μ^+ Knight Shift Measurements in $U_{0.965}Th_{0.035}Be_{13}$ Single Crystals

J. E. Sonier,[1,*] R. H. Heffner,[1] D. E. MacLaughlin,[2] G. J. Nieuwenhuys,[3] O. Bernal,[4] R. Movshovich,[1] P. G. Pagliuso,[1] J. Cooley,[1] J. L. Smith,[1] and J. D. Thompson[1]

[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[2]*Department of Physics, University of California, Riverside, California 92521*
[3]*Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands*
[4]*Physics Department, California State University, Los Angeles, California 90032*

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

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An intriguing feature of the heavy-fermion compound $U_{1-x}Th_xBe_{13}$ 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 [4]. Later zero-field muon spin rotation (μSR) measurements [5] 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 [6]. On the other hand, it could originate from a spin-density wave instability [7] or the formation of long-range antiferromagnetic correlations [8,9] within a single SC phase. However, these latter interpretations fail to explain [10] the large specific heat jump at T_{c2}.

Early μSR measurements on polycrystalline samples of $U_{0.967}Th_{0.033}Be_{13}$ showed a constant or perhaps weakly increasing μ^+ Knight shift upon cooling below T_{c1} [11]. In the SC state the temperature dependence of the Knight shift K reflects the change in the static spin susceptibility χ_s due to the formation of Cooper pairs. For the case of orbital s-wave ($L = 0$) spin singlet ($S = 0$) pairing, Yosida [12] calculated from the BCS theory that $\chi_s(T)$ vanishes as $T \rightarrow 0$ 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 μ^+-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 μ^+ sites which facilitate a determination of χ_s in the SC state. We find that upon cooling through T_{c1}, χ_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 μ^+ 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. [13]. 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 μSR 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 Ag plate attached to a cold finger. The magnetic field $\mathbf{H}$ was applied parallel to the crystallographic $\hat{\mathbf{c}}$ axis and transverse to the initial μ^+-spin polarization direction. As a local spin-1/2 probe, the muon is sensitive only to magnetic interactions and precesses about the local magnetic field B_μ with a Larmor frequency $\omega = \gamma_\mu B_\mu$, where $\gamma_\mu/2\pi = 13.553\,42$ 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 μ^+-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 σ is the μ^+-spin depolarization rate. From the amplitude ratio and the frequencies of these two signals, we have determined that the μ^+ stops at the $(0, 0, 1/4)$ site, halfway between nearest-neighbor U atoms. Muons stopping between U atoms adjoined along the $\hat{\mathbf{c}}$-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 μ^+ stop between U atoms adjoined along the $\hat{\mathbf{a}}$- and $\hat{\mathbf{b}}$-axis directions, where the net dipolar field is antiparallel to $\mathbf{H}$. These muons precess at a frequency $\omega_\perp$ that is lower than those stopping in Ag.

The Knight shift at the two magnetically inequivalent μ^+ sites is given by

$$K_{\parallel,\perp} = (\omega_{\parallel,\perp} - \omega_{\mathrm{Ag}})/\omega_{\mathrm{Ag}}\,. \tag{1}$$

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). We attribute the reduction of $K_\parallel$ above $T \approx 50$ K 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 μ^+ sites from plots of K vs χ_{mol} in the normal state (see Fig. 2), where χ_{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 χ^{-1}_{mol} is shown in the inset of Fig. 2 compared with that for proposed CEF splittings of U^{4+} $J = 4$ [17] and U^{3+} $J = 9/2$ [14] manifolds in cubic symmetry. The CEF models have been corrected by adding a molecular-field constant of 57 emu/mol, compared to 52 emu/mol in $CeCu_2Si_2$ [18]. Although the data are consistent with $J = 9/2$, the $J = 4$ energy scheme results in similar behavior when the hybridization proposed in the quadrupolar Kondo model [17] is included in the calculation of $\chi^{-1}_{\mathrm{mol}}(T)$—as was shown for the case of pure UBe_{13} [19]. A linear fit to $\chi^{-1}_{\mathrm{mol}}(T)$ above 100 K yields an effective moment of $3.62(1)\mu_B$/U.

Equation (1) can be expressed in terms of the individual contributions to K, so that for the axial symmetry of the μ^+ site

$$K_\parallel = (A_{\mathrm{c}}^{\parallel} + A_{\mathrm{dip}}^{zz})\chi_{5f} + K_{\mathrm{dem,L}} + K_0 + K_{\mathrm{dia}} \tag{2}$$

and

$$K_\perp = \left(A_{\mathrm{c}}^{\perp} - \frac{1}{2}A_{\mathrm{dip}}^{zz}\right)\chi_{5f} + K_{\mathrm{dem,L}} + K_0 + K_{\mathrm{dia}}\,, \tag{3}$$

where A_{c} and A_{dip}^{zz} are the contact hyperfine and dipolar coupling constants pertaining to the interaction of the μ^+ with the $5f$ electrons (i.e., $A \equiv H_{\mathrm{hf}}/N_A\mu_B$, where H_{hf} is the hyperfine field, N_{A} is Avogadro's number, and μ_B is the Bohr magneton), χ_{5f} is the isotropic molar $5f$-electron susceptibility, $K_{\mathrm{dem,L}} = 4\pi(1/3 - N)\rho_{\mathrm{mol}}\chi_{\mathrm{mol}}$ is the correction for the demagnetization and Lorentz fields (where $N \approx 1$ is the demagnetization factor and $\rho_{\mathrm{mol}} = 0.012\,27$ mol/cm^3 is the molar density), K_0 is the isotropic T-independent contribution from the non-$5f$ conduction electrons, and K_{dia} is due to flux expulsion in the SC state.

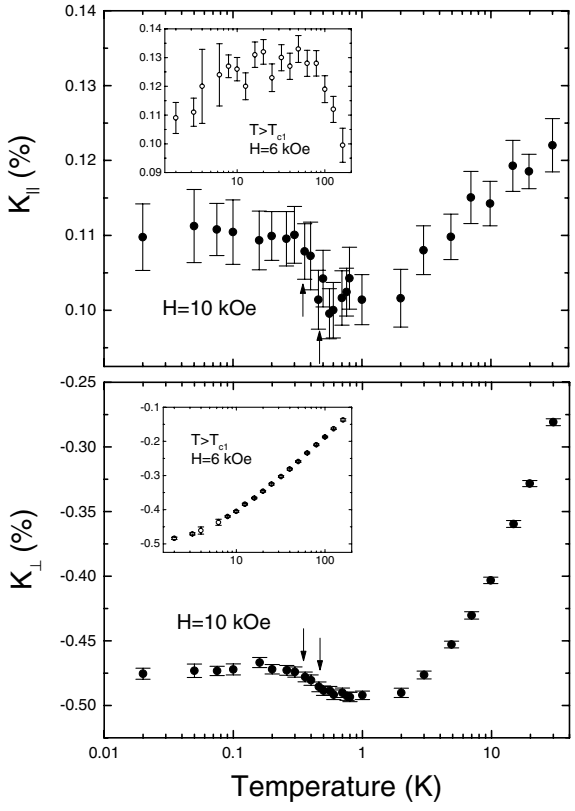

FIG. 1. Temperature dependence of $K_\parallel$ and $K_\perp$ measured at TRIUMF in an applied field $H = 10$ kOe. Insets: Data taken above T_{c1} at PSI, where the maximum available field was $H = 6$ kOe.

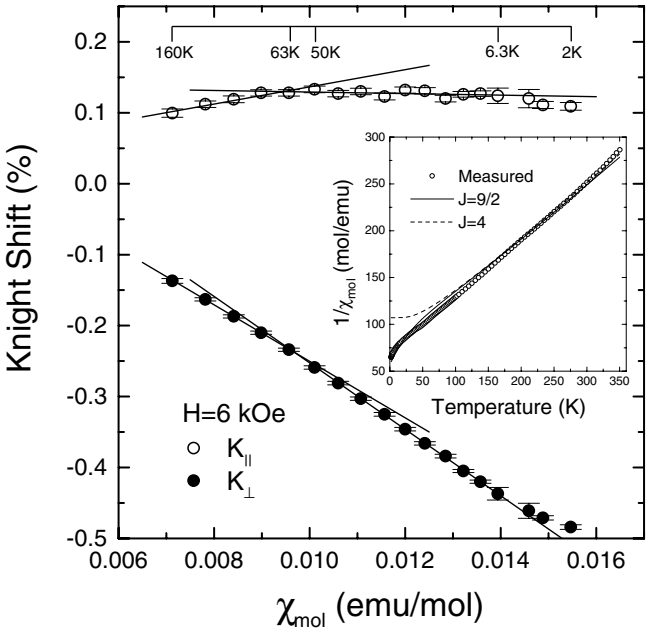

FIG. 2. Plot of the normal-state μ^+ Knight shift at $H = 6$ kOe vs the bulk molar susceptibility. Inset: Temperature dependence of the inverse susceptibility. Dashed and solid lines are calculations using Eq. (3) of Ref. [16] for the CEF schemes described in the text.

The total normal-state susceptibility is given by $\chi_{\rm mol} = \chi_{5f} + \chi_0$, where χ_0 is the T-independent non-$5f$ contribution. From the normal-state plot of $K_\parallel - K_\perp$ vs $\chi_{\rm mol}$ at 10 kOe (see Fig. 3), $\chi_0 = 0.0039(2)$ emu/mol was obtained from the intercept of the extrapolated linear line, where $\chi_{5f} \propto 1/T \to 0$ and $K_\parallel = K_\perp \equiv K_0 = 1846(90)$ ppm. In general, $A_{\rm c}^{\parallel} = A_{\rm c}^{\perp}$, in which case the slope of the solid line $(3/2)A_{\rm dip}^{zz}$ gives $A_{\rm dip}^{zz} = 2066(22)$ Oe$/\mu_B$. This value agrees with the result $A_{\rm dip}^{zz} = 2062$ Oe$/\mu_B$ obtained from a simple dipolar-field calculation for U moments sitting on the corners of a cubic lattice of edge length 5.134 Å. We note that the value of $A_{\rm dip}^{zz}$ obtained from the 6 kOe data is only 1693(28) Oe$/\mu_B$. Although this may imply that $A_{\rm c}$ is anisotropic, the time spectra recorded at 6 kOe had a larger time resolution and far fewer muon-decay events than the spectra taken at 10 kOe. Thus, it is likely that there is a systematic uncertainty in the temperature dependence of the μ^+-Knight shift at 6 kOe.

$A_{\rm c}$ represents the transferred hyperfine coupling between the μ^+ spin and the U $5f$ electrons via the conduction s electrons. Substituting the value of $A_{\rm dip}^{zz}$ into Eqs. (2) and (3) gives the normal-state temperature dependence of $A_{\rm c}^{\parallel}$ and $A_{\rm c}^{\perp}$ shown in Fig. 4. The offset of the 6 kOe data stems from the discussion in the previous paragraph. The decrease above 50 K is likely due to the mixing of the wave functions associated with the different CEF levels. The strong reduction of $A_{\rm c}^{\perp}$ and lack of change of $A_{\rm c}^{\parallel}$ for $T_{c1} \lesssim T \lesssim 4$ K is the source of the nonlinearity above $\chi_{\rm mol} \approx 0.014$ emu/mol in Fig. 3. This is not a muon induced effect, since similar departures from linearity have been observed in K-$\chi_{\rm mol}$ plots for the ^{9}Be NMR Knight shift in UBe_{13} [20] and the ^{63}Cu and ^{29}Si NMR Knight shifts in $CeCu_2Si_2$ [21]. A decrease of $A_{\rm c}^{\perp}$ over nearly the same temperature range is also observed in pure UBe_{13} [22]. This anomaly roughly coincides with peaks in the resistivity and specific heat at $\sim$2.5 K in UBe_{13} [23], which are completely suppressed when 3.55% Th is added. The decrease of $A_{\rm c}^{\perp}$ in both the pure and doped systems is not necessarily inconsistent with this latter behavior, because most of the μ^+ stopping in $U_{0.965}Th_{0.035}Be_{13}$ do not reside near a Th impurity.

In the SC state the flux expulsion term $K_{\rm dia}$ in Eqs. (2) and (3) is related to the value of the magnetic penetration depth λ and the coherence length ξ_0. To our knowledge there have been no measurements of the absolute value of λ in $U_{0.965}Th_{0.035}Be_{13}$. However, the lack of any increase in the μ^+-spin depolarization rate σ below T_{c1} is consistent with a value $\lambda(0) \gg 12\,100$ Å, as reported in pure UBe_{13} [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 [26], we calculate that $|K_{\rm dia}| \ll 72$ ppm. Since we observed no field dependence for $K_{\parallel,\perp}$ below T_{c1} in the range 5 kOe $\le H \le$ 15 kOe, we conclude that the internal field is essentially uniform and the diamagnetic shift $K_{\rm dia}$ is negligible.

Because $A_{\rm c}^{\parallel}$ is temperature independent in the normal state, we make the reasonable assumption that it remains so below T_{c1}, allowing χ_s (i.e., χ_{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

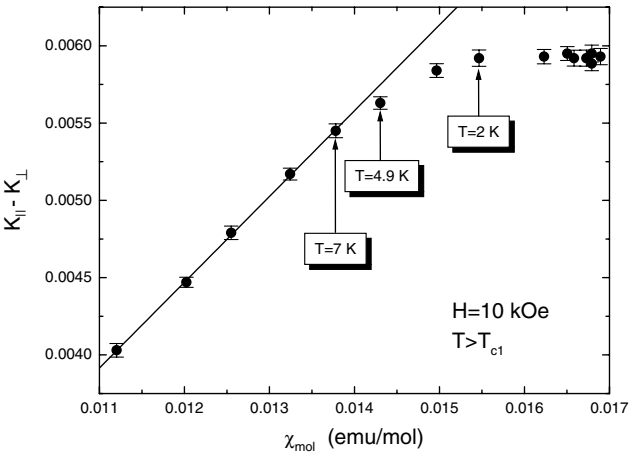

FIG. 3. Plot of $K_\parallel - K_\perp$ vs the bulk molar susceptibility for $T > T_{c1}$ and $H = 10$ kOe. The solid line is a linear fit to the data above 5 K.

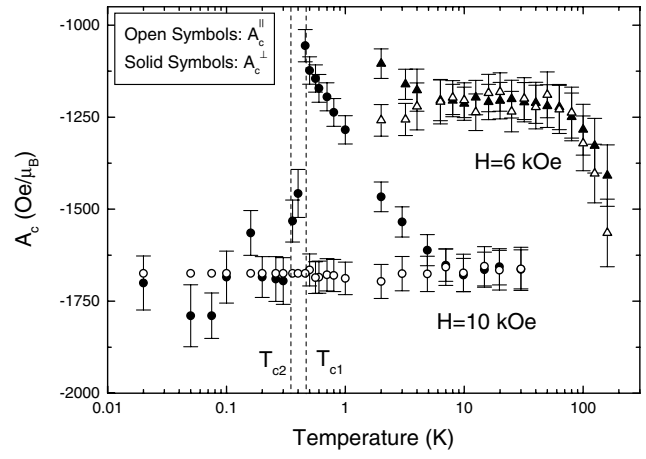

FIG. 4. Temperature dependence of $A_{\rm c}^{\parallel}$ (open symbols) and $A_{\rm c}^{\perp}$ (solid symbols) at $H = 6$ and 10 kOe. Note we have assumed that $A_{\rm c}^{\parallel}$ is unchanged below T_{c1}. The data for $A_{\rm c}^{\perp}$ below T_{c1} were obtained under this assumption.

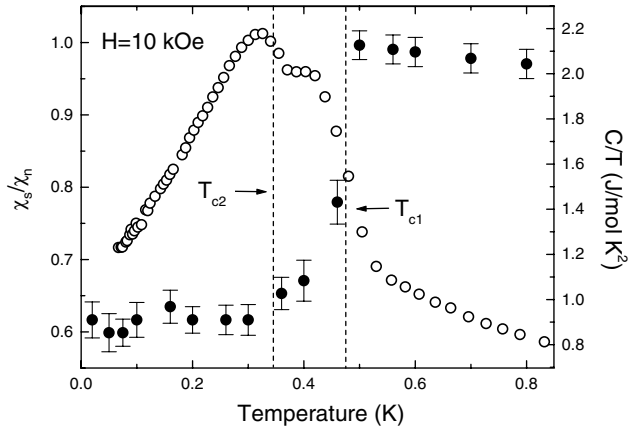

FIG. 5. Temperature dependence of the specific heat (open circles) and magnetic susceptibility (solid circles).

$\chi_s(T_{c2})/\chi_n = 1 - 2l_{\rm SO}/\pi\xi_0$ [27], where χ_n is the normal-state spin susceptibility at T_{c1}, $\chi_s(T_{c2})/\chi_n = 0.61$, and $\xi_0 \approx 77$ Å from $H_{c2}(0)$ [26]. This gives a SO scattering mean free path of $l_{\rm SO} \approx 47$ Å. The average distance between Th atoms $\approx$15 Å represents a lower limit for the mean free path l between collisions of the electrons with the Th impurities. Since $l_{\rm SO}$ 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 χ_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 $\hat{\Delta}(\mathbf{k}) = i(\mathbf{d}\cdot\boldsymbol{\sigma})\sigma_y$, a possible scenario is that (i) one component corresponds to $\mathbf{d} \parallel \mathbf{H}$, so that χ_s decreases below T_{c1}, and (ii) the second component corresponds to $\mathbf{d} \perp \mathbf{H}$, in which case χ_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 χ_{5f} in Eq. (3) we find that the magnitude of $A_c^{\perp}$ rapidly increases to a constant value below T_{c2} (see Fig. 4).

In conclusion, our study of $U_{0.965}Th_{0.035}Be_{13}$ has identified different behavior for the temperature dependence of the spin susceptibility χ_s below the two transitions observed in the specific heat. A possible explanation for the absence of a change below T_{c2} is that $U_{0.965}Th_{0.035}Be_{13}$ 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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*Present address: Department of Physics, Simon Fraser University, Burnaby, BC, Canada V5A 156.

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