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Unconventional heavy-fermion superconductor $CeCoIn_5$: dc magnetization study at temperatures down to 50 mK

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dc magnetization measurements on $CeCoIn_5$ reveal a first-order phase transition at H_{c2} for both $H\|a$ and c axes in the isothermal magnetization $M(H)$ below 0.7 K, indicating a strong Pauli paramagnetic suppression in the even-parity pairing. $M(T)$ in the normal state above H_{c2} exhibits non-Fermi-liquid behavior down to 150 mK, implying the existence of antiferromagnetic fluctuations behind the unconventional superconductivity. We observed an unusual peak effect for $H\|c$ in fields 5–30 kOe below 150 mK($=0.06T_c$), whose anomalous temperature dependence cannot be simply explained by ordinary mechanisms.

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Since in 1979,[1] HF superconductivity has been attracting interest in the field of strongly correlated electron systems. Recent experimental and theoretical progress indicates that most of the HF superconductors are likely to be of an unconventional type. Until recently, to our best knowledge, $CeCu_2Si_2$ was the only Ce-based HF superconductor at ambient pressure. The superconductivity in $CeCu_2Si_2$, however, is rather difficult to understand because of the complicated magnetic phase diagram.[2]

Quite recently, two tetragonal Ce-based HF compounds have been discovered by Petrovic *et al.* to become superconducting at ambient pressure: $CeXIn_5$ [$X=$Ir (Ref. 3) and Co (Ref. 4)]. To our best knowledge, $CeCoIn_5$ has the highest $T_c(=2.3$ K) among the HF superconductors known at present. The specific heat,[4] thermal conductivity,[6] and NMR relaxation rate[8] of $CeCoIn_5$ show power-law temperature dependencies below T_c, suggesting an unconventional superconductivity with anisotropic energy gap. Very recently, the NMR Knight-shift measurement[7,8] has revealed even-parity pairing in the superconducting state, and the angle-dependent thermal-conductivity measurement[9] has identified that the gap symmetry is $k_x^2-k_y^2$, pointing to the fact that the pairing interaction is mediated by magnetic fluctuations. An interesting observation with respect to this point is the non-Fermi-liquid (NFL) behavior in the specific heat divided by temperature C/T, showing a remarkable upturn on cooling when the superconductivity is suppressed by magnetic field.[4,5] To our best knowledge the origin of the NFL behavior has not been clarified yet.

One of the features of the HF superconductors is that the orbital limiting field is relatively high despite low T_c, because of the small Fermi velocity of the carriers. In addition, the HF superconductors possess quite large normal-state paramagnetic susceptibility at sufficiently low temperature, reflecting the high density of states. These facts lead to an interesting situation in which the paramagnetic energy near H_{c2} becomes a significant fraction of the superconducting condensation energy.[10,11] It was theoretically pointed out that a second-order transition at H_{c2} changes into a first-order one below ~ 0.56 T_c for the singlet pairing, provided that the normal-state spin susceptibility is large enough.[12,13] Subsequent theoretical studies predicted that in the case of a clean limit ($l \gg \xi_0$) a first-order transition from the mixed state to the Fulde-Ferrell-Ovchinnikov-Larkin (FFLO) state occurs[14–17] before the system turns into the normal state. However, to our best knowledge no system has been found to show a first-order transition at H_{c2}, and experimental evidence for the existence of the FFLO state is still controversial. Ce-based HF superconductors would provide a good opportunity to study these issues since Kramers degeneracy of the f-electron configuration $(4f^1)$ ensures a substantial spin contribution in the susceptibility. In fact, very recently it has been claimed as a result of torque[18] and thermal-conductivity[9] measurements that a first-order phase transition (FOPT) occurs at H_{c2} in $CeCoIn_5$, although the phase diagram is not known well.

We have performed high-resolution dc magnetization measurements on high-quality single crystals of $CeCoIn_5$ at temperatures down to 50 mK and in fields up to 125 kOe, in order to examine the superconducting phase diagram in detail. A clear FOPT is observed at H_{c2} for both a and c directions, with features in the superconducting phase diagrams and magnetic properties of this unconventional superconductor.

Two high-quality single crystals of $CeCoIn_5$, used in the present experiment, were grown by an In self-flux method as described in Ref. 20. The crystal has a tetragonal $HoCoGa_5$-type structure with $a=4.612$ Å and $c=7.549$ Å. The weight of the samples is 6.9 mg (sample #1) and 18.7 mg (sample #2). Both samples showed the same T_c of 2.3 K. Low-field magnetization data as well as x-ray diffraction indicated an inclusion of a small amount of a pure cobalt phase

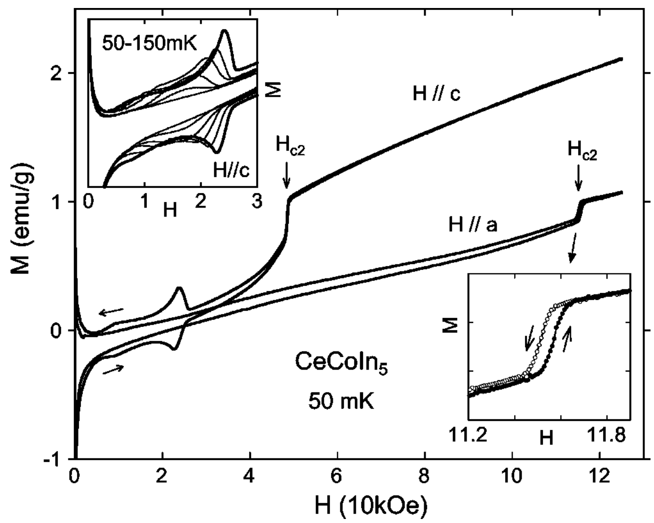

FIG. 1. Isothermal dc magnetization curves $M(H)$ of a single crystal of $CeCoIn_5$ at base temperature of 50 mK in fields applied along the tetragonal c and a axes with the enlarged plot around the upper critical field (lower inset). The upper inset shows the low-field part around the peak effect at several temperatures below 150 mK. The temperature for each curve is 50, 70, 90, 110, 120, and 150 mK in order from the outside.

in sample 2, whereas no foreign phase was found in sample 1 within an experimental sensitivity. Since sample 1 is considered to be of higher quality, we mainly present the results for sample 1 in this paper, although the magnetization results were qualitatively the same for the two samples except for the low-field part. From the de Haas–van Alphen experiment near H_{c2},[23,24] the electron mean free path l of the sample was estimated to be in excess of 2000 Å, well in the clean limit $l \gg \xi_{a,c}(<100$ Å).[21] The dc magnetization measurements in the temperature range 50 mK–2 K have been carried out by a capacitive Faraday magnetometer.[22] In all measurements, a field gradient of 800 Oe/cm was applied to the sample in addition to uniform magnetic fields. By detecting only the magnetic force proportional to the field gradient, we could obtain the true magnetization of the sample. Due to a small dimension of the sample, field distribution inside the sample was less than 100 Oe. A superconducting quantum interference device magnetometer (MPMS, Quantum Design) was also utilized to measure the dc magnetization in temperatures above 2 K and in fields below 7 T.

Figure 1 shows the isothermal magnetization curves of $CeCoIn_5$ at the base temperature of 50 mK in fields up to 125 kOe applied along the a and c axes. These data were taken by slowly scanning the field after zero-field cooling the sample from a temperature well above T_c. The irreversibility of the magnetization due to flux pinning is very small, demonstrating the high quality of our sample. The magnetization curves show a clear discontinuous jump at 49 kOe for $H\|c$ and at 116 kOe for $H\|a$. Since the irreversibility in the $M(H)$ curve completely disappears after the jump and no further anomaly is found at higher fields, we may regard the position of the jump as the upper critical field H_{c2}. The obtained H_{c2} coincides well with the previous one determined by ac susceptibility and specific-heat measurements.[4,23–25] A small but distinct hysteresis is found in the transition for both directions; the width of the hysteresis is 150 Oe for $H\|c$ and 750 Oe for $H\|a$ (the lower inset). Accordingly, the observed transition at H_{c2} is considered to be of first order at this temperature. The superconducting condensation energy, $H_c^2/8\pi$, can be estimated by integrating the magnetization curve: $M-\chi_n H$, where χ_n is the magnetic susceptibility for the normal state. We obtain $H_c^2/8\pi \approx 1.3\times 10^5 \mathrm{erg/cm^3}$, which is extraordinarily large compared to the other HF superconductors.

Interestingly, a remarkable peak effect is observed for $H\|c$; a sharp hysteresis peak can be seen at 2.3 T well below H_{c2}. In addition, a small but appreciable peak is found at around 0.9 T as well. Surprisingly, temperature dependence of the peak effect is extremely strong as shown in the inset of Fig. 1; as the temperature increases slightly, the higher-field peak rapidly shifts to the lower-field side, whereas the lower peak moves to the higher-field side. It seems that both peaks merge at ~ 1.6 T and at 150 mK, and disappear at higher T. It should be noted that the similar peak effect, though less pronounced, was also observed in sample 2, implying that the observed peak effect is an intrinsic phenomenon.[19] We will come back to this point later.

In order to show the temperature dependence of the transition at H_{c2}, we display the magnetization curves $M(H)$ at several selected temperatures between 0.45 K and 1.8 K in Fig. 2. Arrows indicate the position of H_{c2} defined by the anomaly in the $M(H)$ curves, which decreases monotonously with increasing temperature. In the data for $H\|a$ (the upper part of Fig. 2), the discontinuity of the magnetization is still discernible in the data at 0.61 K, whereas at 0.84 K no clear feature of a first-order transition is seen at H_{c2}. Therefore, a critical point is likely to exist at $T_{\mathrm{cr}}=0.7\pm0.1$ K. The $M(H)$ results for $H\|c$ (the lower part of Fig. 2) shows similar temperature variation, with $T_{\mathrm{cr}}=0.7\pm0.1$ K.

Temperature dependencies of the dc magnetization $M(T)$ at several fixed fields are shown in Fig. 3. The data below 2.5 K were collected by warming the sample gradually after zero-field cooling (ZFC), and subsequently cooling under the field (FC). The difference between the ZFC and FC data is rather small. The magnetization significantly decreases for both directions when the superconducting state sets in. Such behavior can be seen even near $H_{c2}(0)$. The observation is consistent with the appearance of the FOPT at H_{c2} in the $M(H)$ curve.

We next move on to the $M(T)$ data in the normal state. As can be seen in Fig. 3, the magnetization is anisotropic in the whole temperature range. The magnetization behavior above 100 K is well reproduced by assuming a localized $4f$ electron $(4f^1)$ under the crystal field (CF) with an antiferromagnetic molecular field.[26] Temperature dependence of the magnetization, especially for $H\|c$, turns to saturate below 50 K, suggesting a Kondo screening, as usually observed in the HF compounds. Surprisingly, the magnetization in $CeCoIn_5$ starts to increase again upon cooling below 20 K,[4] contrary to the ordinary HF's which remain in a Fermi-liquid state with T-independent susceptibility as $T\rightarrow 0$. Whether this unusual increase of $M(T)$ is intrinsic or not would be a matter

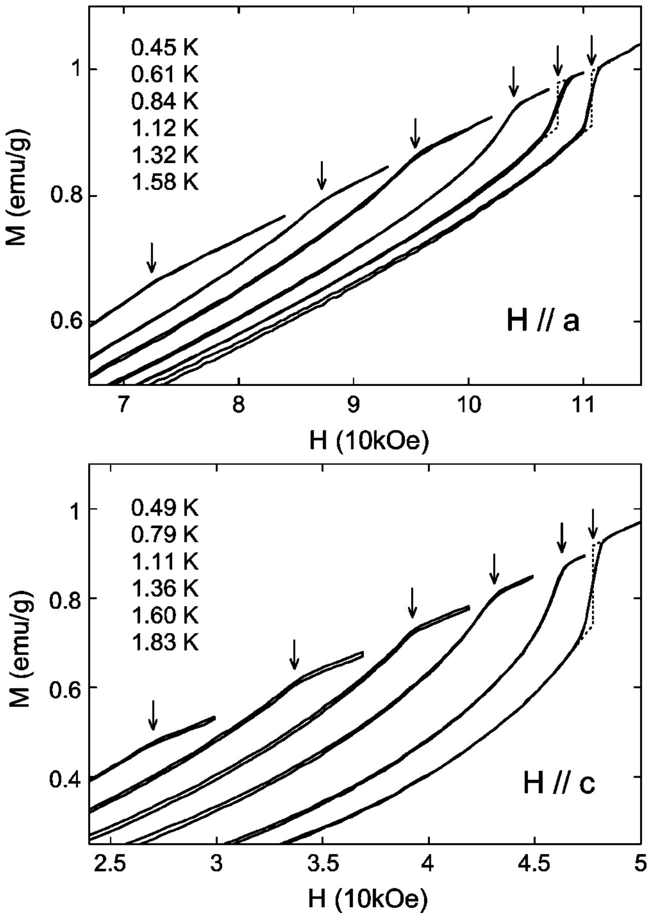

FIG. 2. Isothermal magnetization curve $M(H)$ at several selected temperatures above 0.45 K. The upper part is the results for $H\|a$, and the lower one for $H\|c$. Arrows indicate the position of H_{c2}. The data points were taken up to 125 kOe, not all of which are shown for clarity.

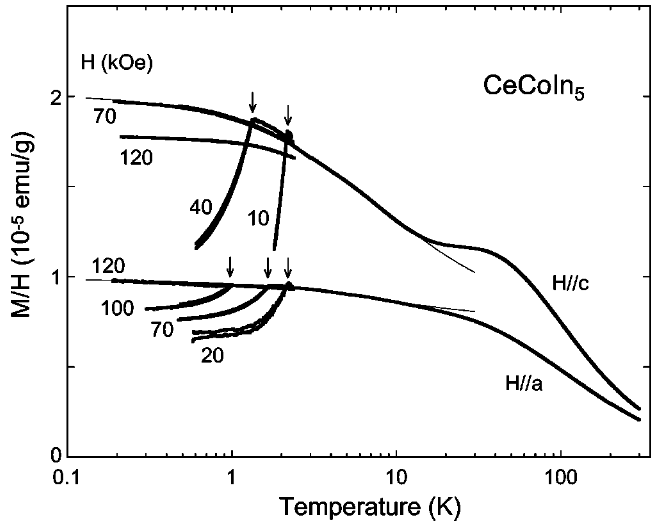

FIG. 3. Thermal variation of the magnetization $M(T)$ for both a and c directions. Both the zero-field cooled and field-cooled data is plotted. The data above 2 K was obtained at the field of 10 kOe. Arrows indicate the position of T_c. Thin solid line is a fit to the function $\chi=\chi_0+C/(T+a_0)$, with $\chi_0=7.6\times10^{-6}$, $C=2\times10^{-5}$, and $a_0=8$ for $H\|a$, and $\chi_0=7.6\times10^{-6}$, $C=1\times10^{-4}$, and $a_0=8$ for $H\|c$.

of interest. We found that $M(T)$ obtained in the present experiment shows a continuous increase at relatively high field ($\geqslant 70$ kOe) and sufficiently low temperatures down to 0.15 K, indicating that the upturn in $M(T)$ is an intrinsic effect, and is not due to magnetic impurities. In fact, our data of M/H can be well expressed by the form $\chi=\chi_0+C/(T^{\alpha}+a_0),(\alpha=0.8\sim1)$ for nearly two decades in temperature, as shown by thin solid lines for the case $\alpha=1$ in Fig. 3. Neither the CF nor the Kondo effects can explain such behavior. It should be noticed that similar Curie-Weiss-like NFL behavior of $M(T)$ has also been pointed out in $CeCu_{6-x}Au_x$ near the vicinity of a quantum critical point ($x=0.1$) of the antiferromagnetic long-range order.[27,28] Our observation therefore suggests that $CeCoIn_5$ is very close to the antiferromagnetic criticality. In fact, by further increasing magnetic field, the NFL behavior becomes weaker and the magnetization tends to recover Fermi-liquid behavior. Further indication of the critical behavior has also been found in a logarithmic increase of the normal state C/T in magnetic field and a T-linear dependence of the resistivity $\rho(T)$.[4,5] Recent high-pressure experiments also show that $CeCoIn_5$ is in the proximity of antiferromagnetism.[29] These facts indicate the importance of antiferromagnetic fluctuations in $CeCoIn_5$, which are presumably responsible for the occurrence of the unconventional superconductivity.

Figure 4 shows the superconducting phase diagrams of $CeCoIn_5$ determined from the present results. The isothermal $M(H)$ curves revealed that the transition at H_{c2} becomes first order below $T_{\rm cr}\sim0.7$ K for both directions. From the $\mathrm{d}H_{c2}/\mathrm{d}T|_{H\sim0}$ value, one can roughly estimate the orbital limiting field H_{c2}^0 as 350 kOe (150 kOe) for $H\|a$ (c), respectively. Those values are in good agreement with the ones determined by the recent specific heat measurements.[25] For both directions, therefore, the actual H_{c2} is suppressed at low T presumably due to the spin paramagnetic effect by nearly a

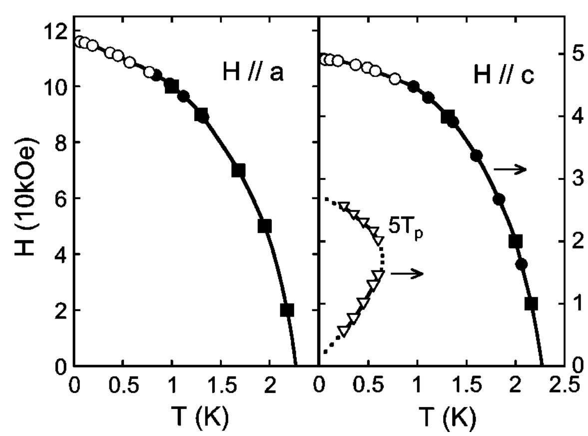

FIG. 4. H-T phase diagram of $CeCoIn_5$. Circles and squares denote H_{c2} determined by the $M(H)$ and the $M(T)$ data, respectively. Open circles indicate the first-order transition. Inverse triangles indicate the position of the hysteresis peaks observed in the $M(H)$ data at various temperatures (denoted as T_p) below 150 mK. For clarity, T_p is magnified by a factor of 5.

factor of 0.3. Interestingly, by comparing the two plots in Fig. 4, one can see that the H_{c2} curves for both directions can be scaled to each other, except for a slight enhancement of H_{c2} for $H\|a$ below T_{cr}. Combining with the anisotropy in H^0_{c2}, this observation implies that the spin part of the susceptibility for $H\|c$ is larger than that for $H\|a$. Assuming $H_{c2} \approx H_P = H_c/\sqrt{4\pi\chi_s}$, we roughly estimate the spin part of the susceptibility χ_s to be 1.3×10^{-5}emu/g for $H\|c$ and 2.4×10^{-6}emu/g for $H\|a$. The large spin susceptibility for $H\|c$ is consistent with the observation that the magnetization jump for $H\|c$ at $H_{c2}(T)$ is larger than that for $H\|a$. The observed $T_{cr}(\sim0.3\ T_c)$ is lower than what is predicted by the theory of the strong Pauli limit $(0.56\ T_c)$,[12,13,30] possibly because the orbital current effect is not negligible.[31]

In the case of a strong Pauli paramagnetic effect and the system is very clean, it has been predicted by a number of theoretical works that the FFLO state, in which the gap amplitude is spatially modulated, appears between the mixed state and the normal state on cooling below $\sim0.56T_c$.[14–17] We examined the magnetization data very carefully, however, we could not find any phase boundary branching from the $H_{c2}(T)$ curves; it seems that the FFLO state is absent in $CeCoIn_5$ despite the strong paramagnetic effect. Although the sample is considered to be clean ($l\sim2000$ Å$\gg\xi_{a,c}$), determining whether the FFLO state survives the residual weak scattering or not would be an interesting issue. Further experimental and theoretical studies are needed to resolve this point.

Finally, we briefly discuss the peak effect for $H\|c$. In type-II superconductors, a peak effect is often observed just below H_{c2}. It mostly originates from a synchronization effect in which softening of the shear modulus of the vortex lattice as H approaches H_{c2} enhances the pinning efficiency; its temperature dependence of the peak position approximately follows the $H_{c2}(T)$ curve, and is very weak at low T. Other mechanisms for the peak effect also give a weak temperature variation at low T where the thermal variation of the superconducting gap is small. On the contrary, temperature dependence of the peak effect observed for $H\|c$ is extremely strong; it disappears at $T\sim0.06\ T_c$ as shown in Fig. 4. Evidently, the peak effect in $CeCoIn_5$ is of an unconventional type, and requires an explanation. The anomalous temperature dependence suggests a phase transition in the superconducting state, although a possibility of certain anomalous vortex dynamics effects should not be excluded.

In conclusion, the present magnetization data clearly reveals a FOPT at H_{c2} below $T_{cr}\sim0.3\ T_c$. While no other phase boundary seems to branch off from T_{cr}, the anomalous peak effect found at very low temperatures $T\leqslant0.06\ T_c$ suggests an ordered phase in the superconducting state. The NFL behavior observed at fields above H_{c2} indicates the importance of magnetic fluctuations behind the unconventional superconductivity.

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