High-field specific heat of $CeCu_2Si_2$ and $CeAl_3$

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We have measured the low-temperature specific heat, C, of both a superconducting and a nonsuperconducting sample of $CeCu_2Si_2$, as well as a sample of $CeAl_3$, in fields to 23 T. Contrary to all our previous $C(H)$ work on nonsuperconducting Ce-based heavy-fermion systems (HFS's), the superconducting $CeCu_{2.2}Si_2$ sample has a small response to field, similar to the results for the other heavy-fermion superconductors UPt_3 and UBe_{13}. Thus, the previous correlation that U-based HFS's have small changes of C with field and that Ce-based HFS's have large changes must be discarded. We attempt to correlate other measured properties with our $C(H)$ data for all HFS's for which such data exist, a total of seven systems, with only limited success. The possibility of a hidden variable linking the lack of large changes in C in 23 T with the occurrence of superconductivity in HFS's is discussed.

INTRODUCTION

Although difficult technically, the measurement of the high-field specific heat of heavy-fermion systems (HFS's) promises to reveal important information about both the formation of the heavy-fermion ground state (large m^*) and superconductivity in these systems. The reason for this is due to several things: (1) Heavy-fermion systems are near to magnetism, as shown by doping experiments,[1–4] neutron scattering,[5–7] high-temperature Curie-Weiss behavior of the susceptibility,[8] and, for UPt_3, the temperature dependence—$T^3 \ln T$—found[9] in the low-temperature specific heat. Additionally, there is even evidence[6] that UPt_3 is an antiferromagnet at 5 K, albeit with a very small ($\sim 0.02\mu_B$) ordered moment. (2) The characteristic effective bandwidth estimated for HFS's is very small ($\propto 1/m^*$). Thus, for large applied fields, $\mu_{\text{eff}} H \sim k_B T_{\text{char}}$. (3) Recent neutron irradiation experiments[10] on UPt_3 and UBe_{13} demonstrate quite clearly the closeness of these systems to magnetism. Thus, magnetic fields are expected to cause important changes in HFS's. Since the very existence of the temperature-dependent heavy-fermion ground state is best seen in the low-temperature specific heat (where a rapid increase is seen in $C/T \propto m^*$ below 10 K for most HFS's), C as a function of H measurements should be quite revealing.

Until the present work, a collection of $C(H)$ data for a number of HFS's large enough to allow an overview and concomitant conclusions has been lacking, in large part due to the difficulty of the measurement. Some theoretical work directed at explaining the prior results has been undertaken already.[11] We present here new results for $C(H)$ to 23 T for $CeAl_3$, nonsuperconducting $CeCu_2Si_2$ and superconducting $CeCu_2Si_2$, as well as a summary of recent $C(H)$ data on $CeCu_6$,[12] UPt_3,[13] UBe_{13},[12,14] nonsuperconducting $UBe_{12.94}Cu_{0.06}$,[12,14] and UPt_4Au.[15] Hopefully, the present work will stimulate further theoretical analysis.

EXPERIMENT

The $CeAl_3$ sample was prepared via arc melting using the highest purity Ce available, that from Ames Laboratory. The sample was annealed at 1000 °C for 56 days. No anomalies in the specific heat was detectable at 2.5 or 4 K from the well-known second phases.[8,16] The nonsuperconducting (ns) $CeCu_2Si_2$ sample was slightly deficient in Cu ($CeCu_{1.9}Si_2$) and has been well characterized elsewhere.[17] The superconducting (s) $CeCu_2Si_2$ sample was prepared with an excess of Cu ($CeCu_{2.2}Si_2$) and was annealed for 4 days at 1000 °C. The superconducting transition temperature for the sample is 0.68 K. Characterization of this sample may also be found elsewhere.[17]

The fields up to 12 T were obtained using a superconducting magnet. Fields to 23 T were obtained at the Francis Bitter National Magnet Laboratory. The low-temperature calorimeter has been described elsewhere.[18,19]

RESULTS AND DISCUSSION

Specific heat divided by temperature, C/T, data for $CeAl_3$, ns-$CeCu_2Si_2$, and s-$CeCu_2Si_2$ between 2.4 and 10 K are shown in Figs. 1–3, respectively. The percent change in the C/T value upon application of the field, calculated as

$$100\times\left[\frac{C}{T}(H=23T)-\frac{C}{T}(H=0)\right]\Big/\frac{C}{T}(H=0)\ ,$$

is shown in Table I, along with such data for five other HFS's. Since the size of the change in C/T with field is temperature dependent, Table I lists values at 2.4 K, a temperature achieved for all the measurements. It is abundantly clear from the data shown in Figs. 1–3 that the magnitude of the change in the specific heat with field increases with decreasing temperature. This has also been observed to much lower temperatures for, e.g.,

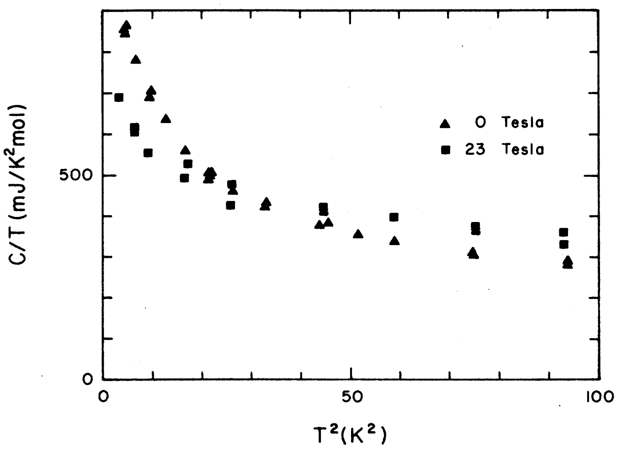

FIG. 1. Low-temperature specific heat divided by temperature vs temperature squared of $CeAl_3$ in 0 and 23 T applied field.

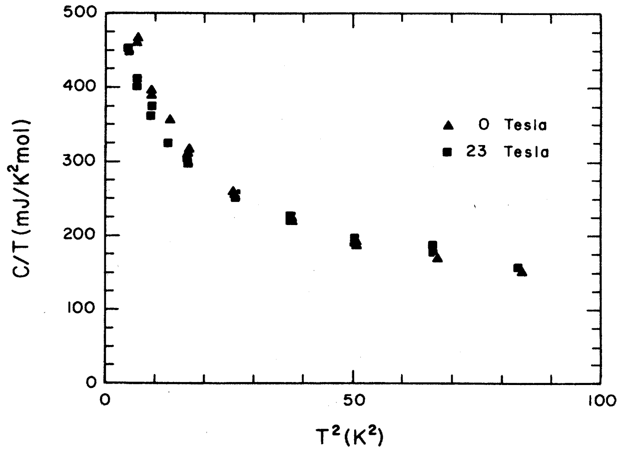

FIG. 3. Low-temperature specific heat divided by temperature vs temperature squared of s-$CeCu_2Si_2$ in 0 and 23 T applied field. Note the significantly smaller change of C with high field in this sample compared with the data presented in Fig. 2 for ns-$CeCu_2Si_2$.

$CeAl_3$.[16] Thus, the choice here, based on technical considerations, of 2.4 K as the temperature for intercomparison is not optimal, but is a usable basis for comparison.

Previous $C(H)$ data[16,20] for $CeAl_3$ extended only up to 8 T and concentrated on the very low-temperature ($T < 1$ K) behavior. The reduction of the low-temperature specific heat at 1 K by an 8 T applied field is[16] 18%, while at the peak in $C(H=0)$ at 0.35 K the reduction in C caused by 8 T is 30%. Comparing these results to our data in Fig. 1, it is clear that for $CeAl_3$ (and $CeCu_6$ as well) there exists a temperature (relatively insensitive to field for those HFS's listed, expect for UPt_3) at which the change in C with field is zero. Below this T_{crossing} (tabulated in Table I) temperature in $CeAl_3$ (also $CeCu_6$), the relative change $[C(H)-C(0)]/C(0)$ becomes more positive as T decreases. In contrast, for $CeCu_2Si_2$ above a certain temperature the change in C with H goes to zero. (In both types of cases it is important to compare these relative change results at the same temperature.)

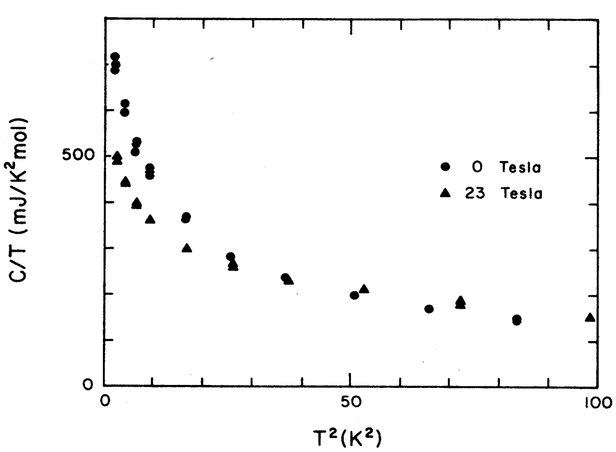

FIG. 2. Low-temperature specific heat divided by temperature vs temperature squared of ns-$CeCu_2Si_2$ in 0 and 23 T applied field.

From examining the data presented in Figs. 2 and 3, the behavior of the specific heat of s-$CeCu_2Si_2$ with field is qualitatively quite different from that of ns-$CeCu_2Si_2$, with the change in C/T with field much larger for the ns sample. [Since no directional dependence for χ in field is observed for our $CeAl_3$ and both $CeCu_2Si_2$ polycrystalline samples, no directional dependence for $C(H)$ is expected either.] Until these data were taken, the only existing high-field specific-heat data for $H > 8$ T for $CeCu_2Si_2$ were on a nonsuperconducting sample,[21] where the field response is large. Since the available high-field specific-heat data for U-based HFS's show a small field response (see Table I), we had established[12] a tentative correlation that Ce HFS's had large $\Delta C(H)$, while U HFS's had a small $\Delta C(H)$. This had implied that the formation and characteristic energy of the heavy-fermion ground state might be different in Ce and U HFS's, as theoretically addressed in Ref. 11. Our new data on s-$CeCu_2Si_2$ show a similar small change in C with field as seen in UPt_3 and UBe_{13}. Arriving at some phenomenological model capable of explaining these differences is a daunting task, given the large number of existing other measurements (e.g., ρ, χ, pressure, neutron scattering) on HFS's. Although the following discussion is certain to omit some possibilities for phenomenological correlations, here we attempt to provide an overview of possible phenomenology to describe this broad set of data on $C(H)$ for HFS's completed by data presented here for the first time.

First, consider $CeAl_3$ versus $CeCu_6$. Even though the zero-field, low-temperature specific heats of both, as well as the magnetic susceptibilities, are equal[8] within a few percent, the change of C(2.4 K) with high field for the two materials is a factor of 2 different in size. Several phenomenological explanations of this difference are pos-

TABLE I. Field dependence of the specific heat of heavy-fermion systems and related parameters (from Ref. 8 unless otherwise noted).

	γ (at $T=2.4$ K) (mJ/mole K^2)	% change (at $H=X$) $\left[\equiv \frac{C(H)-C(0)}{C(0)}\right]$	T_{crossing} (K)	χ $\left[\frac{\text{memu}}{\text{mole}}\right]$ at 1.7 K	$T_{\rho\max}$ (K)
ns-$CeCu_2Si_2$	585	-22% (12 T)		44.5	5–6.5
		-30% (23 T)			
S-$CeCu_2Si_2$	485	$<5\%$ decrease (12 T)		8.7	20–24
		$\sim -11\%$ (23 T)			
$CeAl_3$	770	-13% (12 T)	4.2	27	35
		$\sim -22\%$ (23 T)	4.5		
$CeCu_6$	645	-24% (14.5 T)	2.3	27	14
		-46% (24 T)	5.6		
UPt_3	445	0 (17 T, c axis)		4.2	
	445	$+19\%$ (19 T, $\perp$ c axis)	4	8.3	
ns-$UBe_{13}Cu$	510	$+9\%$ (22.5 T)		16	
UBe_{13}	510	$+4\%$ (11 T)		15	
UBe_{13}	510	5–10% (18 T)		15	2.4
UPt_4Au	500	$\sim 5\%$ (12 T)		13	

[a]Determined by higher temperature Curie-Weiss behavior of χ.
[b]$C(P)$ data (Ref. 31) only taken to 4.5 kbar, where ΔC is 20%. Due to the linearity of the lower pressure ΔC data, and in order to have an intercomparable number, this 4.5 kbar result has been doubled as an estimate.

sible. From Table I, one possibility is $\Delta C(H) \propto T_{\rho\max}^{-1}$, where the temperature of the maximum in the resistivity defines a characteristic energy, perhaps related to the onset of coherence in the heavy-fermion ground state. The smaller is this characteristic energy, or effective bandwidth, the larger is the change with field of the specific heat. Another explanation of the larger $\Delta C(H)$ in $CeCu_6$ versus $CeAl_3$ is based on the fact[22–24] that $CeCu_6$ is known to have a strong directional dependence for $C(H)$ below 1 K and in fields to 7.5 T. For H parallel to the [001] direction in single-crystal $CeCu_6$, C is[22–24] a rather rapid function of H, while in the other two crystalline directions much smaller changes in C with H are observed. This has been explained[25] by a model using crystal-field effects. Although the crystal-field effects, and therefore directional dependence of $C(H)$, are expected to be similar in $CeAl_3$, not only are single crystals of $CeAl_3$ not readily available (due to the phase diagram), polycrystalline $CeAl_3$ has essentially no preferred orientation. In contrast, polycrystalline samples of $CeCu_6$ can have a significant preferred orientation and, in order to observe the largest possible depression of C with H in $CeCu_6$, the high-field data in $CeCu_6$ in Ref. 12 were taken with the polycrystalline sample significantly aligned in the [001] direction. Thus, this may explain the factor of 2 difference observed in ΔC(23 T) for $CeCu_6$ and $CeAl_3$ stated in Table I. Experiments down to 0.4 K and 15 T are planned on a single crystal of $CeCu_6$.

In comparing our high-field data for s-$CeCu_2Si_2$ and ns-$CeCu_2Si_2$, there are several possible explanations. Let us consider them each in turn.

(1) It might be that the field dependence of the specific heat of HFS's is dependent on some characteristic energy. We have known for some time that this T_{char} *is not* T_{Kondo} as calculated from some effective bandwidth, i.e., $T_K \propto 1/\gamma$. This is clear from Table I, since materials with similar γ values have much different $\Delta C(H)$. What other characteristic energy is there in all these systems that would be a likely candidate? Some sort of measure of the coherence temperature seems appealing. The upper limit for T^2 dependence of the electrical resistivity apparently does not work (see Table I). Is there a correlation between $\Delta C(H)$ and the coefficient, A, of the T^2 term at low temperatures in the resistivity? A universal relationship between A and the specific heat γ for HFS's has already been claimed.[26] Unfortunately for this zero-field correlation, the values for A (shown in Table I) for UBe_{13} and high-quality $CeCu_6$ do not obey this universal relationship of A/γ^2=constant. Also, it is immediately clear that $\Delta C(H)$ is not correlated with A (e.g., our previously characterized[17] samples of s- and ns-$CeCu_2Si_2$ have different $\Delta C(H)$—as measured here—and the same A).

The temperature of the peak in the low-temperature resistivity, below which coherency of the local spin moments stops the spin-flip scattering, as seen in Table I, changes qualitatively in the right direction between the s- and ns-$CeCu_2Si_2$ samples for $\Delta C(H) \propto 1/T_{\rho\max}$ to work. [As mentioned above, this would also explain $C(H)$ for $CeCu_6$ versus $CeAl_3$]. The drawback is the lack of a maximum at low temperatures in the resistivity for UPt_3 and UPt_4Au, and the low value of $T_{\rho\max}$ for UBe_{13}. (UPt_3 does have[27] a very broad maximum in ρ versus T at about 800 K.)

TABLE I. (*Continued*).

μ_{eff}[a] (μ_B)	$T_{Kondo}=0.67/\gamma(R)$ (K)	$\Delta C \begin{bmatrix} P=9\text{ kbar} \\ T=1\text{ K} \end{bmatrix} \equiv \frac{C(P)-C(0)}{C(0)}$ (Refs. 24 and 31)	T_{max} for $\rho \sim \rho_0 + AT^2$ (K)	A for $\rho \sim \rho_0 + AT^2$ ($\mu\Omega$−cm/K^2)
2.61	9.5		1–1.5	10 (Ref. 17)
2.37	12.1	40%[b]	1–1.5	10 (Ref. 17)
2.63	7.2	54 (8.2 kbar)	0.3	35
2.69	8.6	33%	0.09	122 ($\rho_0 \sim 10$) (Ref. 32)
		21%	~1.5	26 ($\rho_0 \sim 100$) (Ref. 33)
2.6	12.5			1 (Ref. 34)
31	10.9 11.1	28%	<0.9	116 (Ref. 35)

(2) Another qualitative, phenomenological means of trying to regularize these $C(H)$ results is to say that $\Delta C(H)$ depends on how near to magnetism a given HFS is. Thus, a system like $CeCu_6$, for which antiferromagnetic correlations have been observed[7] by neutron scattering, would have a large $\Delta C(H)$. Also, the Wilson ratio ($\propto \chi/\mu_{eff}^2\gamma$) may be used as a yardstick for how magnetic a system is. Unfortunately, although it is generally agreed[28] that μ_{eff} is altered from its higher temperature value (shown in Table I) by Kondo compensation via the conduction electrons, there exists no agreed-upon method for then determining μ_{eff} at low temperatures. Although neutron scattering data may be used to approximate μ_{eff}, this is an arguably inaccurate process. Second, at least in the case of ns-$CeCu_2Si_2$, it has been argued[29] rather convincingly that the large value of χ measured is due mainly to impurity effects.

(3) The impurities which produce a larger χ in our ns-$CeCu_2Si_2$ as compared to our s-$CeCu_2Si_2$ sample may also be responsible for the 17% difference in γ's (585 versus 485, respectively, at 2.4 K). One could then argue that the larger suppression of C with H of the ns sample is an impurity effect. Thus the 30% suppression of γ observed with 23 T at 2.4 K in ns-$CeCu_2Si_2$ would be made up of a 17% suppression (impurity effect) plus a 13% intrinsic effect very similar to the 11% suppression observed for s-$CeCu_2Si_2$.

(4) Wohlleben has argued[30] that the hidden variable responsible for the factor of 5 variation in measured $\Delta C(H)$ values is that lattice instabilities create the large γ in the heavy-fermion superconductors and therefore these superconducting HFS's have a small response of C to H. The nonsuperconducting HFS's have "true" narrow-band-caused large γ values with large $\Delta C(H)$ values, and the magnetic interactions inherent in a narrow band prohibit superconductivity. This explanation fails to distinguish why, via miniscule Cu doping, ns-UBe_{13} has a small $\Delta C(H)$ just like s-UBe_{13}, and exactly the same specific heat above 0.9 K.

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