**μ⁺-Knight Shift Measurements in U$_{0.965}$Th$_{0.035}$Be$_{13}$ Single Crystals**

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Muon spin rotation ($\mu$SR) measurements of the temperature dependence of the $\mu$⁺-Knight shift in single crystals of U$_{0.965}$Th$_{0.035}$Be$_{13}$ have been used to study the static spin susceptibility $\chi_s$ below the transition temperatures $T_{c1}$ and $T_{c2}$. While an abrupt reduction of $\chi_s$ with decreasing temperature is observed below $T_{c1}$, $\chi_s$ does not change below $T_{c2}$ and remains at a value below the normal-state susceptibility $\chi_0$. In the normal state we find an anomalous anisotropic temperature dependence of the transferred hyperfine coupling between the $\mu$⁺-spin and the U 5f-electrons.

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An intriguing feature of the heavy-fermion compound U$_{1-x}$Th$_x$Be$_{13}$ is that for $0.019 \lesssim x \lesssim 0.045$ a second phase transition $T_{c2}(x)$ appears at a temperature below the superconducting (SC) transition $T_{c1}(x)$ [1]. The nature of the lower transition $T_{c2}$ is still a matter of considerable debate. Initially $T_{c2}$ was identified as a second distinct SC transition from measurements of a specific heat peak [1], the pressure dependence of $T_c(x)$ [2] and the increased slope of $H_{c1}$ vs. $T$ [3]. The observation of a $T^3$ dependence of the $^9$Be NMR spin-lattice relaxation rate below $T_{c2}$ suggested a SC state characterized by line nodes in the energy gap [1]. Later zero-field $\mu$SR measurements [3] clearly revealed the onset of small moment magnetism ($\approx 10^{-3} \mu_B$/U) below $T_{c2}$. The appearance of a small internal field could arise from a SC state that breaks time-reversal symmetry [3]. On the other hand, it could originate from a spin-density wave instability [3] or the formation of long-range AFM correlations [4] within a single SC phase. However, these latter interpretations fail to explain [1] the large specific heat jump at $T_{c2}$.

Early $\mu$SR measurements on polycrystalline samples of U$_{0.967}$Th$_{0.033}$Be$_{13}$ showed a constant or perhaps weakly increasing $\mu$⁺-Knight shift upon cooling below $T_{c1}$ [1]. In the SC state the temperature dependence of the Knight shift $K$ reflects the change in the static spin susceptibility $\chi_0$ due to the formation of Cooper pairs. For the case of orbital $s$-wave ($L=0$) spin singlet ($S=0$) pairing, Yosida [4] calculated from the BCS theory that $\chi_s(T)$ vanishes as $T \to 0$ K. Modifications to this temperature dependence are expected for spin-orbit scattering by impurities and unconventional pairing states.

In this Letter we report on the temperature dependence of the $\mu$⁺-Knight shift in single crystals of U$_{0.965}$Th$_{0.035}$Be$_{13}$. These measurements differ from earlier studies on polycrystalline samples in that there are two magnetically inequivalent $\mu$⁺-sites which facilitate a determination of $\chi_s$ in the SC state. We find that upon cooling through $T_{c1}$, $\chi_s$ rapidly decreases, but remains independent of temperature below $T_{c2}$. Our study also reveals a temperature dependence in the normal state of the transferred hyperfine coupling at one of the two $\mu$⁺-sites, roughly coinciding with features observed in resistivity and specific heat data for pure UBe$_{13}$.

The single crystals of U$_{0.965}$Th$_{0.035}$Be$_{13}$ were grown from an Al flux as described in Ref. [5]. From zero-field specific heat measurements the upper and lower transitions occur at $T_{c1} = 0.47(5)$ K and $T_{c2} = 0.35(2)$ K, respectively. The $\mu$SR measurements were carried out using a top loading dilution refrigerator on the M15 beam line at the TRI-University Meson Facility (TRIUMF), Canada and using a $^4$He gas-flow cryostat on the πM3 beam line at the Paul Scherrer Institute (PSI), Switzerland. The crystals were mounted on a Mg plate attached to a cold finger. The magnetic field $\mathbf{H}$ was applied parallel to the crystallographic $\mathbf{c}$-axis and transverse to the initial $\mu$⁺-spin polarization direction. As a local spin-1/2 probe, the muon is sensitive only to magnetic interactions and processes about the local magnetic field $B_\mu$ with a Larmor frequency $\omega = \gamma_\mu B_\mu$, where $\gamma_\mu/2\pi = 13.55342$ MHz/kOe. The applied field results in a uniform polarization of the localized U 5f-moments, which reside at the corners of a cubic lattice. The Fourier transform of the $\mu$⁺-spin precession signal in U$_{0.965}$Th$_{0.035}$Be$_{13}$ shows two distinct symmetric lines with an amplitude ratio of 1:2. In the time domain, each signal was best fit by a Gaussian relaxation function $G(t) = \exp(-\sigma^2 t^2/2)$, where $\sigma$ is the $\mu$⁺-spin depolarization rate. From the amplitude ratio and the frequencies of these two signals, we have determined that the $\mu$⁺ stops at the (0, 0, 1/4) site, half way between nearest-neighbor U atoms. Muons stopping between U atoms adjoined along the $\mathbf{c}$-axis direction experience a net dipolar field from the 5f-moments which is parallel to $\mathbf{H}$, and thus precess at a frequency $\omega_\parallel$ that is greater than those stopping in Ag (which provide a zero-shift reference frequency). On the other hand, twice as many $\mu$⁺ stop between U atoms adjoined along the...
The Knight shift at the two magnetically inequivalent \( \mu^+ \)-sites is given by

\[
K_{\parallel,\perp} = \left( \omega_{\parallel,\perp} - \omega_{\text{Ag}} \right) / \omega_{\text{Ag}},
\]

where \( \omega_{\parallel,\perp} \) is the frequency of the muon precession parallel or perpendicular to the \( b \)-axis or the field \( H \). These muons precess at a frequency \( \omega_{\perp} \) that is lower than those stopping in Ag.

Figure 1 shows measurements of the temperature dependence of \( K_\parallel \) and \( K_\perp \) below 30 K at \( H = 10 \) kOe and above 2 K at 6 kOe (insets). The reduction of \( K_\parallel \) above \( T \approx 50 \) K is attributed to crystal electric field (CEF) excitations, which have been inferred from specific heat [14] and NMR spin-lattice relaxation [15] studies in pure UBe\(_{13}\). The effect on the hyperfine coupling is observable for both \( \mu^+ \)-sites from plots of \( K \) vs. \( \chi_{\text{mol}} \) in the normal state (Fig. 2), where \( \chi_{\text{mol}} \) is the isotropic bulk molar susceptibility. The plots are essentially linear between 5 and 50 K (where \( K \) follows a Curie-Weiss behavior) and at temperatures above 63 K, with a change of slope between the two regions. The temperature dependence of \( \chi_{\text{mol}} \) is shown in the inset of Fig. 2 compared with that for proposed CEF splittings of \( U^{4+} \) and \( U^{3+} \) manifolds in cubic symmetry. The CEF can be expressed in terms of the molecular-field model developed by Hao et al. [24]. Using the simple theoretical model developed by Hao et al. for the reversible magnetization of a type-II superconductor [25] and the value \( H_{c2}(0) \approx 55 \) kOe [28], we calculate that \( |K_{\text{dia}}| \ll 72 \) ppm. Since we observed no field dependence for \( K_{\parallel,\perp} \) below \( T_{c1} \) in the range 5 kOe \( \leq H \leq 15 \) kOe, we conclude that the internal field is essentially uniform and the diamagnetic shift \( K_{\text{dia}} \) is negligible.

Because \( A_0^\parallel \) is temperature independent in the normal state, we make the reasonable assumption that it remains
so below $T_{c1}$, allowing $\chi_s$ (i.e., $\chi_{5f}$ in the SC state) to be determined from Eq. (2). As shown in Fig. 5, $\chi_s(T)$ exhibits two different behaviors (in agreement with the raw Knight shift data in Fig. 1) which coincide with the two phase transitions in the specific heat. The decrease of $\chi_s(T)$ between $T_{c1}$ and $T_{c2}$ is consistent with a phase in which the Cooper pairs have a substate of opposite spin projection (i.e., $S_z = 0$). However, the data cannot distinguish between even and odd parity spin states possessing this substate, because Fermi-liquid corrections and spin-orbit (SO) scattering by impurities may be significant. For the case of an even parity SC phase we can estimate the importance of SO scattering from the relation $\chi_s(T_{c2})/\chi_n = 1 - 2l_{SO}/\pi\xi_0$ [27], where $\chi_n$ is the normal-state spin susceptibility at $T_{c1}$, $\chi_s(T_{c2})/\chi_n = 0.61$ and $\xi_0 \approx 77 \text{ A}$ from $H_{c2}(0)$ [26]. This gives a SO scattering mean free path of $l_{SO} \approx 47 \text{ A}$. The average distance between Th atoms $\approx 15 \text{ A}$, represents a lower limit for the mean free path $l$ between collisions of the electrons with the Th impurities. Since $l_{SO}$ is of the same order of $l$, modification of $\chi_s(T)$ due to SO scattering cannot be ruled out.

The lack of a temperature dependence for $\chi_s$ below $T_{c2}$ is characteristic of a spin-triplet ($S = 1$) odd-parity ($L = 1$) superconductor with parallel spin pairing, except that $\chi_s < \chi_n$. This unusual behavior suggests that the component of the order parameter corresponding to the phase $T_{c2} < T < T_{c1}$ stops or slows down its growth at $T_{c2}$, where a second component develops. In terms of the $d$-vector [28] of the triplet order parameter $\hat{\Delta}(k) = i(d \cdot \sigma)\sigma_y$, a possible scenario is that (i) one component corresponds to $d \parallel H$, so that $\chi_s$ decreases below $T_{c1}$ and (ii) the second component corresponds to $d \perp H$, in which case $\chi_s$ is unchanged below $T_{c2}$. The idea of a two-component $d$-vector is similar to the weak spin-orbit coupling model recently developed for UPt$_3$ [29] from detailed $^{195}$Pt NMR Knight shift measurements [30]. Finally, substituting $\chi_s(T)$ for $\chi_{5f}$ in Eq. (3) we find that the magnitude of $A_{\perp}$ rapidly increases to a constant value below $T_{c2}$ (see Fig 4).

In conclusion, our study of $U_{0.965}\text{Th}_{0.035}\text{Be}_{13}$ has identified different behavior for the temperature dependence of the spin susceptibility $\chi_s$ below the two transitions observed in the specific heat. A possible explanation for the absence of a change below $T_{c2}$ is that $U_{0.965}\text{Th}_{0.035}\text{Be}_{13}$ is an odd parity spin-triplet superconductor. However, we stress that this may not be the only interpretation of our measurements. A definitive identification of the pairing state will require further measurements as a function of magnetic-field direction to unambiguously determine the relative orientation of the $d$-vector and $H$.

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[1] H.R. Ott, H. Rudigier, Z. Fisk and J.L. Smith, Phys. Rev. B 31, 1651 (1985).
[2] S.E. Lambert et al., Phys. Rev. Lett. 57, 1619 (1986).
[3] U. Rauchschwalbe et al., Europhys. Lett. 3, 751 (1987).
[4] D.E. MacLaughlin et al., Phys. Rev. Lett. 53, 1833 (1984).
[5] R.H. Heffner et al., Phys. Rev. B 40, 806 (1989); ibid, Phys. Rev. Lett. 65, 2816 (1990).
[6] M. Sigrist and T.M. Rice, Phys. Rev. B 39, 2200 (1989).
[7] U. Rauchschwalbe et al., Europhys. Lett. 3, 751 (1987).
[8] D.E. MacLaughlin et al., Phys. Rev. Lett. 53, 1833 (1984).
[9] B. Batlogg et al., Phys. Rev. Lett. 55, 1319 (1985).
[10] F. Kromer et al., Phys. Rev. B 60, 4176 (1999).
[11] R.H. Heffner and M.R. Norman, Comments Condens. Matter Phys. 17, 361 (1996).
[12] M. Sigrist and T.M. Rice, Phys. Rev. B 39, 2200 (1989).
[13] K. Machida and M. Kato, Phys. Rev. Lett. 58, 1986 (1987).
[14] R. Felton et al., J. Math. Phys. 37, 1255 (1986); ibid, Phys. Rev. B 39, 11345 (1989).
[15] K. Yosida, Phys. Rev. 110, 769 (1958).
[16] J.L. Smith, Phil. Mag. B 65, 1367 (1992).
[17] R.H. Heffner et al., Phys. Rev. Lett. 55, 1319 (1985).
[18] F. Kromer et al., Phys. Rev. Lett. 81, 4476 (1998).
[19] R.H. Heffner and M.R. Norman, Comments Condens. Matter Phys. 17, 361 (1996).
[20] M. Sigrist and T.M. Rice, Phys. Rev. B 39, 2200 (1989).
[21] K. Yosida, Phys. Rev. 110, 769 (1958).
[22] J.L. Smith, Phil. Mag. B 65, 1367 (1992).
[23] R. Felton et al., Europhys. Lett. 2, 323 (1986).
[24] W.G. Clark et al., J. Appl. Phys. 63, 3890 (1988).
[25] D.L. Cox, Phys. Rev. Lett. 59, 1240 (1987).
[26] P.G. Pagliuso et al., Phys. Rev. B 60, 4176 (1999).
[27] E.A. Goremychkin and R. Osborn, Phys. Rev. B 47, 14280 (1993).
[28] P.W. Anderson, Phys. Rev. Lett. 57, 1255 (1986); ibid, Phys. Rev. B 39, 11345 (1989).
[29] K. Machida and T. Ohmi, J. Phys. Soc. Jpn. 67, 1122 (1998); K. Machida, T. Nishira and T. Ohmi, J. Phys. Soc. Jpn. 68, 3364 (1999).
[30] W.G. Clark et al., Phys. Rev. B 53, 1255 (1986); ibid, Phys. Rev. B 53, 1833 (1984).

FIGURE CAPTIONS

Figure 1. Temperature dependence of $K_\parallel$ and $K_\perp$ measured at TRIUMF in an applied field $H = 10$ kOe. Inset: Data taken above $T_{c1}$ at PSI, where the maximum available field was $H = 6$ kOe.

Figure 2. Plot of the normal-state $\mu^+\text{Knight shift}$ at $H = 6$ kOe vs. the bulk molar susceptibility. Inset: Temperature dependence of the inverse susceptibility. Dashed and solid lines are calculations using Eq. (3) of Ref. [17] for the CEF schemes described in the text.

Figure 3. Plot of $K_\parallel - K_\perp$ vs. the bulk molar susceptibility at $T > T_{c1}$ and $H = 10$ kOe. The solid line is a linear fit to the data above 5 K.

Figure 4. Temperature dependence of $A_c^\parallel$ (open symbols) and $A_c^\perp$ (solid symbols) at $H = 6$ kOe and 10 kOe. Note: We have assumed that $A_c^\parallel$ is unchanged below $T_{c1}$. The data for $A_c^\perp$ below $T_{c1}$ was obtained under this assumption.

Figure 5. Temperature dependence of the specific heat (open circles) and magnetic susceptibility (solid circles).
H=6 kOe

- $K_{\parallel}$
- $K_{\perp}$

$\chi_{mol}$ (emu/mol)

1/$\chi_{mol}$ (mol/emu)

Temperature (K)

Knight Shift (%)

Measured

$J=9/2$

$J=4$

$2K$

$6.3K$

$50K$

$63K$

$160K$
$H = 10 \text{ kOe}$

$T > T_{c1}$
Temperature (K)

$A_c (\text{Oe/}\mu\text{B})$

Open Symbols: $A_c^\parallel$
Solid Symbols: $A_c^\perp$

$H=10 \text{ kOe}$

$H=6 \text{ kOe}$

$T_{c2}$

$T_{c1}$
$H = 10 \text{ kOe}$

- $T_{c1}$
- $T_{c2}$

**Graph:**
- $\chi_s / \chi_n$ vs. temperature (K).
- $C/T$ (J/mol K$^2$) vs. temperature (K).

**Legend:**
- $\circ$: Experimental data
- $\bullet$: Theoretical predictions

**Note:**
- The graph shows the magnetic susceptibility normalized to the paramagnetic susceptibility ($\chi_s / \chi_n$) and the specific heat divided by temperature ($C/T$) as functions of temperature, with two critical temperatures $T_{c1}$ and $T_{c2}$ indicated.