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Normal and Superconducting State Properties of Rare-earth Intermetallic Compounds; $CeRu_2$, $CeCo_2$, $Yb_3Rh_4Sn_{13}$

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We have measured the electrical resistivity, Hall effect, magnetization and specific heat to investigate the normal and mixed state properties of $CeRu_2$, $CeCo_2$ and $Yb_3Rh_4Sn_{13}$. All the compounds exhibit a so-called peak effect in the DC magnetization or the AC susceptibility, which has been argued in relation to the inhomogeneous superconducting phase proposed by Fulde-Ferrell and Larkin-Ovchinnikov. We observed a related anomaly also in the transport properties evidencing the stronger pinning force. For $CeCo_2$, we found a clear deviation from the ordinary BCS prediction in the specific heat.

KEYWORDS: peak effect, superconductivity, transport property, specific heat

§1. Introduction

The anomalous peak effect, observed in the magnetization near the upper critical field H_{C2} for several U and Ce compounds such as UPd_2Al_3, UPt_3 and $CeRu_2$,[1-7] has recently attracted much attention in relation to the inhomogeneous superconducting phase proposed by Fulde-Ferrell and Larkin-Ovchinnikov (FFLO).[8-10]

We have recently found a similar peak effect also in $CeCo_2$[11] and $Yb_3Rh_4Sn_{13}$[12], whose characteristics resemble those in $CeRu_2$. $CeCo_2$ has a largely enhanced Pauli paramagnetic susceptibility (= 5.3 to 8.0×10^{-5} emu/cm^3 depending on how to estimate the impurity contribution) compared to the ordinary metals and to $CeRu_2$ (=2.5×10^{-5} emu/cm^3), though it is slightly suppressed compared to YCo_2 or $LuCo_2$ which is known to be a typical exchange enhanced paramagnet.[13] For $CeCo_2$, the valence change of Ce from +3 is thought to be responsible for the suppression of the magnetic susceptibility; the density of states decreases according to the shift of the Fermi level relative to the Co d-band.[14] The experimental value of the magnetic susceptibility is still largely enhanced compared to that estimated from the specific heat coefficient γ ;i.e., the Wilson ratio is approximately four. In contrast, the enhanced magnetic susceptibility in $CeRu_2$ has been thought to be directly related with the Ce valence fluctuation. In either case, the large spin susceptibility leads to the lower paramagnetic limiting field and the weaker pinning force state.[15,16]

$Yb_3Rh_4Sn_{13}$ is one of the rare examples of Yb compounds exhibiting superconductivity. The overall behavior of the temperature dependent magnetic susceptibility suggests the Yb valence to be close to +2. The magnetic susceptibility shows a sharp increase at low temperatures, however, the temperature dependence can not be simply explained by the Curie-like contribution from some impurities in the sample. Even if we assume the susceptibility at low temperature (~5×10^{-6}emu/cm^3) to be intrinsic, it is less than 1/5 of that in $CeRu_2$. Interestingly, all these three compounds exhibit a peak effect with a striking resemblance. It is one of the purpose of this paper to compare the superconducting and normal state properties of these compounds.

For comparison with the theories,[8-10,15,16] a key parameter is the existence range of the peak effect in the superconducting *H-T* phase diagram. Most of the experimental investigations on the peak effect so far have been restricted to the DC magnetization, AC susceptibility and elastic properties. We show that transport measurements can be used to accurately evaluate the existence range of the peak effect. We have reported only a brief result on the electrical resistivity, Hall effect and transverse even voltage in the flux flow state in $CeRu_2$.[17]

We also show several evidences of a deviation from the conventional BCS predictions in the superconducting state of $CeCo_2$.[11,18]

§ 2. Experiment

Single crystals of $CeRu_2$ and $CeCo_2$ were grown by an induction zone melting method in a vacuum better than 10^{-8} Torr. The raw materials were 99.99% pure Ce, Ru and Co. The starting composition was selected as $CeTr_{1.7}$ (Tr = Ru, Co) after consideration of the alloy phase diagram. The sweep speed for zone melting was 1 mm/hr. The obtained ingots, about 10 mm in diameter and 20 mm in length, have several large grains with C15-Laves phase structure, from which single crystal samples were carefully spark-cut. $Yb_3Rh_4Sn_{13}$ single

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crystals have been fabricated by the tin-flux method as originally reported by Remeika et al.[19] The purity of the starting elements is 99.9% for Yb, 99.99% for Rh and 99.999% for Sn. The obtained single crystals have a $Pr_3Rh_4Sn_{13}$ structure[19] (type I cubic structure with a lattice constant of 9.681Å).

The electrical resistivity and Hall resistivity were measured by the conventional DC four-probe method using Keithley 182 nanovoltmeters. The specific heat was measured by means of a quasi-adiabatic method down to 0.1 K using a dilution refrigerator. The magnetization and the magnetic susceptibility were measured by a Quantum Design SQUID magnetometer in fields of up to 55kOe. The AC-susceptibility was measured up to 80kOe and down to 0.24 K using a dilution refrigerator.

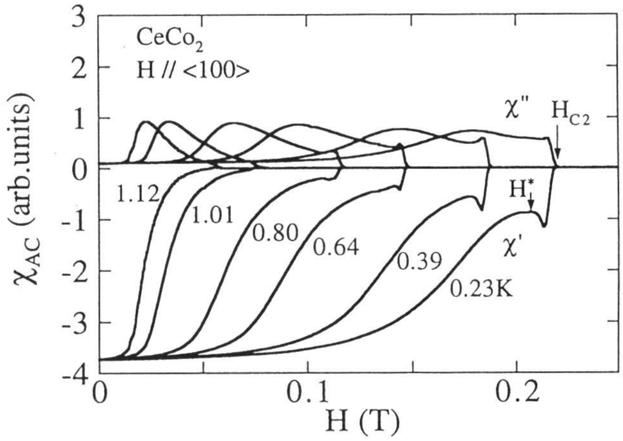

Fig. 2. Field dependence of the AC magnetic susceptibility for $CeCo_2$.

§ 3. Results and discussion

Figure 1 shows examples of the field dependences of the magnetization for $CeRu_2$ and $Yb_3Rh_4Sn_{13}$. There clearly observed a peak effect below H_{C2} for both compounds, and a close similarity between the hysteresis curves for the two compounds is apparent. Above the lower critical field (H_{C1}), the magnetization first increases with increasing field up to a field H* where it drops sharply and shows a minimum (a maximum for decreasing field) below the upper critical field H_{C2} at lower temperatures. In this paper, H_{C2} is defined as the field where the magnetization starts to deviate from the linear dependence in the normal state. Below H^*, there is a finite field range of reversible magnetization reflecting the small pinning force.

For $CeCo_2$, the AC susceptibility measurements have been made instead of the DC magnetization as shown in Fig. 2, since its T_C is lower than the workable range of the SQUID magnetometer. There exists a clear anomaly both in the real and the imaginary parts of the AC susceptibility. The similar anomaly observed in $CeRu_2$ has been found to correlate directly with H^* for the peak effect.

Figure 3 shows the typical H-T phase diagrams for the three compounds determined by the magnetization and the AC susceptibility measurements; the upper critical field H_{C2} and the critical field H^* where the peak effect appears for the ascending field sweep. The phase diagrams have a common characteristic irrespective of the difference in the absolute values of T_C and H_{C2};i.e., note the similarity with the predicted phase diagram for the FFLO phase.[10] If pressed to say the difference, however, the H_{C2} vs. T plot for $CeCo_2$ is rather linear down to the lowest temperature compared to the others. In addition, H^* is always closer to H_{C2} over the investigated temperature range. At a glance, there exists a tricritical point near T_t = ~6K for $Yb_3Rh_4Sn_{13}$ and ~5.3K for $CeRu_2$, which defines the upper limit of the existence range of the peak effect. However, we must note that it is not easy to conclude whether the peak exists or not near T_C, since the magnitude of the peak effect is getting smaller and smaller.

For better understanding of the superconducting properties, we first make a brief comparison of the normal state properties in these compounds. Figure 4 shows the low temperature part of the electrical resistivity as a function of T^2. The residual resistivity for $CeCo_2$ (0.97μΩcm) is more than an order of magnitude smaller than the others (~10μΩcm), suggesting the better quality of this compound. In fact for this compound, de Haas-van Alphen oscillations, with the frequency range from 6.34×10^6 Oe to 8.77×10^7 Oe and the estimated cyclotron effective mass up to $10.9m_0$, have been successfully observed.[11] For all the compounds, the electrical resistivity data are nicely on a linear line reflecting a Fermi liquid behavior. The coefficient A in,

$$\rho(T) = \rho_0 + AT^2, \tag{1}$$

is estimated as given in table I, which is found to be of similar magnitude for all the compounds.

Figure 5 shows C/T vs. T^2 plots for $CeCo_2$ and

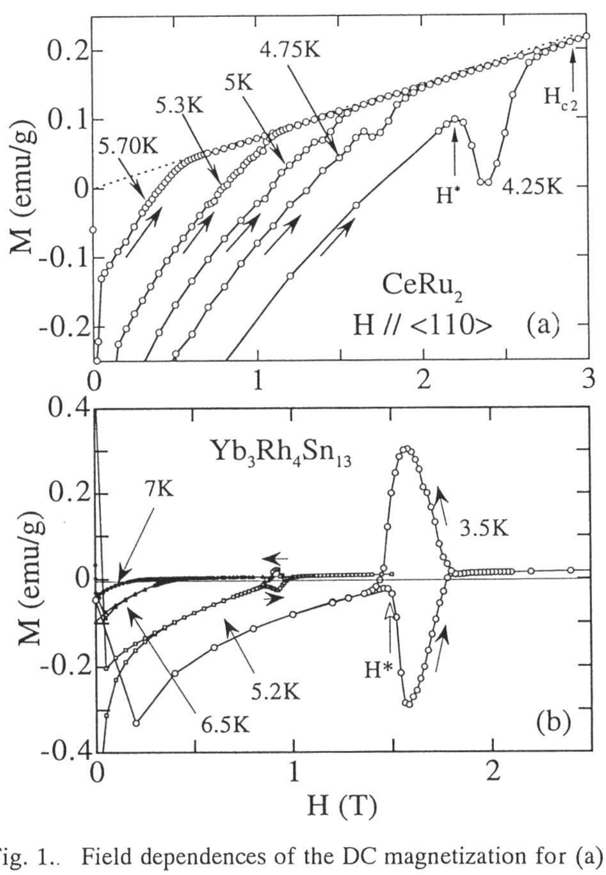

Fig. 1.. Field dependences of the DC magnetization for (a) $CeRu_2$ and (b) $Yb_3Rh_4Sn_{13}$.

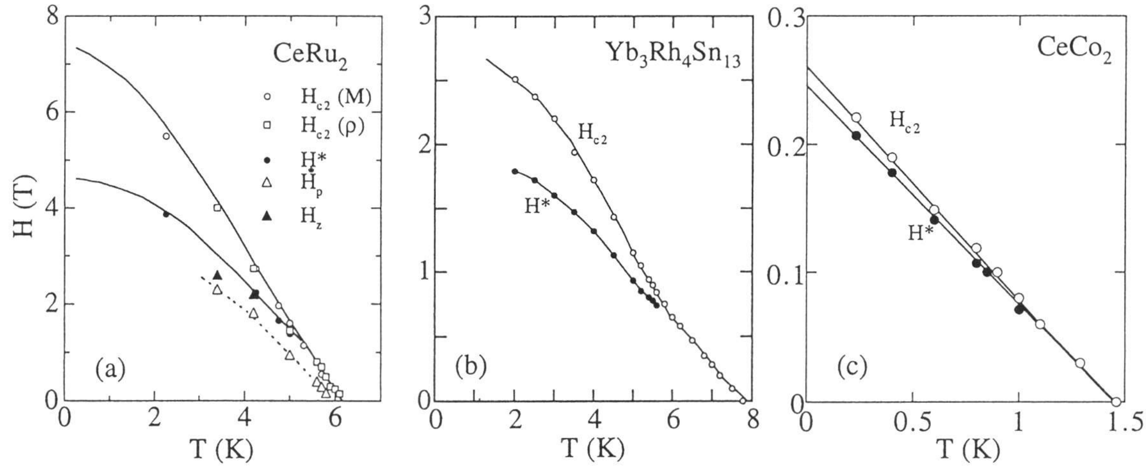

Fig. 3. Superconducting *H-T* phase diagrams for (a) $CeRu_2$, (b) $Yb_3Rh_4Sn_{13}$ and (c) $CeCo_2$. H_{C2} the upper critical field determined from the M and ρ measurements, H^* the lower critical field for the peak effect determined from the DC magnetization, H_p the lower critical field for the peak effect lower critical field where ρ = 0.

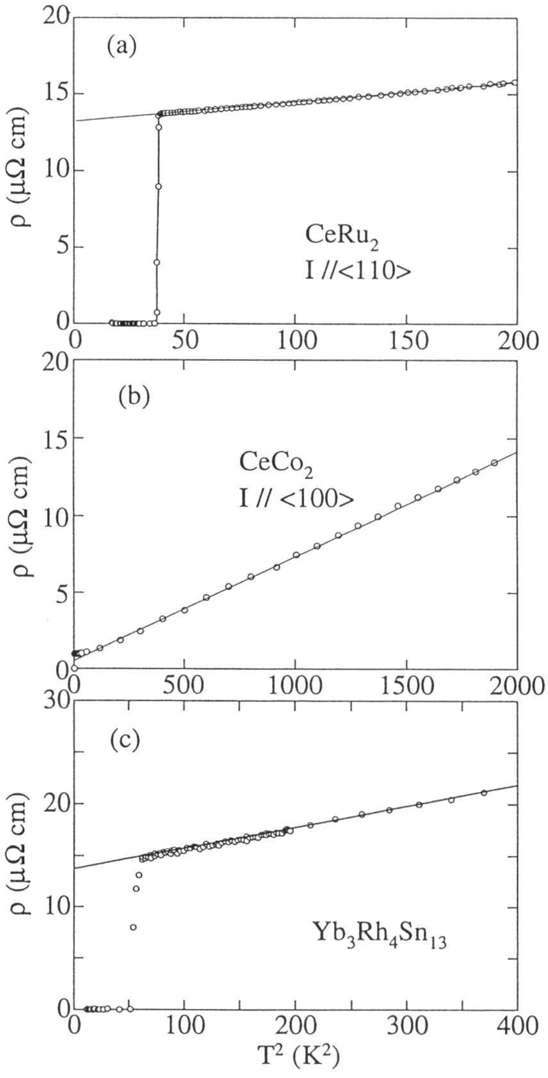

Fig. 4. ρ vs. T^2 plots for (a) $CeRu_2$, (b) $Yb_3Rh_4Sn_{13}$ and (c) $CeCo_2$.

$Yb_3Rh_4Sn_{13}$. There clearly observed a jump reflecting the superconducting transition at a transition temperature T_C. Above T_C, the data are on a linear line,

$$C/T = \gamma + \beta T^2, \tag{2}$$

for both compounds, from which we estimated the Sommerfeld coefficient γ as given in table I. In the table, the reported γ value for $CeRu_2$ is also included. The specific heat jump $\Delta C/\gamma T_C$ is close to the predicted value of 1.43 from the conventional BCS theory for both $Yb_3Rh_4Sn_{13}$ and $CeRu_2$, and there observed no sign of unusual superconductivity in these compounds. In contrast, for $CeCo_2$, $\Delta C/\gamma T_C$ is highly reduced, which will be independently discussed later.

Figure 6 shows the temperature dependence of the Hall coefficient R_H for the three compounds. At room temperature, R_H for $CeRu_2$ and $CeCo_2$ have a similar magnitude of $10^{-10}m^3/C$ typical of normal metals, though the sign is different. With decreasing temperature, there appears a positive anomalous Hall effect contribution for both compounds. The magnitude of the anomalous contribution is about an order of magnitude larger for $CeRu_2$. For both compounds, the anomalous part shows a peak near 30K. Of course, at present stage, we can not rule out the possible contribution from the temperature dependence of anisotropy in the relaxation time. The magnitude of R_H for $Yb_3Rh_4Sn_{13}$ is slightly smaller than the Ce compounds in the investigated range, which suggests $Yb_3Rh_4Sn_{13}$ to be also normal metallic. From the view point of the carrier concentration, all the three compounds are normal metallic.

Next point to be tested is the existence range of the peak effect, which is a key parameter to be compared with the FFLO theory. In the DC magnetization measurements, we notice that it is not easy to judge the existence of the peak effect near T_C, since the magnitude of the anomaly largely decreases with increasing temperature. To estimate the change in

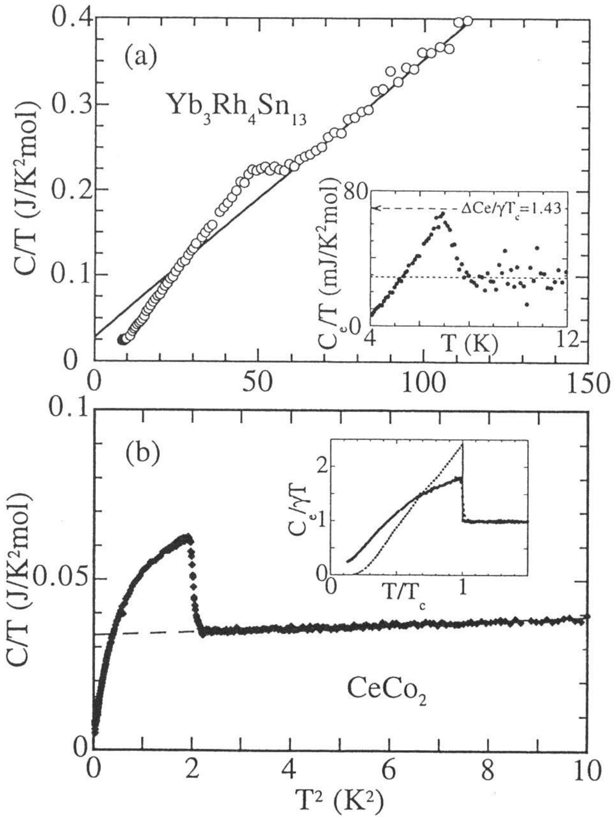

Fig. 5. (a) C/T vs. T^2 plots for $Yb_3Rh_4Sn_{13}$ and (b) Temperature dependence of $C_e/\gamma T_C$ for $CeCo_2$. The broken curve is calculated based on the BCS theory.

Table *I*. Comparison of the normal and superconducting properties for $CeRu_2$, $CeCo_2$ and $Yb_3Rh_4Sn_{13}$.

	$CeRu_2$	$CeCo_2$	$Yb_3Rh_4Sn_{13}$
ρ_0 ($\mu\Omega$cm)	14	0.97	13
T_C (K)	6.1	1.4	7.8
H_{C2} (0) (kOe)	74	2.6	28
$\chi(0)$ (10^{-5}emu/cm^3)	2.5	5.3-8.0	0.54*
γ (mJ/mol.K^2)	28	36	30
A ($10^{-3}\mu\Omega$cmK^{-2})	30	7.3~10	20
l (nm)	100	260	~10
ξ(nm)	6.7	35	10
λ(nm)	110-140	310-460	200
κ	16-21	~10	20
β	1.2	0.1	0.2

pinning force near T_C, we measured the field dependence of the electrical resistivity in the flux flow state. Figure 7 shows the results at 4.2K for $CeRu_2$ and $Yb_3Rh_4Sn_{13}$ for selected values of measuring current *I*. The resistivity is essentially zero up to H_{C2} for small I. For larger values of *I*, the resistive voltage shows up at a critical field H_S, depending on *T* and current density j, where fluxoids trapped in the samples start to move. The electrical resistivity increases monotonously up to H_P above which it drops sharply to zero for all the values of I in the present experiment. Near H_{C2}, it recovers again and approaches the normal state value. The largely enhanced

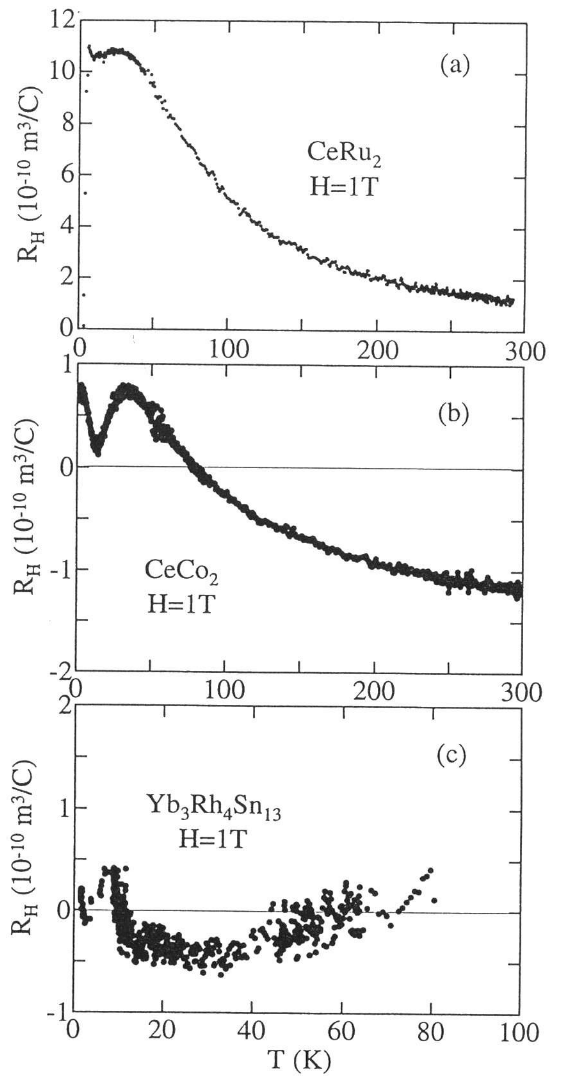

Fig. 6. Temperature dependence s of the Hall coefficient for (a) $CeRu_2$, (b) $CeCo_2$ and (c) $Yb_3Rh_4Sn_{13}$.

pinning force between H_P and H_{C2} is directly correlated with the peak effect observed in the magnetization measurement. The pinning force density f_p for $CeRu_2$ estimated from $f_p = |j_C \times H|$ or $f_p = |j \times H_S|$, where j_C is a critical current density at *H*, is ~10^5N/m^3 between *H*= 0.5T and 1.5T at 4.2K, which is more than three orders of magnitude smaller than the value 5× 10^8N/m^3 estimated at the center of the peak effect from the magnetization measurements. The result at higher temperatures is shown in Fig. 8, where the existence of the peak effect is evident up to 5.7K. In the Hall resistivity and transverse even voltage, we can identify some anomaly related with the peak effect up to 5.8K. The field values H_p at the low field side of the anomaly are plotted in Fig. 3, which shows that the peak effect persists far closer to T_C than was determined from the magnetization measurements. At the moment, we infer that the peak effect persists up to T_C, contrary to the limit of T/T_C=0.55 originally predicted for the FFLO state. In a preliminary measurement, $Yb_3Rh_4Sn_{13}$ exhibits basically the same tendency; the peak effect persists far closer to T_C than was determined from the magnetization. The anomaly related with the peak effect was observed also in $CeCo_2$ below H_{C2},[20]

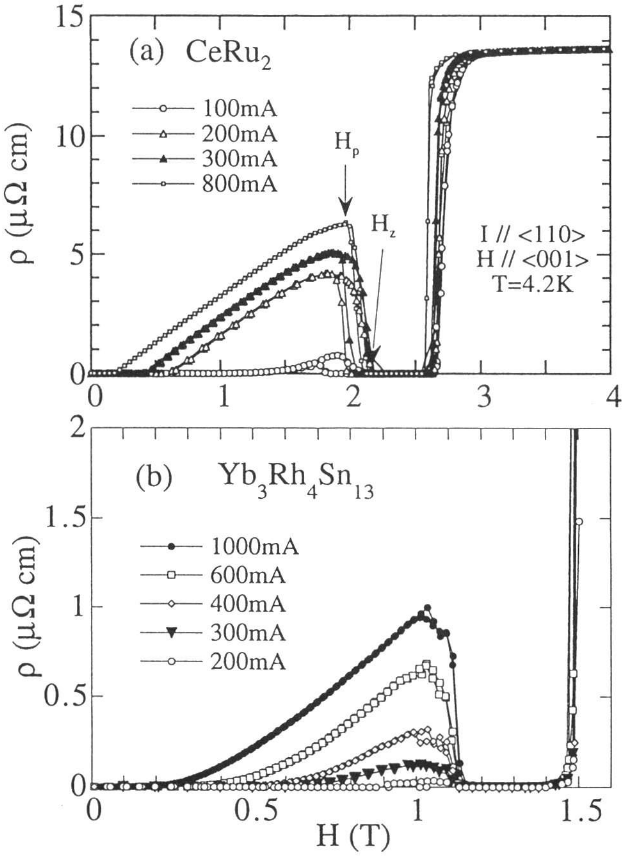

Fig. 7. Field dependences of the electrical resistivity for (a) $CeRu_2$, (b) $Yb_3Rh_4Sn_{13}$ at 4.2K for selected values of current I.

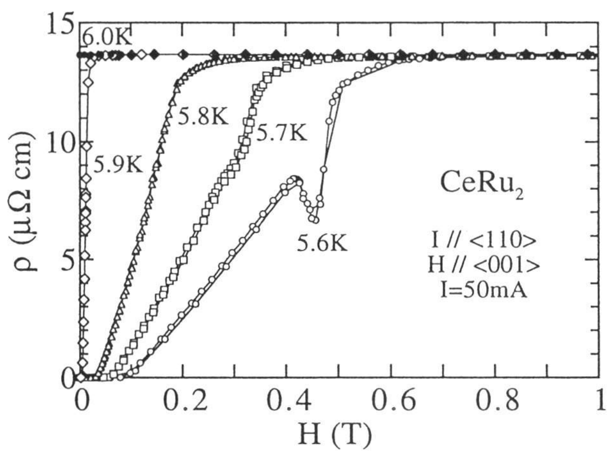

Fig. 8. Field dependences of the electrical resistivity at selected values of measuring temperature for $CeRu_2$.

though the difference in the pinning force density between the peak field region and the lower field region is smaller. In a preliminary work on a higher quality $CeRu_2$ sample with a residual resistivity less than 1μΩcm, we also found the smaller difference in the pinning force density between the field ranges;i.e., f_p is enhanced at lower fields and suppressed in the peak field region compared to the present sample. These facts suggest a large influence of sample quality on the peak effect.

Figure 9 shows the field dependence of the Hall

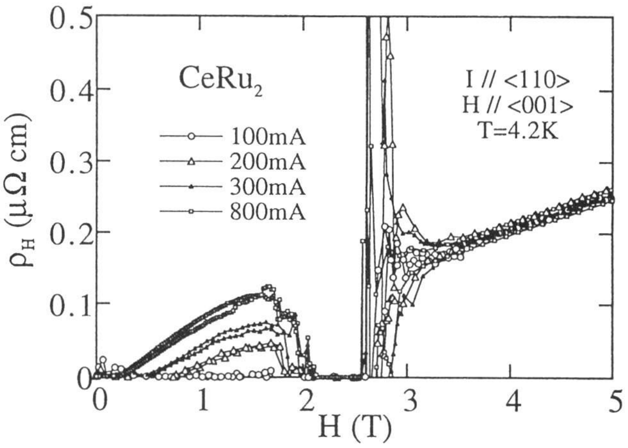

Fig. 9. Field dependence of the Hall resistivity for $CeRu_2$ simultaneously measured with the resistivity in Fig. 7(a).

resistivity for $CeRu_2$ simultaneously measured with the resistivity shown in Fig.7 (a). The field dependence is reminiscent of that of the resistivity. There observed no sign change of the Hall resistivity in the flux-flow state as was reported in the oxide high temperature superconductors,[21] though there exists a large uncertainty in the determination of the Hall resistivity near the peak effect region. When the Hall angle, defined as $\tan(\theta_H)=\rho_H/\rho$, was plotted against H using the data from Figs. 7(a) and 8, two characteristic features in the mixed state are recognized; 1) it depends on the current density, and 2) it is increased below the peak field region and lies above the line extrapolated from the normal state. These facts can not be explained by the simplest Hall effect models given by Bardeen and Stephan,[22] and by Nozieres and Vinen.[23] Such an enahncement of Hall angle below H_{C2} has been predicted for dirty type II superconductors in the microscopic theories by Maki[24] and Ebisawa.[25]

Another condition for the stabilization of the FFLO state was given by Gruenberg and Gunther;[10] the parameter $\beta=\sqrt{2}\,H^0_{C2}/H_P$ should be larger than 1.8, where H^0_{C2} is the orbital critical field at 0K and $H_P=\Delta_0/\sqrt{2}\,\mu_B$ is the paramagnetically limited upper critical field. The parameter β was estimated to be 1.2 for $CeRu_2$, while that for $CeCo_2$ and $Yb_3Rh_4Sn_{13}$ as given in table *I* (only ~0.1 and ~0.2, respectively) does not fulfill the condition. The other superconducting parameters, the Ginzburg-Landau (GL) coherence length ξ, the penetration depth λ and the GL parameter κ are also given in table *I*. The table shows that $Yb_3Rh_4Sn_{13}$ is clearly far from the clean limit condition.

Finally, we discuss anomalous superconducting characteristics found in the specific heat of $CeCo_2$. The most prominent feature from Fig.5(b) is the small specific heat jump $\Delta C_e/\gamma T_C$ ~ 0.85 compared to the ordinary BCS prediction of 1.43, which has been further tested on three different single crystals within 5% accuracy.[18] The small specific heat jump indicates a variation of the gap parameter in $\boldsymbol{k}$ space, which can be due to two possibilities; i.e., conventional s-wave pairing superconductivity with anisotropic Fermi sheets, or unconventional superconductivity.[26] Moreover, a deviation from the BCS prediction has been also found in the temperature dependence of C_e at lower temperatures than T_C. Figure 10

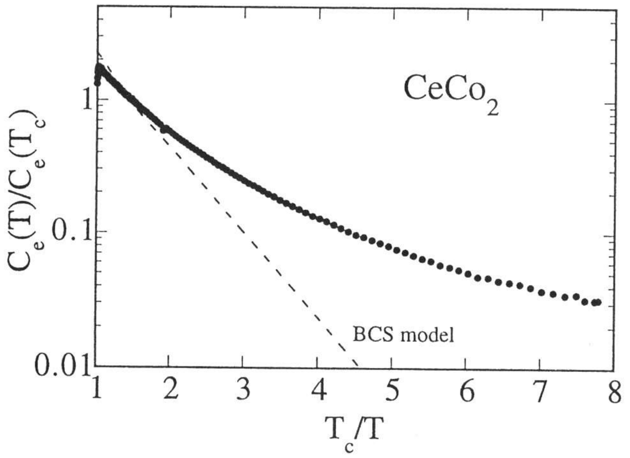

Fig. 10. Electronic part of the specific heat normalized at T_C as a function of T_C/T for $CeCo_2$. The broken curve is calculated based on the BCS theory.

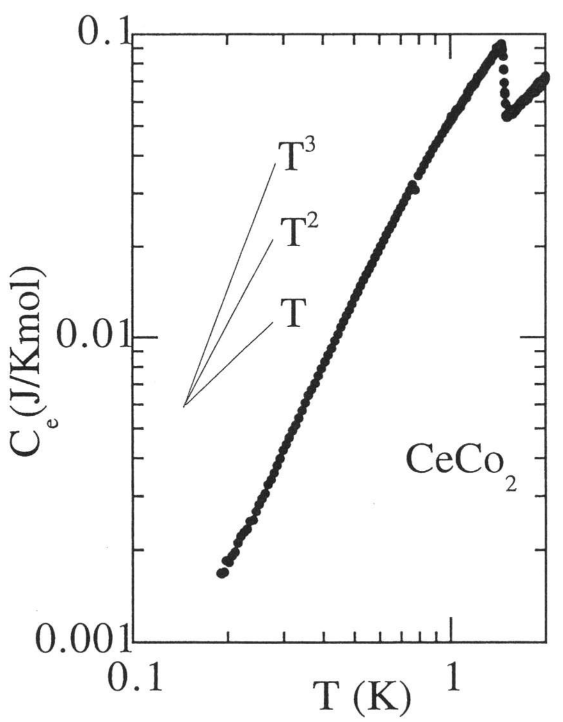

Fig. 11. log(C_e) vs. log (T) for $CeCo_2$.

shows $C_e(T)/C_e(T_C)$ as a function of T_C/T along with the BCS prediction. The experimental data clearly deviate from an exponential dependence predicated from the ordinary BCS theory. Figure 11 shows a double-log plot for C_e vs. T. The dependence at lower temperatures is rather close to the second power dependence (T^2), which suggests that the energy gap possesses lines of nodes on the Fermi surface. The dependence is expected for the unconventional superconductor of d-wave pairing. However, this may not be plausible if we take into account the relatively low value of (dH_{C2}/dT) at T_C. For the detailed discussion of the deviation from the BCS prediction, the specific heat measurement should be extended to the lower temperature range; the field dependence measurement is of particular importance. Furthermore, elaborate experiments on wide variety of properties are desirable.

§ 4. Summary

We found that the flux flow transport measurements can be a useful tool to investigate the mixed state properties in rare earth superconductors. For the three compounds exhibiting the peak effect, carrier density, Sommerfeld coefficient and the T^2 coefficient of resistivity are similar in magnitude. While the magnetic susceptibility is largely different, it gives rise to no essential effect on the basic character of the H-T phase diagrams. Even on the samples ($CeCo_2$ and $Yb_3Rh_4Sn_{13}$) with relatively small superconducting parameter β, basically the same peak effect has been observed. The sample quality, estimated from the residual resistivity, has a clear influence on the peak effect through some pinning mechanism. These facts might give negative support for the original FFLO scenario. Since the peak effect observed has many interesting features such as the recovery of the irreversibility, novel theories which better explain these experimental facts are desirable.

We found clear evidences of a deviation from the ordinary BCS prediction in the superconducting character of $CeCo_2$.

Acknowledgments

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