Knight shifts could not be measured for $H_0 > 5$ kOe, which was the maximum field available from the Helmholtz-pair magnet used for our muon-spin-rotation experiments.) Although there is an apparent disagreement with our results, the stronger applied field used in the NMR experiments might have modified the symmetry of the pairing, and a line of phase transitions may exist between 5 and 15 kOe.

Unpublished spin-polarized–neutron scattering cross sections, which are proportional to the uniform spin susceptibility, have been reported very recently in the heavy-fermion superconductors $CeCu_2Si_2$, UBe_{13}, and UPt_3.[17] No change of cross section was observed below T_c for magnetic fields as low as 6 kOe in any of these systems; a result which, in the case of UBe_{13}, seems to be inconsistent with the results of our muon-spin–rotation study. This may reflect a difference in sample characteristics having to do with either pinning of the order parameter in our case, or increased spin-orbit scattering in the case of the neutron measurements, for example.

To summarize, the temperature dependence of the μ^+ Knight shift in superconducting $U_{1-x}Th_xBe_{13}$ is significant for two reasons. First, the strong reduction of K_μ in pure UBe_{13} suggests either even-parity pairing or, if the parity is odd, pinning of the order parameter to the crystal lattice. Second, the difference in behavior for $x = 0$ and $x = 0.033$ could be due either to spin-orbit scattering, or to a qualitative difference in the order parameter symmetry in these alloys.

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