Coexistent superconductivity and magnetism in Th-doped $CeCu_2Si_2$

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Antiferromagnetic order is found in $Ce_{1-x}Th_xCu_2Si_2$ for $0.1 \le x \le 0.5$, which becomes ferromagnetic in nature for $x = 0.9$. Previous work, which found that superconductivity remains present in Th-doped $CeCu_2Si_2$ up to at least $x = 0.12$, and perhaps as far as $x = 0.2$, is expanded upon to find that superconductivity remains up to at least $x = 0.25$, with $T_c^{\text{onset}} = 0.25$ K. We report the coexistence of a significant bulk ordered moment ($\sim \frac{1}{4}$ of that of a fully ordered spin-$\frac{1}{2}$ system) coexisting with superconductivity in a heavy-fermion system.

With the discovery[1] of superconductivity in highly correlated, high-effective-mass ("heavy fermion") m^* electrons in $CeCu_2Si_2$, a great deal of interest has been focused on $4f$ and $5f$ "heavy-fermion" systems. Some have been found to be superconducting ($CeCu_2Si_2$, UBe_{13}, and UPt_3) while others (e.g., U_2Zn_{17} and UCd_{11}) display the magnetism expected for such highly correlated electrons, while still others (including $CeAl_3$ and $CeCu_6$) display no long-range order.[2] It has become evident with further study of these materials that the nonmagnetically ordered systems are more "nearly magnetic" than previously understood (with the exception of UPt_3, which was always[3] known as a spin-fluctuation system). For example, muon-spin-rotation (μSR) work[4] on $CeAl_3$ has found magnetic correlations that are partly coherent (albeit spatially inhomogeneous and frustrated) below 0.7 K; doping experiments[5] in $CeCu_6$ have shown that small-doping perturbations ($CeCu_{5.91}Ag_{0.09}$) cause long-range magnetic order of apparently antiferromagnetic nature.

The question of whether these ubiquitous magnetic correlations in heavy-fermion systems are tied to the occurrence of superconductivity in $CeCu_2Si_2$, UBe_{13}, and UPt_3 is an often considered but as yet unsolved speculation. A second important and presently unresolved question is the source of the heavy-fermion ground state, i.e., what causes the observed huge effective electron masses.

Recently, significant progress has been made[6] on this latter question in UBe_{13} with the discovery that 40% of the large m^* is due to single-ion effects, and that the many-particle contribution to m^* is extremely sensitive to the U-Be separation. Also, no evidence for nearly magnetic behavior was found[6] in any of the $U_{1-x}M_xBe_{13}$ alloys studied, for all nine of the M elements investigated (M=Hf, Zr, Sc, Li, Y, Pr, Ce, Th, and La) which form nonmagnetic MBe_{13} compounds. Thus, a similar study of $Ce_{1-x}M_xCu_2Si_2$ was undertaken, with M=Y, La, Lu, and Th. We report here on our unusual findings in $Ce_{1-x}Th_xCu_{2.2}Si_2$.

The samples were prepared by arc melting together the purest possible starting elements (including Ames Ce and Th crystal bar), followed by turning and remelting an additional three times, followed by annealing at 900 °C for one week. The slight excess of copper serves to minimize the presence of uncompensated Ce^{3+} spins. X-ray-diffraction studies of all of the samples indicated single phase material, as expected from the fact that $CeCu_2Si_2$ and $ThCu_2Si_2$ form in the same crystal structure with very similar lattice parameters. Lattice parameters and unit cell volumes for the samples are shown in Table I; there is a slight c-axis expansion for $x = 0.2$ and 0.5, as has been previously reported.[7]

The resistivity ρ for samples of $Ce_{1-x}Th_xCu_2Si_2$ published[7] as part of a L_{III} absorption study, shows that the broad maximum at a temperature $T_{\rho\max} \sim 11$ K in pure $CeCu_2Si_2$ shifts to lower temperature ($T \sim 5$ K), sharpens, and becomes more pronounced for 10% Th. $T_{\rho\max} \simeq 5$ and 6 K for $x = 0.2$ and 0.3, respectively. For $x > 0.3$, the peak in ρ becomes less pronounced and again broadens, with $T_{\rho\max}$ stated to be 11 K for $x = 0.4$ and 13 K for $x = 0.5$.

We have measured for the first time the dc magnetic susceptibility for $Ce_{1-x}Th_xCu_{2.2}Si_2$ between 1.8 and 400 K, and report the low-temperature values and the μ_{eff} determined from the higher-temperature Curie-Weiss behavior ($1/\chi$ linear in T) of the susceptibility. Plots of these data for $x = 0.25$ and 0.9 are shown in Fig. 1. The magnetization versus field data show linear behavior to 5.5 T for all samples except $x = 0.9$, which shows a pronounced saturation (see Fig. 1) starting at about 2 T with a saturation moment corresponding to $0.8\mu_B$/Ce-mole.

TABLE I. Lattice Parameters and μ_{eff} for $Ce_{1-x}Th_xCu_{2.2}Si_2$.

x	a (Å)	c (Å)	Unit cell volume (Å^3)	χ^a(1.8 K) (memu/Ce mole)	$\mu_{\text{eff}}(\mu_B)$
0.00	4.105	9.933	167.4	7.4	2.68
0.05	4.097	9.914	166.2	9.2	2.69
0.10	4.101	9.904	166.7	9.3	2.53
0.20	4.095	9.913	166.4	10.7	2.58
0.50	4.097	9.926	166.2	39.0	2.42
0.90	4.092	9.903	165.2	1800.0	2.82
1.0	4.096	9.887	165.9	-0.02^b	

[a] χ(1.8 K) ≡ 14.7, 15.8, and 25.2 memu/Ce mole for $x = 0.25$, 0.30, and 0.40, respectively.
[b] pure $ThCu_{2.2}Si_2$.

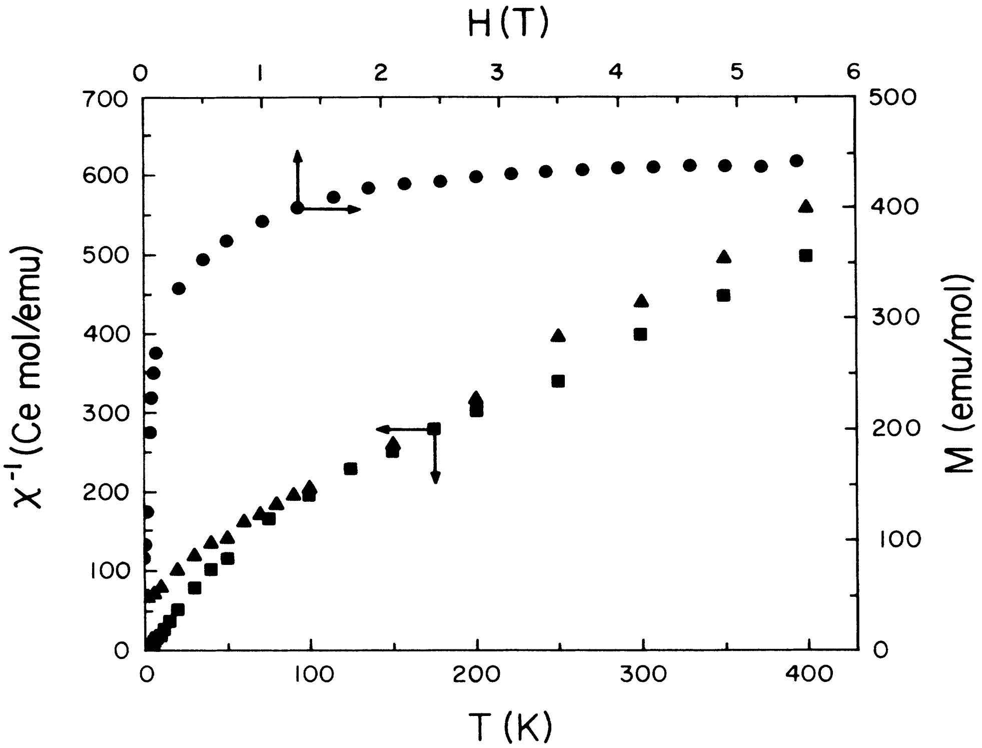

FIG. 1. Inverse magnetic susceptibility per Ce mole for $x = 0.25$ (triangles) and $x = 0.9$ (squares). Note the Curie-Weiss behavior at higher temperatures (i.e., $1/\chi$ is linear in T), from which μ_{eff} is calculated in Table I. The sharp fall in $1/\chi$ for $x = 0.9$ below 20 K coupled with the nonlinear M vs H behavior (circles, use the right-hand axis) points to ferromagnetic behavior at this composition.

The low-temperature χ upon close examination show a slight peak in χ at ~ 4.5 K for $x = 0.2$ and $x = 0.3$, a change in slope for $x = 0.4$ at 4.5 K, and no such anomaly for $x = 0.5$. $d\chi/dT$ plots show the anomalies quite distinctly. By cooling the samples in zero field, then turning on a 100 G field and measuring χ_{dc} versus T, a much more distinct anomaly [although $(\chi_{\text{peak}} - \chi_{1.8\,\text{K}})/\chi_{1.8\,\text{K}}$ is still only 4%] is observed.

Our χ_{ac} measurements show no anomaly within our detection capability for the $Ce_{0.7}Th_{0.3}Cu_{2.2}Si_2$ sample, whereas a distinct round anomaly peaked at 2.7 K is observed for the $x = 0.9$ Th-doped sample. This peak displays no significant frequency dependence over the range from 40 to 5000 Hz.

These results indicate, as a first approximation that is consistent with all the data, that $Ce_{1-x}Th_xCu_{2.2}Si_2$ orders magnetically for $x \geq 0.1$, with the character of the magnetism being antiferromagnetic for $x \leq 0.5$, while the saturation behavior of the M versus H data and the huge $\chi(1.8\text{ K})$ value for $x = 0.9$ indicate ferromagnetic character. The greater localization of the Ce $4f$ electron (as inferred from the increasing magnetic behavior) further explains the slight anomalous increase in the c-axis lattice parameter observed for $x = 0.2$ and 0.5, Table I, and is consistent with the observation[7] based on the L_{III} absorption study that the valence for $CeCu_2Si_2$ is 3.08, decreasing to 3.03 for $Ce_{0.4}Th_{0.6}Cu_2Si_2$.

In order to investigate further our discovery of magnetism in a system where the superconducting T_c has been variously reported to remain nonzero until[7] $x = 0.2$ and to be[8] 0.17 K at $x = 0.12$, we have measured the low-temperature specific heat C and the low-temperature ac susceptibility. The specific-heat data, normalized per Ce mole, versus temperature for $x = 0.0$, 0.1, 0.15, and 0.2 are shown in Fig. 2. A clear anomaly peaked at $T = 2.3$ K is already observed for $x = 0.1$, with $T_{\text{max}} = 2.6$ K for $x = 0.15$ and 4.2 K for $x = 0.2$. [Data for $x = 0.05$ (not shown for clarity) show a slight increase above the pure $CeCu_{2.2}Si_2C$ data below 2 K, but no anomaly down to 1.1 K.] These data imply, based on the published[7,8] superconductivity results, the coexistence of superconductivity and (antiferrolike) magnetic order for $x > 0.05$. In order to further investigate the magnetic character of this transition, the specific heat as a function of field for $x = 0.2$ was measured, Fig. 3. The suppression of the anomaly in size and the shift to lower temperature with H is certainly consistent with some kind of antiferromagnetic order. The entropy associated with the anomaly for $x = 0.1$ (Fig. 2) already implies 0.09 of the entropy (R ln2) associated with the ordering of a spin-$\frac{1}{2}$ system, when extrapolated to $T = 0$; 0.19 of R ln2 is the difference in the entropy between 0 and 7 K between the $x = 0.2$ and $x = 0.0$ samples, normalized per Ce mole.

The question then arises, how do T_{max} and the entropy associated with the transition progress upon further doping, and when does T_c fall to 0? Specific-heat data for $x = 0.25$, 0.30, and 0.40 are shown in Fig. 4, while data for $x = 0.5$ and $x = 0.9$ are shown in Fig. 5. Some variation from a monotonic behavior in T_{max} is apparent, since T_{max} for $x = 0.25$ is only 3.5 K. However, this is

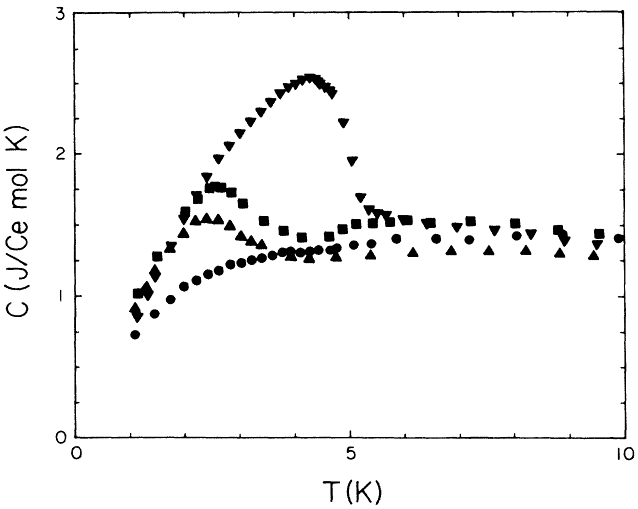

FIG. 2. Specific heat vs temperature for $Ce_{1-x}Th_xCu_{2.2}Si_2$, normalized per Ce mole by subtracting $C_{ThCu_{2.2}Si_2}$ (γ=2.95 mJ/mole-K^2 and Θ_D=350 K) and dividing by $1-x$. (Circles, $x=0$; triangles, $x=0.1$; squares, $x=0.15$; inverted triangles, $x=0.2$.) The progressively more pronounced anomaly with increasing x is thought to be due to antiferromagnetism, as discussed in the text. The entropy of ordering discussed in the text is obtained by integrating $[C(Ce_{1-x}Th_xCu_{2.2}Si_2) - C(CeCu_{2.2}Si_2)]/T$ from $T=0$ up to T_{onset}.

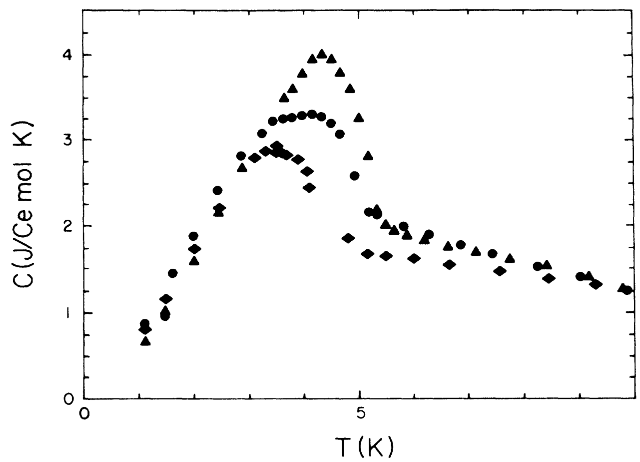

FIG. 4. Specific heat vs temperature data for $Ce_{1-x}Th_xCu_{2.2}Si_2$, normalized as discussed in Fig. 1, with $x=0.25$ (diamonds), $x=0.3$ (triangles), and $x=0.4$ (circles). The concentration of $x=0.3$ has the largest anomaly in the specific heat, normalized per Ce mole.

clearly a broader transition than for $x=0.2$, and $T_{onset}\sim5$ K. In any case, T_{max} does not increase after $x=0.2$, but the transition does broaden. The largest entropy observed is for $x=0.3$, where the entropy associated with the transition is 0.33 of R ln2.

We have measured χ_{ac} for our $x=0.15$, 0.25, and 0.30 samples, which from Figs. 2 and 4 clearly already have substantial magnetic anomalies in their specific heats. The diamagnetic transition for $x=0.15$ is quite broad, with $T_c^{onset}=0.37$ K and a monotonic decrease in χ_{ac} down to our lowest temperature of measurement, 0.05 K, i.e., $T_c^{mid}\sim0.18$ K. For $x=0.25$, $T_c^{onset}=0.27$ K and the transition again extends down to below 0.05 K, i.e., $T_c^{mid}=0.13$ K. Qualitatively, the signal for the $x=0.25$ sample is much weaker than that for $x=0.15$. For $x=0.30$, no diamagnetic response is observed down to 0.05 K.

Thus, as more and more entropy is associated with the antiferromagnetic transition, and as T_N increases from 2.3 K ($x=0.1$) to 4.2 K ($x=0.2$ and 0.3), superconductivity is suppressed in $Ce_{1-x}Th_xCu_{2.2}Si_2$. The region of

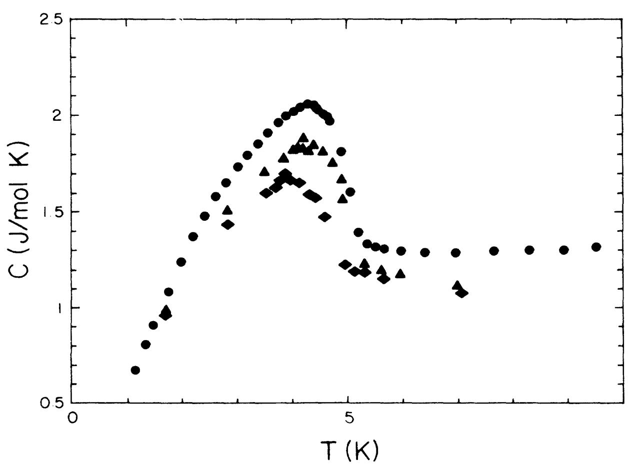

FIG. 3. Unnormalized specific heat (i.e., per formula unit with no subtractions) vs temperature as a function of field (H=0, circles; H=5 T, triangles; H=11 T, diamonds) for $Ce_{0.8}Th_{0.2}Cu_{2.2}Si_2$. The suppression of the transition with increasing field is consistent with some form of antiferromagnetism.

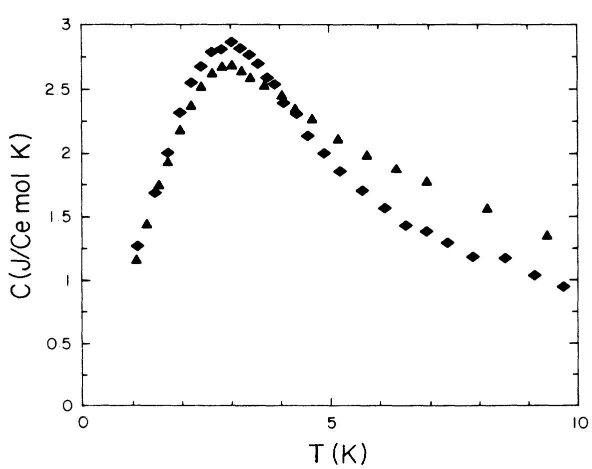

FIG. 5. Specific heat vs temperature of $Ce_{0.5}Th_{0.5}Cu_{2.2}Si_2$ (triangles) and $Ce_{0.1}Th_{0.9}Cu_{2.2}Si_2$ (diamonds), normalized per Ce mole as discussed in Fig. 1. The broadness of the anomalies may indicate sample inhomogeneities.

coexistence of both magnetism and superconductivity is significant, leaving ample opportunity[9] for further measurements at low temperature to investigate what may be an important system for understanding the superconducting pairing mechanism in $CeCu_2Si_2$.

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[9]There is one other report (Ref. 10) of a very small ordered moment (approximately 4% of the moment report here, based on entropy) occurring in $Ce_{0.97}La_{0.03}Cu_{2.2}Si_2$, with $T_c \sim 0.4$ K. If confirmed as intrinsic antiferromagnetism, this would allow an even broader study.

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