Novel Pressure Phase Diagram of Heavy Fermion Superconductor CePt₃Si
Investigated by ac Calorimetry

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The pressure dependences of the antiferromagnetic and superconducting transition temperatures have been investigated by ac heat capacity measurement under high pressures for the heavy-fermion superconductor CePt₃Si without inversion symmetry in the tetragonal structure. The Néel temperature $T_N = 2.2$ K decreases with increasing pressure and becomes zero at the critical pressure $P_{cr} \approx 0.6$ GPa. On the other hand, the superconducting phase exists in a wider pressure range from ambient pressure to about 1.5 GPa. The pressure phase diagram of CePt₃Si is thus very unique and has never been reported before for other heavy fermion superconductors.

KEYWORDS: heavy-fermion superconductor, CePt₃Si, ac calorimetry

Recently, Bauer et al. reported superconductivity in CePt₃Si with a non-centrosymmetric tetragonal structure (space group P4 mmn).¹ Superconductivity with the transition temperature $T_{sc} = 0.75$ K is realized in the long-range antiferromagnetic ordered state with the Néel temperature $T_N = 2.2$ K. A large electronic specific heat coefficient $\gamma = 300 - 400$ mJ/K²·mol and a large slope of upper critical field $dH_{c2}/dT (\approx -8.5$ T/K) at $T_{sc}$ suggest that superconductivity is based on heavy quasiparticles.

CePt₃Si is the first heavy-fermion superconductor lacking the inversion center in the crystal structure.¹,² It has been thought that a material lacking inversion symmetry would be an unlikely candidate for spin-triplet pairing.³,⁴ Interestingly, the upper critical field $H_{c2}(0) (\approx 3$ T) in CePt₃Si exceeds the Pauli-Clogston limit (≈ 1 T), and triplet pairing was suggested in the superconducting state of CePt₃Si.¹ Recent theoretical studies have claimed that the absence of the inversion center does not indiscriminately suppress the spin-triplet pairing state.⁵⁻¹⁰ It should be noted that recently superconductivity was found in a ferromagnet UIr without inversion symmetry under pressure where the Curie temperature approximately becomes zero.¹¹ The relation between anisotropic superconductivity and the non-centrosymmetric crystal structure is the most crucial issue to be clarified at present.

We grew a high-quality single crystal of CePt₃Si and investigated magnetic and electrical properties.¹²,¹³ It was clarified that $H_{c2}(0)$ was approximately isotropic: $H_{c2}(0) = 2.7$ T for $H // ||100|$ and $3.2$ T for $H // ||001|$. In the de Haas-van Alphen experiment, the topology of the Fermi surface in CePt₃Si was found to be most likely similar to that of LaPt₃Si. Large cyclotron masses of 10⁻20 m₀ were detected in CePt₃Si, which indicates the existence of heavy quasiparticles in this compound. In the neutron scattering experiment, a clear antiferromagnetic Bragg peak with $Q = (0,0,1/2)$ was observed below $T_N$ and the magnetic moment was determined as 0.16 $\mu_B$/Ce.¹⁴ The Bragg peak intensity was almost constant below $T_{sc}$, which indicates that the antiferromagnetic state coexists with the superconducting state. A microscopic coexistence between magnetism and superconductivity was also suggested by muon spin relaxation ($\mu$SR) and NMR experiments.¹⁵⁻¹⁷ In particular, in the NMR experiment, the novel behavior of $1/T_1T$ ($1/T_1$: Pt nuclear spin-lattice relaxation rate) was observed below $T_{sc}$, suggesting that a new class of superconducting state is realized in CePt₃Si.

Moreover, the pressure dependence of the superconducting transition temperature $T_{sc}$ was investigated by electrical resistivity measurements.¹⁸,¹⁹ The transition temperature decreases with increasing pressure and finally becomes zero at 1.5 GPa. The Néel temperature $T_N$ also decreases with increasing pressure, but the pressure dependence is not clear above 0.8 GPa because the change in the resistivity at $T_N$ is too weak to be detected. In order to clarify the pressure phase diagram of CePt₃Si, we carried out heat capacity measurement under high pressures.

A detailed description of our sample preparation is given in the previous papers.¹²,¹³,¹⁸ In the present heat capacity measurement, we used a high-quality single-crystal sample, which was cut from the sample used in the previous de Haas-van Alphen experiment. This sample was also used in the pressure experiment for the electrical resistivity and ac susceptibility. The sample size for the ac heat capacity measurement was $0.35 \times 0.25 \times 0.05$ mm³.

Heat capacity was measured by the ac calorimetry method in a piston cylinder pressure cell. The sample was thermally linked with a heat bath and was heated by application of an oscillating heating power $P =$
The heat capacity peak around $T_{\text{m}}$ magnetic susceptibility measurements ($\Delta C$) due to the superconducting transition. The transition temperature $T_{\text{sc}}$ was determined as $T_{\text{sc}} = 2.2$ K, as shown by an arrow. The heat capacity peak around $T_N$ is of the $\lambda$-type, and the peak structure is sharper than those in the previous reports.\(^{1,12}\) This might reflect the high quality of the present sample.

Below 0.5 K, the heat capacity indicates another peak due to the superconducting transition. The transition temperature $T_{\text{sc}}$ is determined as $T_{\text{sc}} = 0.46$ K. The value is lower than those determined by the resistivity and ac magnetic susceptibility measurements ($\sim 0.7$ K).\(^{12}\) The reason for this discrepancy is not clear. Such a discrepancy was also found in the heavy fermion superconductor CeIrIn$_5$.\(^{24}\)

The value of $\Delta C_{\text{ac}} / C_{\text{ac}}(T_{\text{sc}})$ is 0.33 at ambient pressure. Here, $\Delta C_{\text{ac}}$ is the jump of the heat capacity at $T_{\text{sc}}$ and $C_{\text{ac}}(T_{\text{sc}})$ is the value of $C_{\text{ac}}$ just above $T_{\text{sc}}$, namely, corresponding to $\gamma T_{\text{sc}}$, where $\gamma$ is the electronic specific heat coefficient. It is noted that a smaller value of 0.25 was reported in ref. 1. These values are far smaller than the BCS value $\Delta C / (\gamma T_N) = 1.43$. This reduction might be due to the gapless structure of the anisotropic superconducting gap and/or the high sensitivity of the present superconductivity to impurities.

With increasing pressure, the antiferromagnetic ordering shifts to lower temperatures. The peak at $T_N = 2.2$ K becomes weak with increasing pressure and finally becomes a broad hump at 0.47 GPa. The peak was not observed in the $C_{\text{ac}}$ curve at 0.70 GPa. This indicates that the antiferromagnetic ordering disappears at 0.70 GPa. The antiferromagnetic critical pressure $P_{\text{AF}}$ was thus estimated as $P_{\text{AF}} \approx 0.6$ GPa.

Figure 1(b) shows the low-temperature part of $C_{\text{ac}}$ of CePt$_3$Si under high pressures. Experimental data under high pressures are shifted downwards. $T_N$ and $T_{\text{sc}}$ correspond to the Néel temperature and superconducting transition temperature, respectively.
estimated as \( P_{sc} \simeq 1.5 \) GPa.\(^{18}\) The \( T_{sc} \) value at 1.29 GPa might be below the lowest temperature of our measurement, 90 mK. In fact, \( C_{ac} \) shows an upturn structure below 130 mK at 1.29 GPa.

The pressure dependence of \( T_{sc} \) is characteristic, as shown in Fig. 2. As pressure increases, \( T_{sc} \) decreases faster than that of \( T_{N} \). The \( T_{N} \) value decreases faster than that of \( T_{sc} \) with increasing pressure. An interesting point is that the superconducting phase exists above \( P_{AF} \).

The pressure dependence of \( T_{sc} \) is characteristic, as shown in Fig. 2. Namely, \( T_{sc} \) decreases as a function of pressure, becomes approximately constant from 0.6 GPa to 0.8 GPa, decreases further with increasing pressure, and becomes zero at \( P_{sc} \simeq 1.5 \) GPa. The present pressure of 0.6 GPa corresponds to the antiferromagnetic critical pressure \( P_{AF} \simeq 0.6 \) GPa. In the pressure region from \( P_{AF} \simeq 0.6 \) GPa to 1.5 GPa, \( \chi_{ac} \) measurement shows only the superconducting transition. The pressure phase diagram of CePt\(_3\)Si is thus very unique.

Figure 3(a) shows the pressure dependence of \( \Delta C_{ac}/C_{ac}(T_{sc}) \). It is almost constant in the pressure region from ambient pressure to \( P_{AF} \) and decreases steeply above \( P_{AF} \simeq 0.6 \) GPa. The value of \( \Delta C_{ac}/C_{ac}(T_{sc}) \) is, however, about 0.2 at 0.99 GPa. This indicates that the bulk superconducting state survives in the paramagnetic phase, namely above \( P_{AF} \simeq 0.6 \) GPa.

The thermocouple AuFe/Au is a dilute Kondo system and the thermopower \( S(T) \) is given as \( S(T) \propto T \) below 1 K. Therefore, the value of the inverse thermovoltage \( V_{ac}^{-1} \), which corresponds to \( [S(T)T_{sc}]^{-1} \), is approximately proportional to \( C/T \) at low temperatures. Therefore, the pressure dependence of \( V_{ac}^{-1} \) roughly corresponds to the electronic specific heat coefficient \( \gamma \).

Figure 3(b) shows the pressure dependence of \( V_{ac}^{-1} \), together with that of the coefficient \( A \) of the \( T^{2} \) term in the resistivity. Here, the data \( V_{ac}^{-1} \) was obtained just above \( T_{sc} \) under the same conditions of heater power \( P_{0} \), ac current frequency \( \omega \), and thermal conductivity \( \kappa \). At 1.29 and 1.57 GPa, where the superconducting transition does not appear, \( V_{ac}^{-1} \) becomes almost constant below 0.2 K. This constant value is plotted in Fig. 3. The value of \( V_{ac}^{-1} \) decreases with increasing pressure and shows a tendency to saturate above 1.0 GPa, as shown in Fig. 3(b). Similarly, the \( A \) value simply decreases with increasing pressure and there is no anomaly around \( P_{AF} \).

These results indicate that there is no divergent feature in the pressure dependence of the electronic specific heat coefficient \( \gamma \) at \( P_{AF} \) and most likely at \( P_{sc} \).

We will compare the present result for CePt\(_3\)Si with those for the other heavy-fermion Ce-based superconductors. In a prototype superconductor CeCu\(_2\)Si\(_2\), superconductivity occurs in a nonmagnetic state that is close to antiferromagnetic instability.\(^{25,26}\) The electronic state can be tuned by pressure or the stoichiometric composition of a sample. Superconductivity and antiferromagnetism are basically competitive and do not coexist in the compound. This is quite different from the characteristic feature of CePt\(_3\)Si. Namely, superconductivity coexists...
with antiferromagnetism in CePt$_3$Si.

Another example is pressure-induced superconductivity in CeIn$_3$, CeRh$_2$Si$_2$, and CePd$_2$Si$_2$. These compounds show antiferromagnetic ordering at ambient pressure, $T_N$ decreases with increasing pressure. Superconductivity appears around the magnetic critical region where $T_N$ becomes zero, namely around $P_{AF}$. Superconductivity is considered to be mediated by low-energy magnetic excitations around the magnetic critical region where the heavy-fermion state is realized. The superconducting phase exists in a narrow pressure region around the magnetic critical region, and $T_{sc}$ becomes a maximum around the critical pressure $P_{AF}$. These features are quite different from those of CePt$_3$Si where the bulk superconducting phase exists in a wide pressure region above and below $P_{AF}$, and $T_{sc}$ does not show a maximum at $P_{AF}$. The maximum $T_{sc}$ is realized at ambient pressure. The present superconductivity is most robust at ambient pressure. It is suggested from the pressure dependence of $V_{ac}$ that the critical pressure $P_{AF}$ is not of second order but of first one. Therefore, superconductivity in CePt$_3$Si is different from superconductivity associated with magnetic instability around the magnetic critical region.

The relation between antiferromagnetism and superconductivity in CePt$_3$Si is thus very unique. One might speculate that the superconducting and antiferromagnetic phases compete with each other below $P_{AF}$ and the former overcomes the latter above $P_{AF}$. However, it should be noted that both ordering temperatures decrease with increasing pressure up to $P_{AF}$ and that both $T_{sc}$ and $\Delta C_{ac}/C_{ac}$ ($T_{sc}$) decrease above $P_{AF}$. It seems to be difficult to consider these experimental results from a competitive relation between the two states. From the pressure dependence of $T_{sc}$, it is supposed that the coupling between the antiferromagnetic and superconducting states is basically weak. In order to clarify the relation between the two states, further study is needed. In particular, it is needed to investigate the change in the microscopic superconducting properties such as the pairing symmetry across $P_{AF}$.

In conclusion, we constructed the pressure phase diagram of the heavy-fermion superconductor CePt$_3$Si by ac calorimetry. The bulk superconducting phase exists in a wide pressure region from ambient pressure to about 1.5 GPa, which is far above the antiferromagnetic critical pressure $P_{AF} \approx 0.6$ GPa. The overall features of pressure phase diagram of CePt$_3$Si are different from those of the other heavy-fermion superconductors. Furthermore, it is emphasized, on the basis of the results of the present pressure experiment, that superconductivity in CePt$_3$Si is most robust at ambient pressure where the antiferromagnetic ordered state is realized.

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1) E. Bauer, G. Hilscher, H. Michor, Ch. Paul, E. W. Scheidt, A. Gribanov, Yu. Seropegin, H. Noël, M. Sigrist and P. Rogl: Phys. Rev. Lett. 92 (2004) 027003.
2) S. S. Saxena and P. Monthoux: Nature. 427 (2004) 799.
3) P. W. Anderson: Phys. Rev. B. 30 (1984) 4090.
4) M. Sigrist and K. Ueda, Rev. Mod. Phys. 63, (1991) 239.
5) P. A. Frigeri, D. F. Agterberg, A. Koga and M. Sigrist: Phys. Rev. Lett. 92 (2004) 097001.
6) K. V. Samokhin, E. S. Zil’jstra and S. K. Bose: Phys. Rev. B 69 (2004) 094514, Erratum: Phys. Rev. B 70 (2004) 069902(E).
7) I. A. Sergienko and S. H. Curnoe: Phys. Rev. B. 71 (2005) 214510.
8) K. V. Samokhin: Phys. Rev. Lett. 94 (2005) 027004.
9) P. A. Frigeri, D. F. Agterberg and M. Sigrist: New J. Phys. 6 (2004) 115 .
10) V. P. Mineev: Phys. Rev. B. 71 (2005) 012509.
11) T. Akazawa, H. Hidaka, T. Fujiiwara, T. C. Kobayashi, E. Yamamoto, Y. Haga, R. Settai and Y. Ōnuki: J. Phys.: Condens. Matter. 16 (2004) L29; J. Phys. Soc. Jpn. 73 (2004) 3129.
12) T. Takeuchi, S. Hashimoto, T. Yasuda, H. Shishido, T. Ueda, M. Yamada, Y. Obiraki, M. Shiihoto, H. Kohara, T. Yamamoto, K. Sugiyama, K. Kindo, T. D. Matsuda, Y. Haga, Y. Aoki, H. Sato, R. Settai and Y. Ōnuki: J. Phys.:Condens. Matter. 16 (2004) L333.
13) S. Hashimoto, T. Yasuda, T. Kubo, H. Shishido, T. Ueda, R. Settai, T. D. Matsuda, Y. Haga, H. Harima and Y. Ōnuki: J. Phys.:Condens. Matter. 16 (2004) L287.
14) N. Metoki, K. Kaneko, T. D. Matsuda, A. Galatanu, T. Takeuchi, S. Hashimoto, T. Ueda, T. D. Matsuda, Y. Ōnuki and N. Bernhoeft: J. Phys.:Condens. Matter. 16 (2004) L207.
15) A. Amato, E. Bauer and C. Baines: Phys. Rev. B. 71 (2005) 092501.
16) W. Higemoto, to be published.
17) M. Yogi, Y. Kitaoka, S. Hashimoto, T. Yasuda, R. Settai, Y. Ōnuki, P. Rogl and E. Bauer: Phys. Rev. Lett. 93 (2004) 027003.
18) T. Yasuda, H. Shishido, T. Ueda, S. Hashimoto, R. Settai, T. Takeuchi, T. D. Matsuda, Y. Haga and Y. Ōnuki : J. Phys. Soc. Jpn. 73 (2004) 1657.
19) M. Nicklas, G. Sparn, R. Lackner, E. Bauer and F. Steglich: Physica B 359-361 (2005) 386.
20) P. F. Sullivan and G. Seidel Phys. Rev. 173 (1968) 679.
21) H. Wilhelm: Adv. in Solid State Phys. 43 (2003) 889.
22) I. R. Walker: Rev. Sci. Instrum. 70 (1999) 3402.
23) Y. Uwatoko, S. Todo, K. Ueda, A. Uchida, M. Kosaka, N. Mori and T. Matsumoto: J. Phys.: Condens. Matter. 14 (2002) 11291.
24) C. Petrovic, R. Movshovich, M. Jaime, P. G. Pagluisio, M. F. Hundley, J. L. Sarraz, Z. Fisk and J. D. Thompson: Europhys. Lett. 53 (2001) 354.
25) F. Steglich, J. Aarts, C-D Bredl, W. Lieke, D. Meschede, W. Franz and H. Schafer: Phys. Rev. Lett. 43 (1979) 1892.
26) H. Q. Yuan, F. M. Grosch, M. Deppe, C. Geibel, G. Sparn and F. Steglich: Science 302 (2003) 2104.
27) N D. Mathur, F. M. Grosch, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer and G. G. Lonzrich: Nature. 394 (1998) 39.
28) G. Knebel, D. Braithwaite, P. C. Canfield, G. Lapertot and J. Flouquet: Phys. Rev. B. 65 (2002) 024425.
29) R. Movshovich, T. Graf, D. Mandrus, J. D. Thompson, J. L. Smith and Z. Fisk: Phys. Rev. B. 53 (1996) 8241.
30) S. Araki, M. Nakashima, R. Settai, T. C. Kobayashi and Y. Ōnuki: J. Phys.: Condens. Matter. 14 (2002) L377.
31) A. Demuer, D. Jaccard, I. Sheikin, S. Raymond, B. Salce, J. Thomasson, D. Braithwaite and J. Flouquet: J. Phys.: Condens. Matter. 13 (2001) 9335.