Competition between Magnetic Order and Superconductivity in $CeCu_{2.2}Si_2$

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We describe muon spin relaxation measurements of the magnetic heavy fermion compound $CeCu_{2.2}Si_2$. Static magnetic order appears below about 1 K, most likely of spin glass nature. We find that the superconducting transition onsetting at 0.6 K partially destroys the magnetic state and that the magnetic volume fraction decreases within the superconducting state. This observation supports the idea that in $CeCu_{2.2}Si_2$, magnetic order and superconductivity compete with each other rather than coexist.

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The discovery [1] of superconductivity in $CeCu_2Si_2$ by Steglich in 1979 gave birth to the field of heavy fermion superconductivity. Heavy fermion systems, in which the conduction electrons have extraordinarily enhanced effective masses, as evidenced by their large specific heat or Pauli susceptibility, have proven to be fascinating materials [2]. Their spin fluctuations, which had been thought to preclude superconductivity, were subsequently observed to coexist with and possibly even cause it. In several compounds, superconductivity and magnetic order have even been found to coexist. Two materials, (U,Th)Be_{13} [3] and UPt_3 [4], have been observed to possess several distinct superconducting phases, some of which are characterized by a spontaneous magnetic field.

Magnetic order was first detected in $CeCu_{2.1}Si_2$ by Uemura *et al.* using muon spin relaxation (μSR) [5]. They attributed the large static field distribution to either spin glass or incommensurate spin density wave (ISDW) order. Magnetism was subsequently detected [6] with NQR in several samples. To date, neutron scattering has not detected magnetic order, which is understandable in view of the apparent absence of commensurate long range order.

Great variations in the electronic properties of $CeCu_2Si_2$ have been reported, depending on the precise stoichiometry and annealing conditions. These variations have hampered progress in the understanding of $CeCu_2Si_2$, however, they also provide important clues to the underlying physics. Generally, the superconducting properties of $CeCu_2Si_2$ are stabilized through the use of a slight Cu excess [7]. Most likely, the excess Cu resides interstitially, straining the lattice and providing a source of internal pressure. Samples of $CeCu_2Si_2$ (notably crystals) which are not superconducting but rather order magnetically may be made superconducting with the application of pressure [8]. The substitution of La for Ce in $Ce_{1-x}La_xCu_2Si_2$ causes an expansion of the unit cell, giving an effective negative chemical pressure with a corresponding degradation of the superconducting properties [9]. Copper deficiency has been found to cause magnetic order; for example, $CeCu_{1.9}Si_2$ undergoes spin-glass order at 2 K [10] and is not superconducting.

$CeCu_2Ge_2$ is isostructural and isoelectronic to $CeCu_2Si_2$. Jaccard *et al.* have demonstrated [11] that with the application of pressure, its electronic properties are analogous to those of $CeCu_2Si_2$. As the pressure is increased, T_N decreases from 4.1 K (with an estimated ordered moment $\mu = 0.74\mu_B/\mathrm{Ce}$). Under 101 kbar hydrostatic pressure, $CeCu_2Ge_2$ becomes superconducting at $T_{c=0.64}$ K, with $H_{c2=2}$ T, values which correspond to those of $CeCu_2Si_2$ under ambient pressure.

As one varies the pressure, through either mechanical or chemical means, $CeCu_2Si_2$ and $CeCu_2Ge_2$ evolve from a magnetically ordered system to a superconductor. In many samples, superconductivity and magnetism coexist. However, it is unclear to what extent the coexistence occurs on a microscopic scale, although recent bulk measurements [12] of the elastic constants of $CeCu_2Si_2$ were interpreted as evidence against coexistence. Here, we present results of μSR experiments [13,14] of $CeCu_{2.2}Si_2$. We observe an electronic phase separation into regions with and without magnetic order. The gradual loss of magnetic volume fraction below the superconducting T_c indicates that magnetic order and superconductivity compete rather than coexist at a microscopic level.

The sample was prepared at the University of Tsukuba, following the methods described in Ref. [9]. The superconducting transition onsetted at $T = 0.73$ K, with zero resistance at about $T = 0.62$ K. For the μSR measurements, the polycrystalline disk was attached to an extension of the mixing chamber of an Oxford Model 400 dilution refrigerator located on the M15 surface muon channel at TRIUMF.

Complementary to momentum-space probes such as neutron diffraction, μSR is a pointlike probe, analogous to NMR [15]. μSR experiments may be performed in zero external field (ZF−μSR), longitudinal field (LF−μSR), or in transverse field (TF−μSR). ZF−μSR is

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extremely sensitive to the presence of static magnetic fields; static moments as small as $0.005\mu_B$ typically result in internal fields of about 1 G and are readily detected. Rapidly fluctuating paramagnetic moments will not cause observable relaxation of the ZF$-\mu$SR spectra; therefore, the absence of relaxation can indicate either such a paramagnetic state or a nonmagnetic state (for example, a Kondo singlet).

Figure 1 shows several ZF$-\mu$SR spectra taken upon cooling. Above $T = 1$ K, the relaxation rate is small and temperature independent, characteristic of the relaxation from static nuclear dipole moments. At lower temperatures, we see the onset of enhanced relaxation whose magnitude indicates that it is electronic in origin. We do not observe any spin precession; this indicates that the muons experience a broad range of fields. Both incommensurate spin density wave order and spin-glass order result in a broad distribution of fields at the muon site. However, the ISDW has a characteristic peak in its field distribution resulting in a muon polarization function which exhibits several oscillations before being completely relaxed [16]. Therefore, $CeCu_{2.2}Si_2$ is most likely a spin glass. Examining the form of the relaxation at early times, we observe a Gaussian rather than exponential form as $t \rightarrow 0$. This is characteristic of a so-called dense spin glass, where there is a large density of randomly oriented moments [17], in contrast to the such dilute spin glasses as *Cu*Mn [18], where only a few percent of the atoms possess a spin.

Examining the ZF$-\mu$SR spectra in Fig. 1, we note that the amplitude of the relaxing signal is changing. This is apparent in the baseline of the relaxing signal. Just below the onset of relaxation, there is a quick increase in the amplitude of the relaxing signal. However, below $T \sim$ 600 mK, the amplitude of the magnetic signal turns over and then declines steadily with decreasing temperature as shown by the squares in Fig. 2(a). To provide a more detailed measurement of the magnetic volume fraction, we have also performed weak transverse field (WTF) measurements. In the absence of a spontaneous internal magnetic field, the muon spins precess in the applied field at the Larmor frequency. However, in the ordered state, the combination of the external field and the randomly oriented (in a polycrystal) internal field results in a fast depolarization of the muon polarization. Any precessing signal therefore corresponds to muons which experience no significant internal magnetic field, i.e., nonmagnetic (or paramagnetic) regions of the sample. The temperature dependence of the fraction of the muon ensemble *not* experiencing an internal magnetic field is indicated by the circles in Fig. 2(a): We see that it corresponds to the complement of the magnetic fraction found in the zero field measurements (squares). As we discuss below, this observation demonstrates that volume fraction which exhibits static magnetic order changes as a function of temperature. Based on the amplitudes of the signals, we estimate that about 70% of the sample is ordered at 600 mK, whereas by 20 mK, about 40% is ordered. Apparently, some portions of the sample volume which possessed static magnetic order at 600 mK have become reentrant and no longer do so at lower temperatures.

The muon spin relaxation function in both the zero and transverse field measurements exhibits two distinct components. This indicates the presence of physically

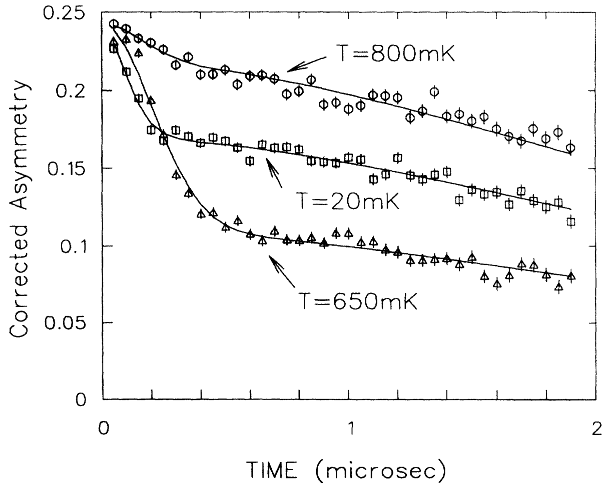

FIG. 1. Zero field μSR spectra of $CeCu_{2.2}Si_2$, taken at $T =$ 0.8, 0.65, and 0.02 K.

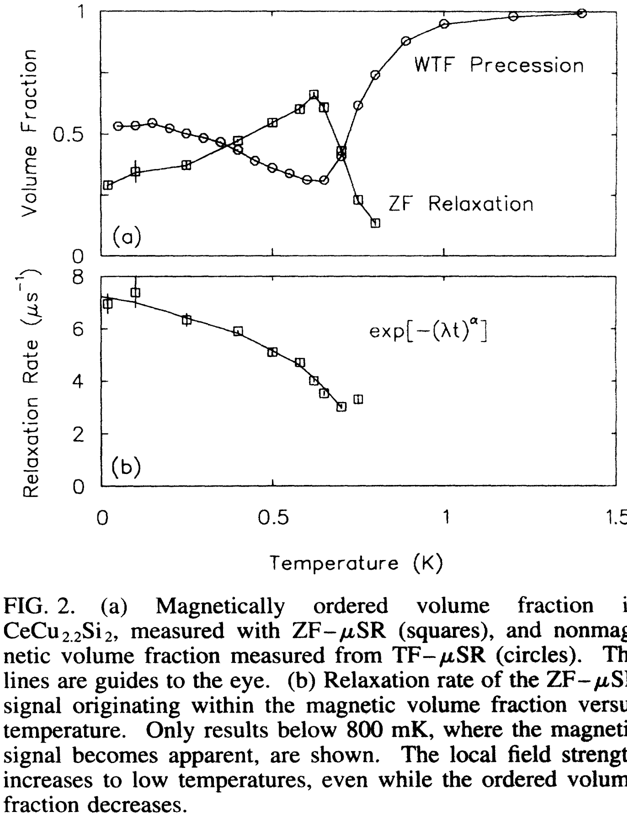

FIG. 2. (a) Magnetically ordered volume fraction in $CeCu_{2.2}Si_2$, measured with ZF$-\mu$SR (squares), and nonmagnetic volume fraction measured from TF$-\mu$SR (circles). The lines are guides to the eye. (b) Relaxation rate of the ZF$-\mu$SR signal originating within the magnetic volume fraction versus temperature. Only results below 800 mK, where the magnetic signal becomes apparent, are shown. The local field strength increases to low temperatures, even while the ordered volume fraction decreases.

separate phases which develop within our specimen. Since the relative fractions associated with the two regions vary with temperature, this separation cannot merely indicate a stoichiometric inhomogeneity. To explain our data, either the size or the number of magnetic regions must actually shrink continuously with decreasing temperature below T_c. μSR, being a real space probe, is not well suited to determining the length scale of the different regions. However, the fact that no sign of a static field is seen in the nominally nonmagnetic signal indicates that these regions must have typical dimensions of at least 10 lattice constants and could in fact be of macroscopic size.

We have attempted to fit the zero field data with a number of trial functions including that corresponding to a homogeneous spin glass, where the moment concentration is a parameter [17]. This model contains the two low-temperature limiting cases of a Gaussian distribution of local fields (for a dense spin glass) and a Lorentzian distribution (for a dilute spin glass). Of all the microscopic model functions we tried, this analysis gave the best fits, but it fails to account for some details of the relaxation function. Most notably, the Gaussian nature of the relaxation at early times is characteristic of nearly static local fields. However, there is no pronounced minimum in the polarization at intermediate times as expected for static randomly oriented moments. In the absence of a microscopic model fit function which adequately fits the data, we have used a generalized power law $\exp[-(\lambda t)^\alpha]$ which corresponds to an exponential with $\alpha = 1$ and a Gaussian with $\alpha = 2$. This phenomenological function gave an excellent parametrization of the data at all temperatures. In most of the temperature range we find that the power $\alpha = 2$ gave the best fits. The only exception to this was around 800 mK, where the fits were more exponential, indicating the dynamic nature of the relaxation around the onset of ordering.

Figure 2(b) shows the temperature dependence of the relaxation rate λ of the magnetic signal. We see that below the onset temperature, the relaxation rate increases monotonically with decreasing temperature. This indicates that within the magnetically ordered regions, the size of the local field increases with decreasing temperature, even while the ordered volume fraction is actually decreasing. The apparent increase at around 800 mK is mainly due to the change in the power α at the transition. Without precise knowledge of the muon stopping site(s) it is impossible to calculate the size of the static moment. However, if we assume that the muon does not occupy a site where the fields largely cancel by symmetry, then to give the observed ~ 50–100 G average internal field would require a Ce moment of about 0.1 μ_B.

Both static and fluctuating magnetic fields can cause relaxation of the muon polarization. The two scenarios may be distinguished in several ways. In the case of rapidly fluctuating moments, the μSR function is either exponential (for concentrated moments) or root exponential (for dilute moments). Gaussian relaxation (which is what we observe) cannot correspond for any rapidly fluctuating spin configuration. Furthermore, the application of an external longitudinal magnetic field will significantly decouple the relaxation when the magnitude of the applied field is roughly comparable to the internal fields. In the case of fluctuating fields, a much greater applied field is required. Figure 3 shows LF$-\mu$SR spectra measured in fields of 105, 344, and 504 G at temperatures of 100 and 620 mK. In both fields, the relaxation is substantially decoupled in an external field of 344 G, indicating that the internal fields are either static or only slowly fluctuating. The residual relaxation of the decoupled signal in Fig. 3 indicates the presence of some slow (on the μs time scale) spin dynamics, both at 100 and 620 mK.

The reduction of the magnetic signal amplitude seen in both transverse and zero fields begins at the superconducting T_c of $CeCu_{2.2}Si_2$. There are several possible interpretations of this effect. The reduction of the fraction of muons seeing the large static moment cannot be due to shielding by supercurrents. The moments must be distributed in a fairly uniform manner throughout the specimen in order to give the observed relaxation. Since the penetration depth is at least 5000 Å , superconducting shielding would be ineffective on interatomic length scales. A change in the spin structure in at least some portion of the sample could result in a cancellation of the ordered moment at the muon site(s). This scenario is also unlikely, as we would not expect the ordered moment in the magnetic regions to continue increasing smoothly through the change in the amplitude while the signal amplitude decreased. In addition, if the spin structure is fairly random as in a spin glass, then a reorientation of the moments would have no significant effect on the total muon polarization.

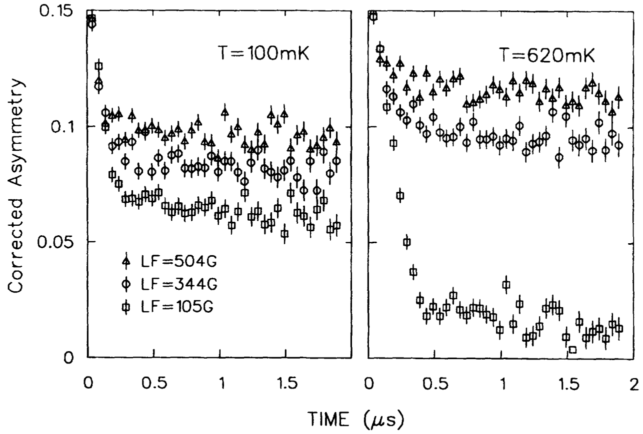

FIG. 3. LF$-\mu$SR spectra for $CeCu_{2.2}Si_2$, measured at T = 100 and 620 mK, in external magnetic fields B = 105 G (squares), 344 G (circles), and 504 G (triangles).

The remaining and most likely explanation is that the magnetic *volume fraction* of the sample is decreasing with decreasing temperature below 600 mK. Since this temperature corresponds to the superconducting T_c, this effect raises the possibility that the superconducting volume fraction is increasing at the expense of the magnetic portion, that the two types of order compete for volume fraction. We attempted to separately determine the superconducting volume fraction by measuring the relaxation of the muon precession signal in transverse field. Following field cooling to establish a uniform flux lattice, the large carrier effective mass results in a long penetration depth, and therefore, only a small increase in the relaxation rate. By contrast, zero field cooling results in an extremely inhomogeneous flux lattice [4], and the relaxation rate at the lowest temperatures is very much enhanced. Comparing data measured at 50 mK following both cooling procedures, we find that the entire nonmagnetic portion of the specimen is superconducting. This precludes the existence of any third (nonmagnetic and nonsuperconducting) phase in the specimen. Because the relaxation rate is so large in the magnetic portion, we are unable to determine if that region is simultaneously superconducting and magnetic.

The mechanism by which the magnetic state is destroyed is unclear, though two general schemes can be envisioned: removal of the moments themselves, or removal of the coupling between the moments. One might expect that the condensation of the conduction electrons into the superconducting state might preclude them from participating in the RKKY interaction between (compensated) cerium moments, thus destroying magnetic order. However, the superconducting coherence length ξ is much larger than the Ce-Ce spacing, so that the RKKY coupling energy scale is at energies higher than the superconducting gap. As such, the RKKY coupling should not be much affected by superconductivity. As to destruction of the moments, we note that the formation of the heavy fermion state already involves a substantial reduction of the cerium moment through Kondo screening. It might be possible that this screening could become more effective in the superconducting state.

To date, antiferromagnetic order and superconductivity have been observed to coexist in UPt_3, URu_2Si_2, UPd_2Al_3, and UNi_2Al_3. In the last three compounds, no anomalous behavior has been seen in the magnetic response in the superconducting state. In UPt_3, there is a slight change in the magnetic Bragg peak intensities below the superconducting T_c [19], which has been interpreted as a coupling between the two order parameters. Here, we are observing a third distinct type of behavior: There is a real space phase separation into regions with and without static magnetic moments with superconductivity appearing at the expense of magnetic order. Apparently, in some region of the $CeCu_2Si_2$ phase diagram, superconductivity and magnetic order compete with each other and do not coexist.

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