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Muon-spin relaxation studies of weak magnetic correlations in $U_{1-x}Th_xBe_{13}$

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Zero-field positive muon-spin relaxation rates in $U_{0.965}Th_{0.035}Be_{13}$ provide definitive evidence for the onset of magnetic correlations at the lower phase transition at temperature T_{c2} below the normal-superconducting transition at T_{c1}. The transition at T_{c2} is found to be second order and mean field like, with a moment $(10^{-3}\text{–}10^{-2})\mu_B/f$ atom. Candidates for the second phase, such as magnetic order and magnetic superconducting states, are discussed.

The interplay between magnetic and superconducting properties of heavy electron (HE) materials, which contain $4f$ or $5f$ elements (Ce, U, ...), remains a subject of considerable interest.[1] At low temperatures the HE state evolves out of the local-moment behavior seen at high temperatures to produce extremely narrow itinerant bands, which can exhibit superconducting and/or magnetic order.[2] It has been known for some time that superconducting states in HE systems show unconventional behavior consistent with anisotropic pairing, and that the pairing mechanisms may be associated with the exchange of spin fluctuations present in the HE state.[2]

In large measure, due to muon-spin relaxation (μSR) measurements such as those presented here, it has recently become clear that some systems previously thought to be only superconducting[3–5] ($U_{0.965}Th_{0.035}Be_{13}$, UPt_3, $CeCu_2Si_2$) or normal and paramagnetic[6] ($CeAl_3$) possess weak static magnetism, with moments $(10^{-3}\text{–}10^{-1})\mu_B/f$ atom. Neither the origin of this weak magnetism nor its relation to HE superconductivity is understood at present.

The $(U_{1-x}Th_x)Be_{13}$ system is particularly intriguing because the substitution of Th for U depresses the superconducting transition temperature[7] T_{c1} in a nonmonotonic fashion,[8] and for $0.2 \lesssim x \lesssim 0.45$ gives rise to a specific-heat anomaly[9] at a temperature T_{c2} below T_{c1}. Batlogg *et al.*[10] have observed a large enhancement of the ultrasonic attenuation at T_{c2}, and have interpreted this as evidence for an antiferromagnetic (AFM) phase transition. Attempts to see this AFM order using both nuclear magnetic resonance[11] and neutron scattering[12] were unsuccessful, however. At a pressure above 9 kbar, Lambert *et al.*[13] reported that superconductivity occurs only for x above and below about 0.03, which suggests that the symmetry of the superconducting state may be different in the two regions. Rauchschwalbe *et al.*[14] found that for $x = 0.03$ the temperature dependence of the lower critical field $H_{c1}(T)$ is quadratic, but with $|dH_{c1}/dT^2|$ larger below T_{c2} than for $T_{c2} < T < T_{c1}$. They interpreted the increased slope below T_{c2} as an increase in the superfluid density n_s, which thus indicates a transition to a second, coexisting superconducting state. Finally, earlier μSR measurements of Heffner, Cooke, and MacLaughlin[3] gave evidence for quasistatic magnetic correlations below T_{c2} for $x = 0.033$.

The nature of this transition has important implications for understanding HE behavior. For example, multiple superconducting transitions in the same material indicate an unconventional order parameter. Furthermore, if the heavy electrons are both superconducting and magnetic in $(U,Th)Be_{13}$ below T_{c2}, it would be the first example of such a state.

In this paper we report zero-field μSR data for $U_{1-x}Th_xBe_{13}$ for $x = 0.035$. Previous μSR data[3] showed an enhanced linewidth below T_{c2}, which implies the onset of weak magnetism. However, the statistical errors were too large to permit a quantitative determination of the temperature dependence of the muon relaxation rate (and hence of the magnetic order parameter) below T_{c2}. Such information is important to characterize the low-temperature phase. In the present high-precision studies we have determined the temperature dependence of the magnetic order parameter. This temperature dependence is in good agreement with a variety of theories of magnetic order [spin-$\frac{1}{2}$ mean-field ordering, spin-density-wave (SDW) instability], but also agrees with the temperature dependence of the conventional BCS superconducting order parameter. The latter might be expected if the transition at T_{c2} is to a superconducting state with unconventional magnetic Cooper-pair symmetry.

The μSR experiments reported here were carried out at the Paul Scherrer Institute (formerly SIN), Villigen, Switzerland, using the surface muon beam at the Low-Temperature Facility. The sample was attached to the mixing chamber of a ^{3}He-^{4}He dilution refrigerator, and temperatures were controlled to ± 0.01 K. The ambient magnetic field at the sample position was nulled to within 0.1 Oe using bucking coils. Data were obtained in a single forward counter, and approximately 10^7 counts were collected per data point. The samples were prepared by arc melting the starting ingredients in elementary form, and the superconducting transition temperature $T_{c1}=0.55 \pm 0.03$ K and the second transition temperature $T_{c2}=0.39 \pm 0.03$ K were determined from ac susceptibility and specific-heat measurements, respectively.

Random local magnetic fields at positive muon (μ^+) sites give rise to a distribution of μ^+ Larmor frequencies. The resulting μ^+ depolarization is given by the Kubo-Toyabe relaxation function[15]

$$G_{KT}(t)=\tfrac{1}{3}+\tfrac{2}{3}(1-\sigma_{KT}^2t^2)\exp(-\tfrac{1}{2}\sigma_{KT}^2t^2)\,, \qquad (1)$$

if the distributions of local-field components are Gaussian, with mean zero and rms width σ_{KT}, and vary only over a time scale much longer than $1/\sigma_{KT}$ (i.e., are quasistatic).

The data were fit to a sum of two terms of the form of Eq. (1), one of which accounted for a small background signal produced by muons stopping in the walls of the cryostat. The amplitude and relaxation rate for this spurious temperature-independent signal were determined from separate runs using a Pb sample, which produces no μ^+ depolarization itself.

The observed relaxation functions $G_{KT}(T)$ for $T=0.07$ and 0.80 K are shown in Fig. 1. The increased relaxation rate at the lower temperature is clearly visible, as is the good agreement between the data and the theoretical line shape from Eq. (1). From this we conclude that the increased relaxation rate arises from additional quasistatic fields rather than lifetime broadening. We note, however, that because the increase is small it is not possible to distinguish between (i) an increase in the width of the local-field distribution, due to incommensurate or spatially random magnetism, or (ii) the onset of a nonzero mean local field, due to commensurate magnetic order. In either case, the increase in σ_{KT} below T_{c2} is proportional to the increase in the local field and hence to the magnetic order parameter.

The temperature dependence of the Kubo-Toyabe relaxation rate σ_{KT}, the specific heat, and the ac susceptibility measured on the same sample are given in Fig. 2. At high temperatures σ_{KT} is due to ^{9}Be dipolar fields. It can be seen that there is no appreciable change in σ_{KT} in the neighborhood of T_{c1}. The sharp increase in σ_{KT} is clearly correlated with the low-temperature peak in the specific heat at T_{c2}.

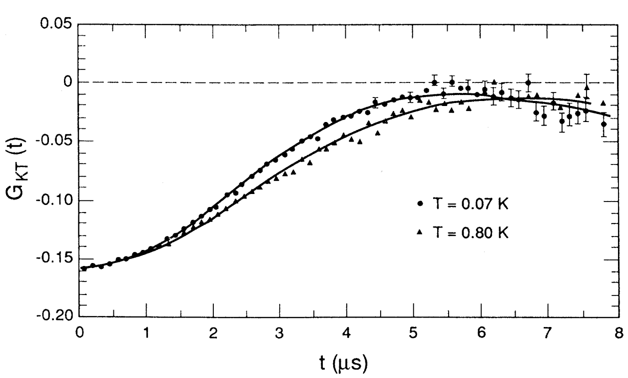

FIG. 1. Zero-field μSR relaxation functions at $T=0.07$ K (●) and $T=0.80$ K (▲). The solid lines are fits to Eq. (1). For clarity not all the data are shown.

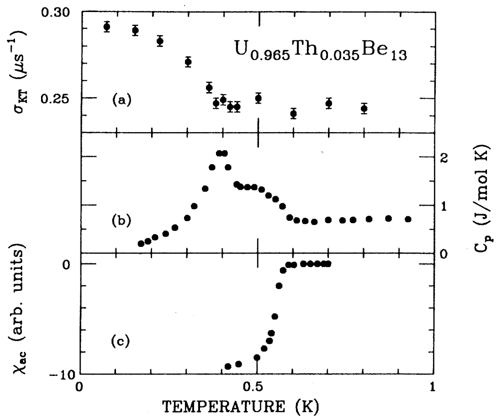

FIG. 2. Temperature dependence of (a) zero-field μ^+ Kubo-Toyabe linewidth σ_{KT}, (b) specific heat C_p, and (c) ac susceptibility χ_{ac} in $U_{0.965}Th_{0.035}Be_{13}$. The anomalous increase of σ_{KT} is associated with the specific-heat peak at T_{c2} rather than the superconducting transition at T_{c1}.

One possible cause of such a change in σ_{KT} is a structural phase transition, so that the dipolar coupling between nuclei (principally ^{9}Be) and interstitial muons is modified. A simple calculation shows that a lattice change of $\sim 5\%$ would be necessary to cause the observed increase of σ_{KT}. Measurements of the thermal expansion coefficient[16] through T_{c2} yield changes 3 orders of magnitude smaller than this, which rules out such an effect. The only viable mechanism for the increase of σ_{KT} is the appearance of weak electronic magnetic moments.

Figure 3 gives the dependence on reduced temperature $t \equiv T/T_{c2}$ of the normalized contribution of the electronic magnetism to the μ^+ linewidth,

$$s(t)\equiv[\sigma_{KT}^2(T)-\sigma_{KT}^2(T_{c2})]^{1/2}/[\sigma_{KT}^2(0)-\sigma_{KT}^2(T_{c2})]^{1/2}\,. \qquad (2)$$

Equation (2) expresses the assumption that nuclear and electronic contributions to σ_{KT} are uncorrelated and therefore add in quadrature. Under this assumption a value of ~ 1.8 Oe is obtained for the electronic contribu-

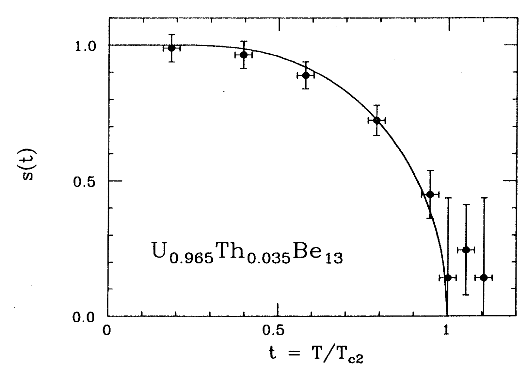

FIG. 3. Dependence on reduced temperature $t \equiv T/T_{c2}$ of normalized zero-field μ^+ Kubo-Toyabe linewidth $s(t)$. Solid curve: spin-$\frac{1}{2}$ mean-field magnetization, BCS pairing amplitude (see text), and sublattice magnetization in theory of Kato and Machida (Ref. 17), for d-wave Cooper pairing.

tion to the local field at $T=0$. Assuming dipolar coupling, this corresponds to an electronic moment of the order $(10^{-3}\text{-}10^{-2})\mu_B/U$ atom, where the uncertainty arises from lack of precise knowledge of the muon stopping site.

The solid line in Fig. 3 is the temperature dependence of the magnetization for two mean-field theories of magnetic order: The Brillouin function for spin-$\frac{1}{2}$ and the theory of Kato and Machida[17] (see below) for a SDW transition at T_{c2}. These theories predict the same temperature dependence within the accuracy of the plot. This curve is also numerically equivalent to the pairing amplitude in the BCS theory of superconductivity. The fit to the data is quite good.

Several explanations of the second phase below T_{c2} have been proposed. Machida and Kato[17,18] suggested that a SDW transition may be favored by residual interactions between HE band quasiparticles, and that such a SDW state could coexist with HE superconductivity. On the other hand, Pines *et al.*[19] have suggested that the weak magnetism generally observed in HE systems is due to small local moments which result from incomplete Kondo-like screening in the low-temperature HE state. Yet other authors have suggested that the transition at T_{c2} is to a second superconducting phase. Volovik and Gor'kov[20] pointed out that exotic "magnetic" superconducting states, analogous to the A_1 state of superfluid ^{3}He, could carry either a spin or an orbital moment and hence could exhibit a form of magnetism. Sigrist and Rice[21] considered a model phase diagram based on a crossing of different representations of odd parity superconducting states, and suggested that the lower transition in (U,Th)Be_{13} is between triplet states of different symmetry. The transition has also been interpreted[22] as being from one essentially conventional superconducting pairing to another, which differs only in the distribution of the pairing amplitude over the Fermi surface. We discuss below the implications of these various interpretations, together with the current experimental situation.

An argument against a SDW below T_{c2} is that the superconducting transition at T_{c1} generally utilizes virtually all of the Fermi surface in Cooper pair formation. If, however, the superconducting energy gap possesses nodes, as in (U,Th)Be_{13}, the required ungapped Fermi surface might exist in the vicinity of superconducting gap zeros, making possible a SDW structure.[17,18] This might also account for the small value of the observed moment.

Rauchschwalbe *et al.*[14] have suggested that because $|dH_{c1}/dT^2|$ increases below T_{c2} the transition is to a state of increased superfluid density, and hence to a second superconducting phase. We point out, however, that $H_{c1}(T)$ is proportional to n_s/m^*, where m^* is the effective mass associated with the screening supercurrents. It is plausible that m^* might also change at T_{c2}, particularly if the transition at T_{c2} were purely magnetic. This is because the Fermi-liquid state is still developing at $T\lesssim 1$ K in UBe_{13}, and the quasiparticle mass is therefore likely to be affected by competing or additional interactions. For example, the onset of AFM is known to decrease the linear specific-heat coefficient in HE systems,[23] where magnetic order tends to reduce f-moment spin fluctuations, which are a large contributor to m^*. A loss of Fermi surface to a magnetic transition (as for a SDW) could also decrease m^*. On the other hand, magnetic excitations (such as magnons) could lead to an increase in m^*. The behavior of m^* and n_s at T_{c2} remains an open question in need of further investigation.

The behavior which we find for the order parameter is also consistent with a conventional BCS theory and may therefore indicate a low-temperature superconducting phase which possesses orbital or spin moments. To date only magnetic states of triplet superconductivity have been treated in detail.[21] The large reduction in μ^+ Knight shift[24] below T_{c1} is evidence for singlet pairing in undoped UBe_{13}, however. Although this reduction becomes smaller in Th-doped specimens, presumably due to spin-orbit scattering by Th impurities, it seems unlikely that doping would change the parity of the pair wave function. Singlet states, which do not exhibit a net spin polarization, can nevertheless possess orbital supercurrents[20] which could in principle contribute to μ^+ local fields. This possibility should be investigated further theoretically; a calculation of the μ^+ relaxation rate would be particularly valuable.

To conclude, our data give definitive evidence that the transition at T_{c2} involves very weak associated magnetic correlations, and that the development of the magnetic order parameter is characteristic of a second-order, mean-field-like phase transition. This resolves the apparent discrepancy between previous ultrasound[10] data and the lack of a magnetic signature from either neutron scattering[12] or NMR.[11] These data also rule out certain theoretical models[22,25] and constrain others. For example, the model of Kato and Machida[17] generally yields a first-order SDW transition for p-wave Cooper pairing, but a second-order transition for d-wave pairing. Only the latter is consistent with our data. A mean-field development of the order parameter below a magnetic transition[3] in UPt_3 at ~ 6 K was also found in neutron-scattering experiments.[26] In the case of UPt_3, however, the mean-field behavior is altered below the superconducting transition temperature $T_c \sim 0.4$ K, whereas in (U,Th)Be_{13} the magnetic order parameter evolves entirely in the superconducting state. This may indicate additional superconducting phases in UPt_3, or that the magnetism is of a different origin in UPt_3 than in (U,Th)Be_{13}.

Further study is required to determine whether the transition at T_{c2} involves magnetic ordering or a transition to a second superconducting state. Additional experiments are under way to help answer this question, and to investigate to what extent weak magnetism is found in other regions of the (U,Th)Be_{13} phase diagram.

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