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First-Order Superconducting Phase Transition in $CeCoIn_5$

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The superconducting phase transition in heavy fermion $CeCoIn_5$ ($T_c = 2.3$ K in zero field) becomes first order when the magnetic field $H \parallel [001]$ is greater than 4.7 T, and the transition temperature is below $T_0 \approx 0.31T_c$. The change from second order at lower fields is reflected in strong sharpening of both specific heat and thermal expansion anomalies associated with the phase transition, a strong magnetocaloric effect, and a steplike change in the sample volume. This effect is due to Pauli limiting in a type-II superconductor, and was predicted theoretically in the mid-1960s.

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The behavior of superconductors in a magnetic field has primary scientific and technological importance. It underlies such diverse areas as magnetic imaging, energy transmission and storage, ultrasensitive instrumentation and electronics, and many other fields of technology and medicine. At the same time, it reflects a very fundamental property of matter—the behavior of electrons in a magnetic field. BCS theory, presented in 1957 (Ref. [1]), gave a microscopic explanation of a number of phenomena observed during the previous half century of research on superconductivity. The theories put forth in the early 1960s, which addressed the effect of a magnetic field on superconductivity, were the first extensions of BCS that made predictions of new phenomena and provided tests of BCS theory's predictive powers [2–7]. A magnetic field can suppress superconductivity via two effects: orbital pair breaking of superconducting pairs in the superconducting state and Pauli paramagnetism due to electron spins, which lowers the relative energy of the normal state. It was shown that, when the Pauli effect is sufficiently strong relative to the orbital effect, the superconducting phase transition may change from second order (BCS result for zero field) to first order [2–4]. This is due to a competition between two energies basic to the understanding of superconducting and normal states of metals: condensation energy of superconducting pairs and magnetic energy of the normal electron spins due to Pauli paramagnetism. This prediction is very straightforward, and yet eluded confirmation for almost 40 years.

A number of conventional superconductors were proposed as candidates for observation of the first-order superconducting transition in a magnetic field, due to their high orbital critical field H_{c20} (weak orbital pair breaking) and, therefore, relatively strong Pauli limiting effect, in the early and mid-1960s. Experimental search, however, came up with null results, which was attributed to a high spin-orbit scattering rate in all of the compounds investigated [4]. Here we present specific heat, magnetocaloric, thermal expansion, and magnetostriction data for $CeCoIn_5$ that demonstrate that the superconducting phase transition indeed changes from second to first order at a critical point with temperature $T_0 = 0.31T_c$, in very good agreement with a theoretical estimate for $CeCoIn_5$. Recently, a first-order phase transition at low temperature in $CeCoIn_5$ was inferred from the step in thermal conductivity in $CeCoIn_5$ at $H_{c2} \parallel [001]$, which was suggested to be "likely due to an entropy jump" [8]. Our specific heat, thermal expansion, and magnetostriction data offer a direct proof of the first-order phase transition in $CeCoIn_5$ with $H \parallel [001]$.

$CeCoIn_5$ is a recently discovered ambient pressure heavy fermion superconductor [9] with the record high superconducting transition temperature $T_c = 2.3$ K for this class of compounds. A number of thermodynamic and spectroscopic measurements indicate a spin-singlet, even pairing state, with lines of nodes in the superconducting energy gap [10,11]. Recently, Izawa *et al.* [8] reported the fourfold modulation of thermal conductivity of $CeCoIn_5$ in a magnetic field in support of the $d_{x^2-y^2}$ order parameter, similar to high temperature superconductors.

The first-order superconducting phase transition in $CeCoIn_5$ occurs in a magnetic field close to the superconducting critical field $H_{c2} = H_{c2}(T = 0) = 4.95$ T, with the field along the [001] crystallographic direction. The change from the second-order nature of the transition, observed at zero and low magnetic field, to first order at high field occurs at $T_0 \approx 0.72$ K $= 0.31T_c$. We used a variety of techniques to investigate the region of interest of the H-T phase diagram, including measurements of specific heat at constant magnetic field, magnetocaloric effect, thermal expansion, and magnetostriction.

Figure 1 shows specific heat as a function of temperature for several values of a magnetic field in the high field region. The data represented with open symbols were collected with the standard heat pulse technique. When

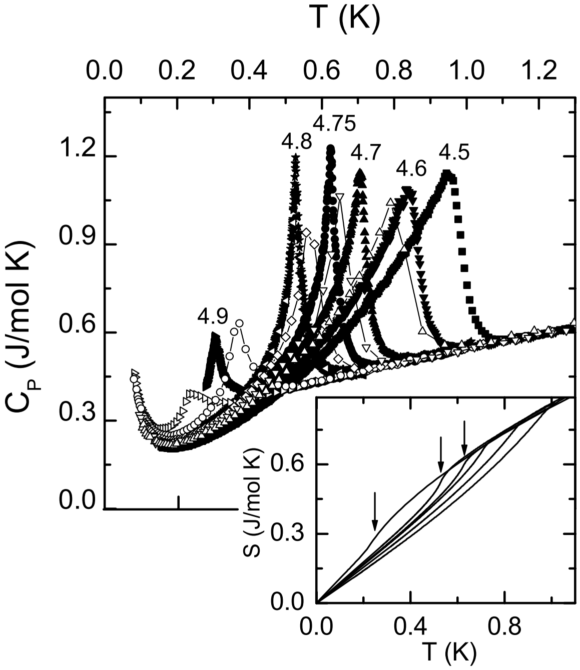

FIG. 1. Specific heat vs temperature of $CeCoIn_5$. Closed symbols—decay method, for indicated fields in Tesla; open symbols—heat pulse method: (△) 4.62 T, (▽) 4.72 T, (◇) 4.77 T, (◁) 4.8 T, (∘) 4.87 T, (▷) 4.925 T. Inset: calculated entropy S; left to right: 4.925, 4.8, 4.75, 4.7, 4.6, and 4.5 T. Arrows indicate steplike features in S at T_c for $H > 4.7$ T.

the phase transition becomes first order, it sharpens substantially. In this regime the temperature decay method, where specific heat is extracted directly from the temperature trace of the system coming to equilibrium, was particularly useful to resolve the specific heat anomaly (solid symbols). The two data sets for $H = 4.8$ T, obtained with the temperature decaying down (stars) and up (dots), as well as the data collected with the heat pulse method (left open triangles), overlap each other (it is difficult to tell stars and dots data apart), indicating good internal thermal equilibrium of the cell.

The specific heat anomaly for the second-order phase transition (e.g., 4.5 T data) displays a characteristic step at T_c (predicted to be $\Delta C/C = 1.43$ in the BCS theory), and then gradually drops below T_c. In $CeCoIn_5$, $\Delta C/C$ drops steadily from the very high value of 4.5 at zero field [9] to ≈ 1.1 at $H = 4.5$ T. The temperature width of the anomaly at half maximum ΔT_{HM} scaled by T_c for 4.5 T is $w(4.5\ \mathrm{T}) = T_{HM}/T_c|_{4.5\ \mathrm{T}} \approx 25\%$.

As we move into the regime of the first-order phase transition, the maximum of the specific heat anomaly rises, e.g., $\Delta C/C(4.8\ \mathrm{T})=1.9$, and it becomes substantially narrower, $w(4.8\ \mathrm{T})=6\%$. It should be kept in mind that this sharpening of the anomaly takes place in the region of the phase diagram where the boundary between the normal and superconducting states is crossed at more of a glancing angle during the temperature sweep as $H \rightarrow H_{c2}$. As a result, the anomaly should broaden if it remains second order, in contrast to the evolution of the data.

The inset of Fig. 1 shows the entropy S of $CeCoIn_5$ as a function of temperature for various values of the magnetic field [12]. There is a clear difference in the temperature evolution of the entropy for the field below and above $H_0 \approx 4.7$ T. Below this field ($T_c > 0.7$ K), the transition manifests itself by a kink in S. For fields above 4.7 T, there is a steplike feature in S at T_c, as expected for a first-order phase transition.

To elucidate the low temperature behavior and determine the temperature T_0 of the critical point (and corresponding field H_0) at which the superconducting transition changes from second to first order, with higher precision, we studied the phase diagram of $CeCoIn_5$ by sweeping magnetic field. This was done under close to adiabatic (constant entropy) conditions, regulating the bath temperature to be that of the sample, which was weakly thermally coupled to the bath. The behavior of the system is then governed by the magnetocaloric effect.

Figure 2 shows several sweeps of magnetic field up and down, starting at different temperatures. Below H_0, there is a sharp change in temperature as the magnetic field crosses the phase boundary. Temperature drops when the phase boundary is crossed as the field is swept up, since the system goes from the low entropy to the high entropy phase, and the temperature has to decrease to keep the entropy constant [13]. The temperature swing is reversed (temperature rises) on the down field sweep. The change in the temperature of the sample after crossing the first-order phase boundary ΔT_{pb} is a measure of the latent heat associated with transition. T_c corresponds to the maximum of the derivative $\frac{dT}{dH}$, and ΔT_{pb} is determined by extrapolations of the fits to the H vs T curves outside of the transition region to T_c. An example of such a procedure is displayed in Fig. 2(a) for the data with $T_c = 0.41$ K, where the horizontal dotted line segment represents ΔT_{pb}. The difference ΔT_{pb} should equal zero for a second-order phase transition. This is indeed observed, within experimental scatter, for the data with $T_c > T_0$, as illustrated in Fig. 2(b) for the data with $T_c = 0.74$ K. Figure 2(b) displays the measured ΔT_{pb} as a function of T_c. The crossover from the first-order transition with nonzero ΔT_{pb} to the second-order transition with $\Delta T_{pb} = 0$ occurs at a sharply defined critical temperature $T_0 = 0.72 \pm 0.05$ K, which is indicated by the arrow.

We also observed the change from second- to first-order nature of the superconducting transition of $CeCoIn_5$ via thermal expansion measurements, depicted in Fig. 3. The coefficient of thermal expansion, $\alpha(T) = l^{-1}dl/dT$, was determined down to 50 mK by utilizing an ultrahigh-resolution capacitive dilatometer. Thermal expansion along the crystallographic [001] direction was measured for two different platelike single crystals in magnetic fields up to 8 T applied along [001]. For one of

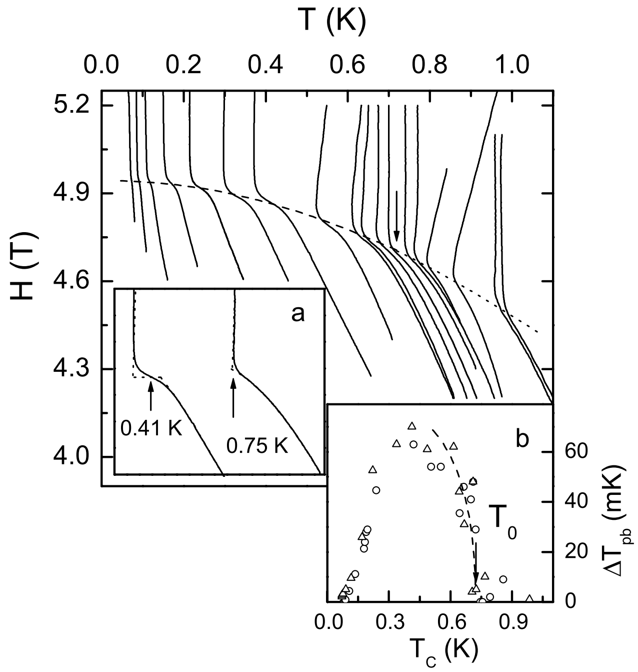

FIG. 2. H vs T during quasiadiabatic magnetic field sweeps. Dotted (dashed) line is a phase boundary in second (first) order transition region. Arrow indicates T_0. Inset (a): field sweep with $T_c = 0.41$ K $< T_0$ and $T_c = 0.74$ K $< T_0$. Dotted lines are cubic fits to the data as well as ΔT_{pb}. Inset (b): change in temperature ΔT_{pb} at T_c vs T_c. (○) field swept up; (△) field swept down. Arrow indicates T_0. Dashed line—guide to the eye to ΔT_{pb} for T_c just below T_0.

the crystals, isothermal magnetostriction measurements were performed as well at $T = 0.2$ K and at $T = 1.5$ K.

In the low field range $H \leq 4$ T, a steplike anomaly in α, indicative of a second-order transition, is observed, which shifts towards lower temperatures upon increasing H. With increasing fields (see Fig. 3) the signature in α

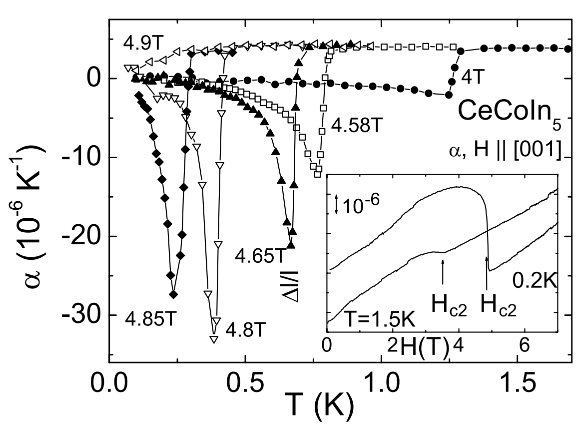

FIG. 3. Thermal expansion coefficient α vs T of $CeCoIn_5$ for fields $4\,T \leq H \leq 4.9\,T$ applied along [001]. The inset shows the relative length change $\Delta l/l$ vs H at $T = 1.5$ K and $T = 0.2$ K. The arrows indicate anomalies at H_{c2}.

sharpens anomalously and becomes peaklike, with extremely high absolute values of α. This again indicates a change of the nature of the superconducting transition from second order to first order for magnetic field on the order of 4.6 T. A first-order transition should result in a jump in the sample length, corresponding to a divergence of α. Thus, the peaklike signature in α indicates a broadened first-order transition.

We also measured the isothermal magnetostriction of $CeCoIn_5$, which we show in the inset of Fig. 3. Whereas at $T = 1.5$ K the kink in $\Delta l/l$ at $H = 3.55$ T indicates a second-order phase transition, the jump in $\Delta l/l$, observed for $T = 0.2$ K at $H = 4.86$ T, provides clear evidence for the first-order nature of the transition.

In addition to steps in magnetostriction and thermal conductivity [8], magnetization data also were shown recently to have a step at T_c [14]. We can also estimate the width of the fluctuation region for the second-order superconducting phase transition in $CeCoIn_5$ via the Ginzburg criteria to be $\Delta T/T_c = [(2\pi\xi_0)^{-3}k_B/\Delta C]^2 \approx 10^{-9}$, much smaller than the width of the measured specific heat anomaly $\Delta T/T_c \approx 0.1$ at 4.8 T. The combined evidence from all the available data and our estimate of $\Delta T/T_c$ proves conclusively that the superconducting transition in $CeCoIn_5$ becomes first order below $T_0 = 0.31T_c$.

How do our experimental results compare with theoretical predictions? Pauli paramagnetism leads to an upper limit for the magnetic field $H_p = \Delta_0/\sqrt{2}\mu_B$, called the Clogston paramagnetic limit [15], which the superconductor can support. Here, Δ_0 is the superconducting energy gap, and μ_B is the Bohr magneton. Orbital effects of magnetic field also limit H_{c2}. The relative strength of the orbital pair breaking by a magnetic field and Pauli limiting can be characterized by the parameter $\alpha = \sqrt{2}H_{c20}/H_p$, introduced by Maki [4], where H_{c20} is an orbital critical field in the absence of the Pauli limiting. Maki's calculations [4] show that for $\alpha \geq 1$ the second-order phase transition between the normal state and Abrikosov vortex state becomes unstable and changes to first order at a higher field and, if the orbital effect is neglected ($\alpha = \infty$), this change takes place at the reduced temperature $t_0 = T_0/T_c = 0.55$. [3]

In the early 1960s, an alternative theory, also based on Zeeman energy of electron spins in magnetic field, suggested that a new spatially inhomogeneous superconducting state, now called the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state, may be stabilized close to the critical field H_{c2} at which superconductivity is suppressed to zero [5,6]. The FFLO state forms a wedge between the normal state and the homogeneous Abrikosov vortex state. The tricritical point where the phase boundaries between the three states meet denotes the point of instability of second-order phase transition at low field to the appearance of the FFLO wedge above the critical field within the FFLO scenario. Gruenberg and

Gunther [7] (GG) generalized the FFLO theory and included the orbital effect of magnetic field. The authors conclude that, when the orbital pairbreaking effect is sufficiently small ($\alpha \geq 1.81$), the FFLO state can exist in a type-II superconductor. They also calculated the dependence of the reduced temperature t_0 of a tricritical point on the Maki parameter α. For $\alpha = \infty$ (orbital pair breaking is ignored), $t_0 = 0.55$, same as in Maki's calculations [3].

We now make an assumption that we can use the result of the GG calculation of the instability point of the second-order phase transition for arbitrary α within the FFLO picture, to represent the instability of the second-order phase transition within the Maki's scenario for an arbitrary α, since both theories give the same result in the limit $\alpha = \infty$, where calculations for Maki's scenario exist. To estimate α for $CeCoIn_5$, we use $\Delta_0 = 2.14 k_B T_c$ for a d-wave superconductor and obtain $H_p = 2.25 T_c$ T/K = 5.2 T. The orbital critical field is $H_{c20} = 0.7 H'_{c2} T_c =$ 13.2 T [10]. We therefore obtain $\alpha = 3.6$, corresponding to $t_0 = 0.35$ from Fig. 1, curve b, of Ref. [7]. Alternatively, it is possible to find H_p from curve a of the same figure, which relates H_{c2}/H_p to $\alpha = \sqrt{2} H_{c20}/H_p$. We find $H_p = 5.8$ T, $\alpha = 3.2$, and $t_0 = 0.33$. Both values of t_0 are very close to the value of $t_0 = 0.31$ observed experimentally.

The FFLO state has also attracted great attention, but its unambiguous observation has not been made. In the past decade, the FFLO state was suggested to exist in heavy fermion UPd_2Al_3 (Ref. [16]) and $CeRu_2$ (Ref. [17]), based on thermal expansion and magnetization data, respectively. Subsequent research identified the magnetization feature in $CeRu_2$ as due to the flux motion [18], and the region of the suggested FFLO state in UPd_2Al_3 was shown to be inconsistent with the theoretical model [19]. Most notably, no indication of the FFLO state was *ever* observed via specific heat measurement, which is the primary tool for identification of the thermodynamic details of the phase transition. $CeCoIn_5$ has all the prerequisite properties for the observation of the FFLO state, including that the superconductor must be in the clean limit, since its quasiparticle mean-free path $l_{tr} \approx 14\xi_0$ at T_c [10]. Within the superconducting state, thermal conductivity divided by temperature grows by an order of magnitude as temperature is lowered to $T = 0.2T_c$, and even at 30 mK (1% of T_c) $CeCoIn_5$ is outside of the impurity dominated regime [10]. The agreement between theoretical prediction and experimental observation of the critical point at t_0 shows that the pertinent physics of electronic spin Zeeman energy and Pauli effect drives the behavior of the system. However, within the FFLO picture two transitions are expected: from normal state into FFLO state, and from FFLO state into a usual Abrikosov vortex state. We observe only one phase transition in $CeCoIn_5$ with field $H \parallel [001]$. Therefore, we do not see evidence for a FFLO state with field in this orientation.

In summary, the superconducting transition in $CeCoIn_5$ with field $H \parallel [001]$ becomes first order below $T_0 = 0.31T_c$. This is consistent with long-standing theoretical predictions which take into account both orbital and spin interactions of superconducting electrons with magnetic field. We do not observe the inhomogeneous superconducting FFLO state proposed theoretically almost 40 years ago [5–7]. Instead, the first-order superconducting transition in $CeCoIn_5$ takes place from a normal metal into a mixed vortex state, in accord with the scenario suggested by Maki [3,4] almost 40 years ago [3,4].

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