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Low-temperature order in the heavy-fermion compound $CeCu_6$

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We have used nuclear-quadrupole-resonance (NQR) techniques to study Cu nuclei in two single-crystal samples of $CeCu_6$ between 200 μK and 20 mK. We present measurements of the NQR intensities and spin-lattice relaxation times, T_1, at frequencies corresponding to three different sites in the crystal. Below 5 mK we observe deviations from standard metallic behavior in both signal intensity and spin-lattice relaxation times. These deviations are unusual in that they are site dependent; they reveal the presence of one or more types of order in this system.

Heavy fermion (HF) compounds display a rich variety of magnetic order and exotic superconductivity.[1] However, the ground states of $CeCu_6$ and $CeAl_3$ (Ref. 2) have yet to be determined. These compounds have among the largest linear coefficients of specific heat, γ, in this class of systems.[1] The determination of their ground states would therefore be of special interest. In this paper we present the results of our very low-temperature studies of $CeCu_6$. These measurements indicate the presence of one or more ordering transitions.

Earlier higher-temperature measurements by several groups[3–5] on pure $CeCu_6$ and on a series of alloys suggest that antiferromagnetic order is likely to occur in the pure compound in the limit of zero temperature. Aeppli *et al.*[3] obtained evidence of short-range antiferromagnetic correlations at $T=0.4$ K from neutron-scattering measurements on pure $CeCu_6$. For the alloy series $Ce(Cu_{1-x}Ag_x)_6$ Gangopadhyay *et al.*[4] have made magnetic susceptibility measurements down to 60 mK and have observed evidence of antiferromagnetic ordering for $x<0.10$. For larger x the ordering becomes ferromagnetic or possibly ferrimagnetic. Recently, Löhneysen *et al.*[5] measured the magnetic susceptibility, specific heat, and transport of various samples of $CeCu_{6-x}Au_x$. They conclude that for $x>0.1$ long-range antiferromagnetic order occurs and that for $x=0.1$ this is suppressed to a very low temperature by the competing Kondo effect. Other evidence to support a magnetic ground state is discussed by Kim and Stewart.[6] They point out that the large value of γ may be due to magnetic correlations in addition to an enhanced effective mass.

A static, magnetically ordered ground state is only one possibility. In other HF systems such as $CeCu_2Si_2$ (Ref. 7) or $CeAl_3$ (Ref. 8) dynamic magnetic correlation effects appear to be important. Finally HF superconductivity has been observed in several systems, sometimes in coexistence with magnetic order.[1]

We have carried out pulsed nuclear-quadrupole-resonance (NQR) measurements on Cu nuclei in two different samples of $CeCu_6$. Our measurements as well as the measured ac susceptibility of the same samples[9,10] will be discussed. At zero field the nuclear quadrupole splitting is the result of the interaction of the electric quadrupole moment of the Cu nucleus with the electric field gradient present in the lattice. The crystal structure of $CeCu_6$ is orthorhombic at room temperature with a transition to monoclinic below about 200 K. As a result of the low symmetry of the lattice there are five independent copper sites with a nonzero E field gradient. In addition, the two copper isotopes ^{63}Cu and ^{65}Cu have nuclear quadrupole moments that differ by 6.9%. There are therefore ten different zero-field NQR frequencies which range from 3.6 to 11.3 MHz.[11] The use of NQR provides a comparison of microscopic interactions at specific sites rather than the more general properties that can be obtained through susceptibility measurements and neutron probes. NQR has previously been used to measure spin-lattice relaxation times (T_1) in $CeCu_6$ at temperatures above 60 mK. From changes in the temperature dependence of T_1 the transition from the localized impurity (Kondo) state to the heavy electron state was found to occur at about 6 K. Between 60 and 200 mK a Korringa constant of 11 msec K has been measured[12] on a powdered sample.

We have studied three NQR transitions at frequencies of 3.9, 6.8, and 11.3 MHz. In all cases T_1 and signal intensity have been measured as a function of temperature. Both free induction decays and spin echoes were used. Since the samples are single crystals with mm scale dimensions, we are only exciting and detecting the nuclei within a skin depth at any given frequency. At 11.3 MHz, assuming a resistivity of 5 $\mu\Omega$ cm, characteristic of a high-quality sample at mK temperatures,[10] we calculate a skin depth of approximately 30 μm. The skin depth increases with decreasing frequency as $\omega^{-1/2}$.

The H_1 field is supplied by a small coil wrapped around the sample, oriented along the orthorhombic "a" axis. The

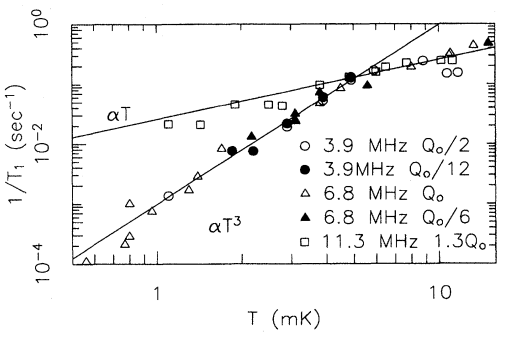

FIG. 1. The spin-lattice relaxation data from sample B demonstrating the Korringa-like dependence ($T_1^{-1} \propto T$) at the 11.3 MHz NQR transition and the abrupt transition to $T_1^{-1} \propto T^3$ dependence for the other measured sites. Five different pulse energies (Q) were employed as a check on eddy current heating from the pulses.

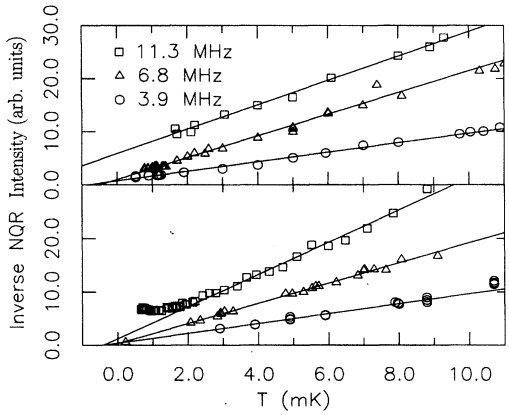

FIG. 2. The inverse NQR intensity is plotted as a function of temperature for sample A (top) and sample B (bottom). A straight line with negative x intercept demonstrates the best fit to the Curie-Weiss law.

electron temperature of the copper plate on which the experiment is mounted is determined by a Pt NMR thermometer with higher resolution provided by a ^{3}He melting curve thermometer above 0.9 mK.[13] Our measurements span the temperature range 200 μK to 20 mK.

Two different samples were measured. A glow discharge mass spectrometer (GDMS) analysis[14] performed on the first sample (A) indicates the presence of magnetic and rare-earth impurities at the 10–100 ppm level. To eliminate possible artifacts introduced by impurity effects we obtained another sample (B) with negligible levels (less than 1 ppm from additional GDMS measurements) of these impurities. Both samples were thermally anchored with a thin layer of silver epoxy.

Spin-lattice relaxation times were measured by the standard technique of saturating the spins and measuring the recovery after various delay times. At the lower temperatures, where the signal intensity is large, the recovery after saturation was monitored by a series of small angle tipping pulses. The value of T_1 at a given temperature appears to be independent of the method used to measure it in these experiments. The pulse length was between 10 and 100 times shorter than the inverse linewidths to ensure saturation. The relaxation curves do not appear to follow a single exponential in all cases; however, the relaxation of the majority of the magnetization occurs with a single time constant, T_1. Figure 1 shows T_1^{-1} for the three different quadrupole resonances in sample B. Above 5 mK the relaxation follows the Korringa law, $T_1T=26$ msec K. Below 5 mK T_1^{-1} becomes site dependent: at the two lower-frequency sites (3.9 and 6.8 MHz) the best fit to the data indicates a T^3 dependence.

The data from sample A show a similar trend to that of sample B, but with a large change in scale factor. Above about 2 mK the data appear to follow a Korringa law but with a constant of 11000 msec K, a factor of 400 *larger* than that of the pure sample. Below 2 mK there is a sudden increase in T_1 for the 3.9 and 6.8 MHz transitions. Because of the length of time involved in reaching thermal equilibrium it was not feasible to take enough data to measure a power-law dependence at low temperatures. Again the 11.3 MHz transition exhibits different behavior below 3 mK. Following saturation, we cannot recover the full signal intensity after many hours, indicating an anomaly in the relaxation time.

The large difference in the Korringa constants for our two samples is clearly of significance, but is difficult to explain. Both exhibit a rapid increase in T_1 with decreasing temperature and show other features which point to a shared physical origin for the observed behavior. The difference between the Korringa constants of our high-purity sample (B) and the sample of Ref. 12 is not understood. The relative difference is, however, much smaller than between our two samples. It is possible that the presence of trace amounts of various impurities affects the spin fluctuation spectrum leading to changes in the nuclear relaxation time.

We turn now to a discussion of measurements of the NQR signal intensity. For a paramagnetic system, the signal intensity obeys the Curie law. In this system we find that the intensity obeys a Curie-Weiss law, indicating antiferromagnetic correlations between nuclei (spins). This functional form fits the data very well over the entire temperature range; the sole exception occurs for the low-temperature data at 11.3 MHz (near and below a peak observed at about 1 mK to be described in more detail below). The value of the Curie-Weiss temperature, Θ, varies with both site and sample; however, there is qualitative agreement between samples A and B in that Θ is largest for the 11.3 MHz resonance and comparable for the two lower-frequency lines. In sample B our best fit to the data yields values of the Curie-Weiss temperature Θ of -0.62 ± 0.1, -0.15 ± 0.1, and -0.1 ± 0.1 mK for the three resonances in order of decreasing frequency. For sample A the same type of fit yields Θ values of -2.5 ± 0.2, -0.42 ± 0.07, and -0.5 ± 0.2 mK, respectively. We plot the inverse signal intensity as a function of temperature for both samples in Fig. 2. We note the quantitative difference, but qualitative similarity, between the samples, also reflected in the T_1 measurements.

The short T_1 for the spins at the 11.3 MHz site in sample B allows for detailed studies of its low-temperature signal intensity. As the cryostat warms up following a demagnetization, the signal intensity *increases* with increasing tem-

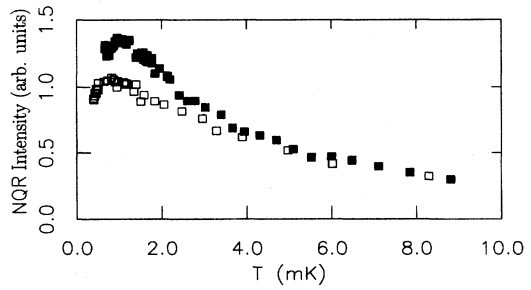

FIG. 3. The NQR intensity from the 11.3 MHz transition as a function of temperature is shown for two different warming rates of the nuclear stage. The run depicted with open circles has a faster warmup.

perature, going through a peak at 1.1 mK (see Fig. 3). The height of this peak depends on our cooling and warming rates, suggesting hysteresis. We studied the line shape, spin-echo decay time, and field dependence of the resonance. There was no substantial change in the line appearance and spin-echo decay time ($T_2=50$ μsec) over the entire temperature range. The application of a field of 100 G resulted in a fourfold splitting of the line.[15] Again there was no substantial change in the temperature dependence of the signal with the field present.

The ac (electronic) susceptibility has also been measured for both samples. Sample A shows two peaks in χ',[9] at 3 and 0.5 mK. Similar features have been reported by Schuberth *et al.*,[16] after subtraction of a baseline due to magnetic Gd^{3+} ions. The susceptibility of sample B shows no maximum at 3 mK; we tentatively attribute the 3 mK feature in sample A to spin-glass ordering of an impurity system. At lower temperatures only a small increase in susceptibility is observed in sample B. There is no indication of the 0.5 mK peak; however, the thermometry was reliable only down to 0.9 mK.

The unique behavior described above for $CeCu_6$ must originate from an ordering transition of either the electronic or the nuclear spin system. Many features are similar to those observed in phase transitions in other systems; however, it appears that not all can be explained by any single phenomenon. In this section we will discuss ordering in other systems in relation to features observed in the NQR and electronic susceptibility of $CeCu_6$.

With regard to electronic order the most interesting possibility is superconductivity. Points to support this interpretation include the temperature dependence of T_1^{-1}, which strongly resembles that of a superconductor; there is an abrupt transition from a Korringa dependence to a T^3 dependence below 5 mK at two of the three sites. (A T^3 dependence has been observed in other exotic superconductors.[17]) Although the temperature dependence of T_1^{-1} at the 11.3 MHz site does not show this dramatic change, a site-dependent T_1 has been observed in exotic superconductors, such as the high-T_c compound $YBa_2Cu_3O_7$.[18] Another feature of superconductivity is a sharp drop in the product of signal intensity and temperature reflecting the decreased penetration depth at and below T_c. This does not appear to explain the observed site dependence of the signal intensity, although the relative magnitudes of H_1 and H_{c1} are unknown and may lead to unanticipated effects. Finally, the ac susceptibility shows no evidence of flux exclusion at 5 mK.

Small moment (typically a fraction of μ_B) electronic antiferromagnetism exists in a number of HF systems, often coexisting with superconductivity.[7] It is instructive to compare our measurements to NQR/NMR measurements on the HF $CeCu_2Si_2$,[7,19] which has a magnetic transition at $T=T_M$, just above the zero-field superconducting transition at $T=T_c$.[20] In the presence of an applied field, the superconducting transition is suppressed, allowing for NMR measurements in the magnetic state only. Several of the features of the magnetic transition in $CeCu_2Si_2$ resemble our measurements. There is a sharp decrease in the product of signal intensity and temperature at T_M with no corresponding change in the line position or appearance. The temperature-independent line shape suggests the absence of the internal field which would be associated with static magnetic order. The lack of a static, internal field, coupled with the anomalous behavior of the spin-echo decay time (T_2) have been interpreted as the signatures of a dynamic magnetic transition in $CeCu_2Si_2$.[7] We note that the T_2 measurements in $CeCu_2Si_2$ reveal a strong field dependence and that at zero field there is no temperature dependence down to well below T_c. Our T_2 measurements, also performed at zero field, are temperature independent. Measurements of $(T_1T)^{-1}$ at the magnetic transition in $CeCu_2Si_2$ show a small increase, followed by a rapid decrease below T_c. Although some of the features of the dynamic magnetic transition are similar to those observed in $CeCu_6$, the site dependence, especially in the T_1 measurements, cannot be readily explained on this basis.

The last class of electronic order that we consider involves a spin-glass transition of uncompensated moments in stray Ce^{3+} ions. Such a transition has been observed in samples of $CeCu_2Si_2$ which have been grown with variations in their stochiometry.[7] The NMR signatures of this transition include an increase in the linewidth and a drop in nuclear signal that mimics a Curie-Weiss law. Finally, the temperature dependence of the intensity has a dramatic field dependence. Although our data can be well described by a Curie-Weiss law, we see no change in linewidth. Additionally, our measurements of the site dependence of the Curie-Weiss constants cannot be explained since the spin-glass transition would be global. The field dependence is also incorrect: since application of 2.5 T dramatically changes the nature of the spin-glass transition in $CeCu_{1.9}Si_2$, which has a zero field $T_g=2.5$ K, we would expect some change with an applied field of 10^{-2} T if T_g were on the order of mK. Finally, there is no indication of a characteristic peak in the ac susceptibility in this temperature range.

With regard to nuclear order, the Curie-Weiss behavior of the nuclear spin system as well as the peak in signal intensity at 1.1 mK are reminiscent of NMR measurements on pure metallic systems that display nuclear order at low temperature.[21] Since these systems have lattices with cubic symmetry, every site is equivalent. In the case of $CeCu_6$ the sites are not equivalent. The different Curie-Weiss constants that we measure could be the result of a spatially varying interaction. Of the two known mechanisms that result in nuclear order in metals, the dipole-dipole interaction is far too small to result in ordering at 1 mK. However, a crude

estimate of the relative magnitude of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in $CeCu_6$ and in metallic Cu shows an enhancement of roughly two orders of magnitude in the HF system.[22] Such a large exchange interaction would result in a significant increase in the ordering temperature, although it still falls below the mK range. A more careful calculation of the RKKY interaction, taking into consideration all of the details of the heavy electrons, would be necessary to make a useful comparison. The first example of nuclear order resulting from the RKKY interaction under thermal equilibrium conditions has just been observed in the intermetallic compound $AuIn_2$ at 35 μK.[23]

In addition to these metals, there are other systems that display nuclear order but with very high T_c (mK range). In solid ^{3}He atomic exchange results in a transition temperature below 1 mK.[24] Such a process is unlikely to exist in $CeCu_6$. The Van Vleck paramagnets also display nuclear order in the mK range. Due to the presence of $4f$ electrons there are large hyperfine fields in these compounds. $PrCu_6$, structurally similar to $CeCu_6$, is a hyperfine enhanced system in which the Pr nuclear spins order ferromagnetically at 2.7 mK.[25] This type of order is unlikely in $CeCu_6$ as the Ce nuclei have no spin and there are no large hyperfine fields at the Cu nuclei.

A phase transition occurring in the low mK regime in either the nuclear or electronic system is highly unusual; however, unusual behavior, such as the coexistence of magnetism and superconductivity, is known to exist in HF compounds. The vast majority of experiments on these compounds have been focused on the electronic system; this is a very low temperature study of the nuclear spin system. Thus it is not surprising that there are no theoretical models available to which we can compare our findings. It is evident that the interactions between the nuclear and electronic systems as well as the ground-state properties of the nuclear spin system in these compounds are of considerable interest.

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