Specific Heat Study of Magnetic and Superconducting Transitions in CePt$_3$Si

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Measurements of specific heat between 80 mK to 4 K and electrical resistivity between 80 mK to 10 K were carried out for polycrystalline CePt$_3$Si samples cut into small pieces (typically ~10 mg). In the specific heat measurements, we observed an antiferromagnetic transition jump at $T_N = 2.2$ K for all the samples, while the heights have large variations. As regards superconductivity, we observed two distinct transition jumps at $T_c^1 \sim 0.45$ K and $T_c^2 \sim 0.75$ K, which were the same for all the samples. From the measurements of specific heat and resistivity, systematic relations were found between antiferromagnetic and superconducting transitions. We conclude that antiferromagnetism, whose transition temperature is 2.2 K, coexists with superconductivity, whose transition temperature is $T_c^2$. In this sample, residual electronic specific heat coefficient in the superconducting state $\gamma_0$ was quite small, and specific heat divided by temperature below $T_c^2$ decreased almost linearly with decreasing temperature. In order to reveal the characteristic properties of the magnetism and superconductivity of the CePt$_3$Si system, it is important to study the two superconducting phases with $T_c^1$ and $T_c^2$, respectively.

KEYWORDS: CePt$_3$Si, non-centrosymmetry, antiferromagnetism, heavy fermion superconductor, specific heat measurement

1. Introduction

Bauer et al. reported that CePt$_3$Si exhibits an antiferromagnetic (AFM) order at $T_N = 2.2$ K and superconducting (SC) transition at $T_c = 0.75$ K, and that normal state electronic specific heat coefficient $\gamma_n$ is approx 0.39 J/(K$^2$·mol).$^1$ This compound is a heavy fermion superconductor having a characteristic crystal structure that lacks inversion symmetry (space group $P4mm$). Therefore, the superconductivity of CePt$_3$Si exists in a particular environment compared with that of a conventional superconductor. Previous theoretical studies have shown that a non-centrosymmetric heavy fermion has several possible states for realizing unconventional superconductivity.$^2$–$^6$

Many experimental studies of superconductivity have been carried out. Previous studies of specific heat by Bauer et al. and Takeuchi et al. have shown marked contrasts between polycrystalline and single crystal samples.$^1,^7$ The former showed a small AFM transition jump at $T_N = 2.2$ K and an SC transition jump at $T_c = 0.75$ K for a polycrystalline sample. The latter showed a large AFM transition jump at the same $T_N$ and an SC transition jump at different $T_c$ of 0.46 K for a single crystal sample. In the single crystal sample, the SC jump was sharp and large, and the residual electronic specific heat coefficient in the SC state, $\gamma_0$, was small, however, its $T_c$ was low compared with that of the polycrystalline sample. In addition, a double anomaly of the SC state in the specific heat measurement was observed by Scheidt et al.$^8$ They suggest that it was a signalling two consecutive phase transitions. On the other hand, Nakatsuji et al. showed that the Meissner effect of SC started increasing from ~0.8 K and the rate of increase changed below ~0.5 K.$^9$ They suggest that the SC domain has a volume fraction. The pressure dependence of the Meissner effect and $T_c$ seemed to indicate that the volume fraction was due to some inhomogeneous property that leads to a spatial variation of local pressure in the sample.$^{10}$

The temperature $T$ dependence of specific heat divided by temperature $(C/T)$ in the SC region preferred a linear $T$ dependence over a $T^{-1}\exp(-\Delta/k_BT)$ dependence.$^7$ In addition, the $T$ dependence of thermal conductivity in the $T$ range of 40 mK to 0.2 K was well fitted by a linear function of $T$.$^{11}$ These results indicate the presence of line nodes in the SC energy gap. On the other hand, the $T$ dependence of nuclear spin-lattice relaxation rate $1/T_1(T)$ did not simply follow an exponential law or a $T^2$-power law. The plot of $1/T_1(T)$ showed a coherence Hebel-Slichter peak at $T_c$, indicating a full-gap state without nodes.$^{12}$ Another NMR measurement indicated that the plot of $1/T_1(T)$ showed no obvious Hebel-Slichter peak and a drastically decreasing ($\propto T^3 \sim T^0$).$^{13,14}$ Therefore, CePt$_3$Si is expected to be an unconventional superconductor. In addition, the pressure $P$ phase diagram of $T_c$ and $T_N$ for this system was unusual compared with that of the previous magnetic superconductor.$^{15–17}$ Although $T_c$ and $T_N$ decreased with increasing $P$, SC still existed even after AFM disappeared. The decreasing rate of $T_c$ slowed down only at around $P_c$, at which AFM disappeared. The pressure corresponding to the maximum $T_c$ in this system was not $P_c$. Some heavy fermion magnetic superconductors show a dome structure for the pressure dependence of $T_c$ at the critical point $P_c$.

2. Experimental

Polycrystalline CePt$_3$Si and Ce$_{1.01}$Pt$_3$Si samples were synthesized by arc-melting Ce of 99.9 % (3N) purity, Pt of 3N5 purity, and Si of 6N purity, using a laboratory-made furnace. The synthesized melt became solidified by quenching on Cu-hearth in Ar atmosphere of 6N purity. The chemical compositions of our samples were deter-
mained from those of the starting materials. The weight loss of the constituent materials was negligible during the preparation. An ingot sample (1~2 g) was cut into two lumps, and one lump was heat-treated. Heat treatment for annealing was carried out under well-controlled conditions: the temperature was maintained at 950°C for one week and lowered to room temperature over three days. We labeled heat-treated and non-heat-treated samples as "annealed" and "as-cast", respectively. Then, each lump was cut into small pieces (~ 10 mg) for measurement. We prepared three CePt$_3$Si as-cast (#1, 2 and 3), two Ce$_{1.01}$Pt$_3$Si as-cast (#4 and 5), and their annealed samples (#1-a, #2-a and so on) to investigate sample dependence. Moreover, we conducted measurements using different pieces from the same batch (#2-a-1, #2-a-2, and so on).

Temperature dependence of specific heat was measured using the adiabatic heat pulse method between ~80 mK and 4 K. Electrical resistivity was measured using the conventional dc four-terminal method down to ~80 mK using the same piece as that used in specific heat measurement. Measurements were carried out using a laboratory-made dilution refrigerator.

### 3. Results and Discussion

Figure 1(a) shows the $T$ dependence of specific heat divided by $T$ ($C/T$) of the CePt$_3$Si as-cast (#1) and Ce$_{1.01}$Pt$_3$Si annealed (#4-a-2) samples. They showed quite different characteristics despite having the same polycrystalline CePt$_3$Si system. The $C/T(T)$ of the Ce$_{1.01}$Pt$_3$Si annealed showed a distinct AFM transition with a large jump at $T_N$ (2.2 K) and SC transition with a sharp jump at low $T_c$ (0.45 K). The residual $\gamma$ extrapolated to 0 K was almost zero. These results were similar to those reported by Takeuchi et al. for their single crystal, as shown by the solid line. On the other hand, the $C/T(T)$ of CePt$_3$Si as-cast exhibited a very small jump of AFM transition and a jump of SC transition appearing at high $T_c$ (0.75 K) compared with that of Ce$_{1.01}$Pt$_3$Si annealed. The AFM transition of this sample had not only a small jump but also a broad tail above $T_N$, from 2.2 K to ~4.0 K. $C/T(T)$ clearly increased at the onset of $T_c$ with decreasing $T$, but the peak broadened. These behaviors were similar to that observed by Bauer et al. for their polycrystalline sample, as shown by the broken line. Figure 1(b) shows the temperature dependence of the electrical resistivity ($\rho$) of the CePt$_3$Si as-cast and Ce$_{1.01}$Pt$_3$Si annealed samples. Measurements were carried out using very small pieces. Because the absolute value might include some ambiguity, $\rho/\rho_{AK}(T)$ values are presented. The residual resistivity ratio (RRR) of CePt$_3$Si as-cast was 20 and that of Ce$_{1.01}$Pt$_3$Si annealed was 120. We confirmed reproducibility by some measurements. All of the measured Ce$_{1.01}$Pt$_3$Si annealed including different batches had RRR exceeding 100. These were remarkably large, but other measured samples indicated RRR ~ 20. A kink of $\rho/\rho_{AK}(T)$ was observed at $T_N$=2.2 K for both samples. The $\rho/\rho_{AK}(T)$ of the Ce$_{1.01}$Pt$_3$Si annealed showed a clear kink at $T_N$ and decreased rapidly below $T_N$ with decreasing temperature. The decrease plateaued immediately just above $T_c$. On the other hand, the kink of the $\rho/\rho_{AK}(T)$ of the CePt$_3$Si as-cast broadened, and the decrease of $\rho/\rho_{AK}(T)$ continued to $T_c$. These results of $C/T(T)$ and $\rho/\rho_{AK}(T)$ indicate that Ce$_{1.01}$Pt$_3$Si annealed has a more regular AFM ordering (which is a long-range ordering with a narrow $T_N$ at 2.2 K) and a more regular lattice (which is an ideal CePt$_3$Si lattice, that is a non-centrosymmetric lattice) than CePt$_3$Si as-cast. Figure 1(c) shows the X-ray diffraction patterns. No extra-phase was observed in the X-ray diffraction patterns of both samples. There was no difference in the accuracy of measurement between the lattice constants of the two samples. The results in Fig. 1 indicate that 1% variations in Ce-concentration and heat treatment yield small structural changes that strongly affect SC and AFM but not powder diffraction patterns. In our speculation, these structural changes concern the
the decrease in the height of the specific heat jump in AFM transition from bottom to top. First, we note both AFM and SC transitions, respectively. The height of the jump in AFM transition, ∆C/T(T_N), decreased gradually without changing T_N, and the broad tail above T_N enlarged gradually from the bottom to top data. This relation is plotted in Fig. 3(b). We observed two peaks for SC transition in both Figs. 2(a) and 2(b). We define T_c^l (~0.45 K) as the temperature of the specific heat peak at lower and T_c^h (~0.75 K) as the onset temperature of the specific heat peak at higher. T_c^l and T_c^h were almost constant for all the samples. However, the heights of the specific heat jump at T_c^l and T_c^h, ∆C/T(T_c^l) and ∆C/T(T_c^h), differed for each sample. As ∆C/T(T_c^l) increased, ∆C/T(T_c^h) decreased. These results indicate that T_c^l does not move to T_c^h and that the SC at T_c^l and T_c^h compete against each other. CePt_3Si as-cast (#1) has only one large peak at T_c^h. However, this peak might include some components of ∆C/T(T_c^h), because it is broadened from T_c^l to T_c^h. Unfortunately, we were unable to prepare a sample that shows only a sharp jump at T_c^h and a small residual γ_c. Next, the relations between the two SC transition jumps, ∆C/T(T_c^l) and ∆C/T(T_c^h), and the AFM transition jump, ∆C/T(T_N), should be noted. In Figs. 2(a) and 2(b), ∆C/T(T_c^l) increased from the top to bottom data, that is, as ∆C/T(T_N) increased, ∆C/T(T_c^l) increased as well. The most typical example of this case is Ce_{1.01}Pt_3Si annealed (#4-a-2). ∆C/T(T_c^l) increased from the bottom to top data. It should be noted that ∆C/T(T_N) and ∆C/T(T_c^h) almost vanished in the sample with the largest ∆C/T(T_c^l). These data of correlation between ∆C/T(T_c^l), ∆C/T(T_c^h) and ∆C/T(T_N) are plotted in Fig. 3(a). These relations are described later. Next, we compare the annealed samples in Fig. 2(b) with the as-cast samples in Fig. 2(a). The ∆C/T(T_N) and ∆C/T(T_c^l) of the annealed samples were almost larger than those of the as-cast samples, while the γ_c of the annealed samples were smaller than those of the as-cast samples. These results are shown in Figs. 3(a) - 3(c) as open and closed symbols for as-cast and annealed, respectively.

The relations of ∆C/T(T_c^l), ∆C/T(T_c^h), C/T(2.4 K) and γ_c versus ∆C/T(T_N) are plotted in Figs. 3(a) - 3(c), respectively. In Fig. 3(a), when ∆C/T(T_N) increases, ∆C/T(T_c^l) decreases and ∆C/T(T_c^h) increases. It is clear that SC at T_c^l and T_c^h compete against each other, and that SC at T_c^h is on competitive relation with AFM at T_N but SC at T_c^l is not. In Fig. 3(b), C/T(2.4 K), which reflects the broad tail above T_N, increased with decreasing ∆C/T(T_N). This enhancement might have some relation with an increase in ∆C/T(T_c^h). In Fig. 3(c), the relation between γ_c and ∆C/T(T_N) is not clear, but at least the γ_c of as-cast was large and the γ_c of annealed with a large ∆C/T(T_N) was small. ∆C/T(T_c^l), ∆C/T(T_c^h) and ∆C/T(T_N) were decided in accordance with Fig. 3(d). These absolute values have some ambiguities because of their broadness. However, it has no significant effects on their relations.

As mentioned above, the present experiment leads us to conclude that the CePt_3Si system is spatially separated into two superconducting regions, SC^l and SC^h, the non-centrosymmetric structure, which is an ordering of Pt and Si atoms occupying the two 1(a)-sites of the P4mm structure. Because, it is considered that non-centrosymmetry is important for both SC of this system and AFM whose magnetic structure consists of ferromagnetic c-planes stacked antiferromagnetically along the c-axis. Therefore, although Ce_{1.01}Pt_3Si annealed has 1% opening Pt and Si sites, it might have two well-ordered 1(a)-sites of P4mm occupied by Pt and Si atoms. Then, the opening sites might be available for removing and ordering Pt and Si atoms when a sample is heated. Conversely, although CePt_3Si as-cast has a stoichiometric composition, it might have some disorders of Pt and Si at the two 1(a)-sites, because there is a quenching process in the preparation of polycrystalline samples.

Figures 2(a) and 2(b) show the C/T(T) of various samples in order to consider sample dependence in detail. Fig. 2(a) shows the results for the as-cast samples and Fig. 2(b) shows those for the annealed samples. In Figs. 2(a) and 2(b), the data were arranged according to
whose transition temperatures are $T_c^1$ ($\sim 0.45$ K) and $T_c^h$ ($\sim 0.75$ K), respectively. SC$^1$ develops in a more regular AFM ordering and a more regular lattice. Ce$_{1.01}$Pt$_3$Si annealed (#4-a-2) is considered to have an almost single phase in which SC$^2$ and AFM with $T_N$ coexist. Because, the volume fraction of this sample exhibited SC$^3$ with a particularly small residual $\gamma_h$ and AFM with the most distinct and largest peak for this sample are probably bulk properties. On the other hand, SC$^h$ does not seem to coexist with AFM having $T_N=2.2$ K at least. In what kind of phase is this SC$^h$ included? To answer this question, the broad tail gradually enlarging above $T_N$ might give us some hints. We suggest that the region of SC$^h$ is included in some magnetic phase which causes enhancement of the broad tail above $T_N$ (for example, a heavy fermion non magnetic phase and an AFM phase with broad $T_N$ from 2.2 to 4.0 K). 21) We suggested in our earlier discussion of Fig. 1 and in refs. 18 and 19 that as-cast samples contain some defects, which are reduced in number by heat treatment and annealing. The annealed samples exhibit large $RRR$, a marked transition at a narrow $T_N$ and a less ferromagnetically anomalous at 3.0 K. A sample having a perfectly regular structure would have perfect non-centrosymmetry. The presence of some defects will affect non-centrosymmetry and produce some par-
pieces. As $\Delta C/T(T_N)$ decreased, a broad tail above $T_N$ enlarged gradually. We observed two SC transition jumps at $T_{lc}^1$ and $T_{hc}^1$, which showed no sample dependence. SC$^1$ and SC$^h$ volume fractions are considered to be spatially separated to each other in a piece. A larger $\Delta C/T(T_l)$ appeared in a piece that showed a larger $\Delta C/T(T_N)$. In contrast, a larger $\Delta C/T(T_h)$ appeared in a piece that showed a smaller $\Delta C/T(T_N)$. Moreover, the piece with the largest jump at $T_{lc}^1$ had a small $\gamma_s$ and the largest RRR, and these properties appeared in both heat-treated and annealed pieces. Thus, SC$^1$ was concluded to coexist with the AFM having $T_N = 2.2$ K in a regular lattice as non-centrosymmetricity. The volume fractions of SC$^1$ and SC$^h$ change with the state of AFM ordering and the defects in crystal structures.

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