Thermodynamic Studies on Non Centrosymmetric Superconductors by AC Calorimetry under High Pressures*†

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We investigated the non centrosymmetric superconductors CePt3Si and UIr by the ac heat capacity measurement under pressures. We determined the pressure phase diagrams of these compounds. In CePt3Si, the Néel temperature \( T_N = 2.2 \) K decreases with increasing pressure and becomes zero at the critical pressure \( P_{C1} \approx 0.6 \) GPa. On the other hand, the superconducting phase exists in a wider pressure region from ambient pressure to \( P_{C1} \approx 1.5 \) GPa. The phase diagram of CePt3Si is very unique and has never been reported before for other heavy fermion superconductors. In UIr, the heat capacity shows an anomaly at the Curie temperature \( T_{C1} = 46 \) K at ambient pressure, and the heat capacity anomaly shifts to lower temperatures with increasing pressure. The present pressure dependence of \( T_{C1} \) was consistent with the previous studies by the resistivity and magnetization measurements. Previous ac magnetic susceptibility and resistivity measurements suggested the existence of three ferromagnetic phases, FM1-3. \( C_{ac} \) shows a bending structure at 1.98, 2.21, and 2.40 GPa. The temperatures where these anomalies are observed are close to the phase boundary of the FM3 phase.

KEYWORDS: CePt3Si, UIr, superconductivity, ac calorimetry

1. Introduction

Recently, the discovery of non centrosymmetric superconductors such as CePt3Si, UIr, CeRhSi3, CeIrSi3, and CeCoGe3 has attracted considerable attention from both theoretical and experimental view points.1-5 In these compounds, two spin degenerate bands are split due to the Rashba-type spin-orbit interaction, which strongly influences the superconducting properties, particularly the pairing symmetry of the Cooper pairs. Theoretical studies suggest a mixed-type pair function with spin triplet and singlet components.6 Many theoretical and experimental studies have been extensively conducted in order to clarify this novel type of unconventional superconductivity. In this paper, we describe our thermodynamic studies on CePt3Si and UIr under high pressure.

CePt3Si crystallizes in the tetragonal structure (space group \( P4\bar{m}nm \)) in which inversion center is absent. Superconductivity is observed at the transition temperature \( T_{sc} = 0.75 \) K below the Néel temperature \( T_N = 2.2 \) K at which antiferromagnetism is observed in CePt3Si.1 Further, a microscopic coexistence between magnetism and superconductivity was suggested based on the neutron scattering, \( \mu \)SR and NMR experiments.7-10 The finding of the superconductivity led to many theoretical and experimental studies for understanding the novel superconductivity in systems without inversion centers. In the NMR experiment, two superconducting order parameters comprising the spin singlet- and triplet-pairing components have been suggested.11 The previous high-pressure study by the resistivity measurement showed that the superconducting transition temperature \( T_{sc} \) decreases with an increase in the pressure and becomes 0 K at around 1.5 GPa.12 On the other hand, the pressure dependence of the antiferromagnetic transition temperature \( T_N \) is not clear because the anomaly in the resistivity at \( T_N \) is too weak to be detected.

UIr is a ferromagnetic compound with the Curie temperature \( T_{C1} = 46 \) K.13,14 UIr crystallizes in the monoclinic PbBi-type structure (space group \( P2_11 \)). There is no inversion center in the crystal structure. The magnetic susceptibility obeys the Curie-Weiss law at temperatures above 500 K, with an effective magnetic moment \( \mu_{eff} = 3.6 \) \( \mu_B / \text{U} \); this value corresponds to the free-ion value of the localized 5f2 and/or 5f3 configurations. In the ferromagnetic state, the magnetization is highly anisotropic and the magnetic property is of the Ising type. The size of the spontaneous magnetic moment oriented along the \( [101] \) direction is 0.5 \( \mu_B / \text{U} \). The cyclotron effective mass in the range of 10 - 30 \( m_0 \) was observed in the de Haas van Alphen experiment. The electronic specific heat coefficient was determined to be \( \gamma = 49 \) mJ/K2·mol.15,16 The itinerant character of the 5f electrons at low temperatures was suggested. Previous high-pressure studies showed that the Curie temperature \( T_{C1} \) decreases with increasing pressure and that superconductivity is observed in a narrow pressure region from 2.6 to 2.7 GPa.2,17,18 A recent study revealed the existence of three ferromagnetic phases FM1-3 and that the superconducting phase exists at a pressure just below the critical pressure of the FM3 phase.19

In order to establish the pressure phase diagram of both the compounds, the thermodynamic measurements are necessary. We carried out the ac heat capacity mea-
measurement on CePt$_3$Si and UIr under high pressures. We present the experimental results in this paper.

2. Experimental

A single crystal of CePt$_3$Si was grown by the Bridge- man method and that of UIr was grown by the Czochral ski method in a tetra-arc furnace. The details of the sample preparation are given in our previous papers.\textsuperscript{12,15}

These values of the residual resistivity ratio RRR (= $\rho_{RT}/\rho_0$) are 100 and 200 for CePt$_3$Si and UIr, respectively. Those values indicate the high quality of the single crystal samples. The ac heat capacity measurement under pressure was measured using a AuFe-Au thermocouple in a hybrid piston cylinder-type cell. The details of experimental techniques for the ac calorimetry are given in ref. [20].

3. Results and discussions

3.1 CePt$_3$Si

The pressure-temperature phase diagram of CePt$_3$Si obtained by the heat capacity measurement is shown in Figure 1. The superconducting transition temperatures $T_{sc}$ previously determined by both resistivity $\rho$ and ac susceptibility $\chi_{ac}$ measurements are also plotted in the figure.\textsuperscript{12} The Néel temperature determined by the resistivity measurement was not plotted because there was ambiguity in the determination of $T_N$ due to the weak resistivity anomaly at the transition temperature. With increasing pressure, $T_N$ decreases faster than $T_{sc}$ and becomes 0 K at around $P_{AF}$ $\simeq$ 0.6 GPa. $T_{sc}$ increases with increasing pressure and becomes approximately constant from 0.6 GPa to 0.8 GPa. It decreases furthermore with increasing pressure and becomes zero at $P_{sc} \simeq$ 1.5 GPa. Thus, the pressure dependence of $T_{sc}$ shows a characteristic feature. The present pressure of 0.6 GPa corresponds to the antiferromagnetic critical pressure $P_{AF}$. CePt$_3$Si is in the paramagnetic state from $P_{AF}$ $\simeq$ 0.6 GPa to 1.5 GPa and it shows only superconducting transitions.

Pressure-induced superconductivity was observed in several cerium compounds such as CeIn$_3$, CeRh$_2$Si$_2$ and CePd$_2$Si$_2$.\textsuperscript{21} These compounds show the antiferromagnetic ordering at ambient pressure. The $T_N$ value decreases with increasing pressure. Superconductivity is observed around the magnetic critical point $P_{AF}$, where $T_N$ becomes zero. The superconducting phase exists in a narrow pressure region around the antiferromagnetic critical pressure $P_{AF}$. The $T_{sc}$ value becomes maximum around the critical pressure. Superconductivity is considered to be mediated by the low-energy magnetic excitations around the magnetic quantum critical point $P_{AF}$. On the other hand, in the case of CePt$_3$Si, the bulk superconducting phase exists in a wide pressure region above and below $P_{AF}$, and $T_{sc}$ does not shows a maximum at $P_{AF}$. The maximum $T_{sc}$ value is realized at ambient pressure. From the pressure dependence of the linear heat capacity coefficient $\gamma$, it was suggested that the critical pressure $P_{AF}$ is not of the second-order quantum critical point but that of the first-order.\textsuperscript{20} Therefore, the superconductivity in CePt$_3$Si may be different from that around the magnetic quantum critical point.

3.2 UIr

Figure 2 shows the temperature dependence of $C_{ac}$ (right side) at ambient pressure. The experimental data obtained by the relaxation method is also plotted (left side). Both the data are scaled around 50 K by experimental data. The temperature dependence of $C_{ac}$ is qualitatively consistent with that obtained by the relaxation method. At ambient pressure, the heat capacity shows an anomaly at around the ferromagnetic transition temperature $T_{C1} = 46$ K.

Figure 3 shows the heat capacity $C_{ac}$ under pressures up to 1.58 GPa. The experimental data under pressures are simply shifted upwards. With increasing pressure, the anomaly at $T_{C1}$ shifts to the lower temperature side and the strength of the anomaly becomes weaker. At 1.58
GPa, a weak anomaly is observed at around 10 K.

Figure 4 shows the heat capacity $C_{ac}$ in the pressure region from 1.58 GPa to 2.61 GPa. The experimental data under pressures are simply shifted upwards. In this region, there is no distinct heat capacity anomaly. However, the curve of $C_{ac}$ at 1.98, 2.21, and 2.40 GPa shows a bending structure as shown in Figure 4. These bending structures are indicated by squares in Figure 5. It is found that the pressure dependence of $T_{C1}$ determined by the present study is consistent with those determined in the previous studies. The transition temperatures $T_{C1}$ obtained from the present study are indicated by circles. The phase boundaries indicated by solid lines are determined by the resistivity and dc magnetization measurements; the ones indicated by broken lines are determined by ac susceptibility measurements. The superconducting region is indicated by a shadow at an enlarged scale. It is found that the pressure dependence of $T_{C1}$ determined by the present heat capacity measurement is consistent with those determined in the previous study. The temperatures where $T_{C2}$ shows bending are indicated by solid lines. Interestingly, these temperatures are close to the boundary of the FM3 phase. Thus, the bending anomaly may be the thermodynamic one related to the phase boundary of the FM3 phase. The anomaly does not appear in $C_{ac}$ at 2.61 GPa where the value of $T_{C3}$ is estimated to be approximately 5 K from the previous studies. The reason for the absence of the heat capacity anomaly is not clear. One possibility is that the critical pressure of the FM3 phase in the present study may be different from that of previous reports due to sample dependence or ambiguity in pressure determination.

Next, we discuss the magnitude of the heat capacity jump $C_{ac}$ shows bending. As discussed later, the temperatures are close to the phase boundary of the FM3 phase. No anomaly is observed in $C_{ac}$ around the phase boundary of the FM2.

The pressure phase diagram of UIr is shown in Figure 5. The transition temperatures $T_{C1}$ obtained from the present study are indicated by circles. The phase boundaries indicated by solid lines are determined by the resistivity and dc magnetization measurements; the ones indicated by broken lines are determined by ac susceptibility measurements. The superconducting region is indicated by a shadow at an enlarged scale. It is found that the pressure dependence of $T_{C1}$ determined by the present heat capacity measurement is consistent with those determined in the previous study. The temperatures where $C_{ac}$ shows bending are indicated by squares. Interestingly, these temperatures are close to the boundary of the FM3 phase. Thus, the bending anomaly may be the thermodynamic one related to the phase boundary of the FM3 phase. The anomaly does not appear in $C_{ac}$ at 2.61 GPa where the value of $T_{C3}$ is estimated to be approximately 5 K from the previous studies. The reason for the absence of the heat capacity anomaly is not clear. One possibility is that the critical pressure of the FM3 phase in the present study may be different from that of previous reports due to sample dependence or ambiguity in pressure determination.

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Next, we discuss the magnitude of the heat capacity jump.

### Table I. Calculated heat capacity jump

| $P$(GPa) | $T_{C1}$ (K) | $\Delta C/T_m^{(SCR)}$ (mJ/K²·mol) | $\Delta C/T_m^{(Stoner)}$ (mJ/K²·mol) |
|----------|-------------|-----------------------------------|-----------------------------------|
| 0        | $T_{C1} = 46$ K | 11                                | 44                                |
| 1.8      | $T_{C2} = 13$ K | 0.11                              | 0.44                              |
| 2.2      | $T_{C3} = 14$ K | 0.22                              | 0.88                              |
| 2.4      | $T_{C3} = 10$ K | 0.30                              | 1.2                               |
| 2.6      | $T_{C3} = 5$ K | 0.6                               | 2.4                               |
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