Heavy Fermion Superconductivity and Magnetic Order in Noncentrosymmetric $CePt_3Si$

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$CePt_3Si$ is a novel heavy fermion superconductor, crystallizing in the $CePt_3B$ structure as a tetragonally distorted low symmetry variant of the $AuCu_3$ structure type. $CePt_3Si$ exhibits antiferromagnetic order at $T_N \approx 2.2$ K and enters into a heavy fermion superconducting state at $T_c \approx 0.75$ K. Large values of $H'_{c2} \approx -8.5$ T/K and $H_{c2}(0) \approx 5$ T refer to heavy quasiparticles forming Cooper pairs. Hitherto, $CePt_3Si$ is the first heavy fermion superconductor without a center of symmetry.

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Correlation effects among electrons belong to the key causes for the occurrence of extraordinary properties of solids at low temperatures. The most exciting phenomenon in this respect is superconductivity (SC). Both high temperature and heavy fermion superconductors attracted great interest throughout the past two decades. The most interesting aspects to solve are the specific mechanisms of pairing and the symmetry of the superconducting condensate [1]. While in conventional superconductors the binding of electrons into Cooper pairs is normally mediated by phonons, the origin of pairing in some heavy fermion superconductors is believed to be connected with spin fluctuations, giving rise to unconventional superconducting phases (see, e.g., Ref. [2]).

Pronounced electron correlations are generally found in systems exhibiting the Kondo effect and thus Ce, Yb, and U based compounds are certainly candidates for the occurrence of superconductivity where renormalized quasiparticles form the Cooper pairs. While heavy fermion superconductors are yet missing in Yb based compounds, such phases were identified for both Ce and U systems.

Ce-based heavy fermion superconductors, however, are still few in numbers. Prototypic $CeCu_2Si_2$ exhibits superconductivity below $T_c = 0.7$ K [3]. The application of pressure in the 20 to 30 kbar range to members of this structure family such as $CeCu_2Ge_2$ [4], $CePd_2Si_2$ [5], and $CeRh_2Si_2$ [6] is sufficient to trigger superconductivity as well. Very recently, a new class of compounds, $CeMIn_5$, was added where at ambient conditions heavy fermion superconductivity occurs for $M =$ Co and Ir at $T_c = 2.3$ and 0.4 K, respectively [7,8]. Again, pressure initiates superconductivity, e.g., in $CeRhIn_5$ below $T_c^{max} = 2.1$ K [9]. The crystal structure of latter compounds can be considered quasi-two-dimensional variants of $CeIn_3$ ($AuCu_3$-type). Cubic $CeIn_3$ becomes superconducting at ~25 kbar [2].

The aim of the present Letter is to report on the discovery of both, heavy fermion superconductivity and long range magnetic order in the compound $CePt_3Si$, to evaluate parameters characterizing the superconducting state and to discuss possible pairing scenarios.

$CePt_3Si$ was prepared by argon arc melting and subsequent heat treatment under high vacuum at 870 °C for three weeks. Crystal structure was determined from kappa-CCD single crystal x-ray data and found to be tetragonal, space group $P4mm$ (No. 99), isotypic with the ternary boride $CePt_3B$ [10,11] (see Fig. 1). Crystallographic data (standardized) are $a = 0.4072(1)$ nm and $c = 0.5442(1)$ nm; Ce in site 1(b) at 0.5, 0.5, 0.1468; Pt(1) in 2(c) at 0.5, 0, 0.6504, Pt(2) in 1(a) at 0, 0, 0 (fixed), and Si in site 1(a) at 0, 0, 0.4118.

$CePt_3Si$ derives from hypothetical $CePt_3$ with cubic $AuCu_3$ structure by filling the void with Si, which in

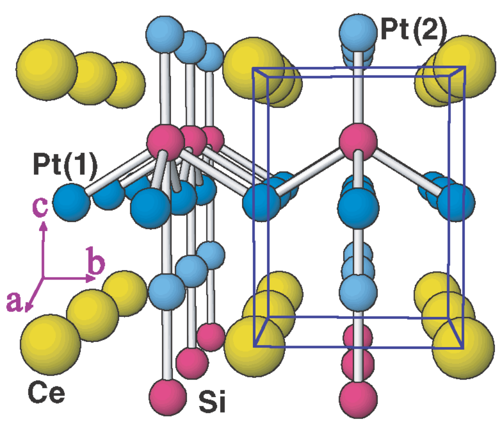

FIG. 1 (color online). Crystal structure of $CePt_3Si$. The bonds indicate the pyramidal coordination $[Pt_5]Si$ around the Si atom. Origin shifted by (0.5, 0.5, 0.8532) for convenient comparison with the parent $AuCu_3$ structure.

addition causes a tetragonal distortion of the unit cell with $c/a = 1.336$. Filling of voids in structures with large cages may dramatically influence physical properties as evidenced in detail for skutterudites $RETM_4X_{12}$ (RE, rare earths; TM, transition metals; X, pnicogen) [12]. Of particular importance with respect to superconductivity is the lack of a center of inversion in the crystal structure of $CePt_3Si$.

Electron microprobe analyses and Rietveld refinements revealed phase purity of the polycrystalline material used for bulk property measurements [13]. The characterization of the paramagnetic state of $CePt_3Si$ from susceptibility measurements (not shown here) reveals a Curie-Weiss behavior with an effective Ce moment $\mu_{eff} = 2.54\mu_B$ and a paramagnetic Curie temperature $\theta_p = -46$ K (data for the fit are taken from the interval $100 \leq T \leq 300$ K). While the former quantity indicates a rather stable 3^+ state of Ce at high temperatures, the large negative θ_p value refers to pronounced antiferromagnetic interactions. In terms of Kondo-type interactions, neglecting crystal field effects, the Kondo temperature would follow from $T_K \approx |\theta_p|/4 \approx 11$ K [14].

Evidence of superconductivity in $CePt_3Si$ is found from resistivity measurements, $\rho(T)$, displayed in Fig. 2 together with data of isostructural nonmagnetic $LaPt_3Si$. $\rho(T)$ of $CePt_3Si$ drops to zero, resulting in $T_c^{mid} = 0.75$ K. At high temperatures, $\rho(T)$ is characterized by a negative logarithmic term, followed by pronounced curvatures at about 75 and 15 K, which may reflect crystal electric field effects in the presence of Kondo-type interactions. Further evaluation of $\rho(T)$ requires knowledge of the phonon contribution which may be taken from homologous and isotypic $LaPt_3Si$ [$a = 0.4115(1)$ nm; $c = 0.5438(2)$ nm]. $LaPt_3Si$ is metallic in the temperature range measured and is simply accounted for in terms of the Bloch-Grüneisen model with a Debye temperature $\theta_D \approx 160$ K [solid line, Fig. 2(a)]. The magnetic contribution to the resistivity, $\rho_{mag}(T)$, is obtained by subtracting from the total measured effect of $CePt_3Si$ both the phonon part (taken from $LaPt_3Si$) as well as the respective residual resistivities. $\rho_{mag}(T)$ exhibits a distinct logarithmic contribution for $T > 100$ K; the maximum around 80 K may indicate the overall crystal field splitting of the $j = 5/2$ Ce $4f^1$ state [dashed line, Fig. 2(a)].

Figure 2(b) illustrates low temperature features of the electrical resistivity of $CePt_3Si$. Besides the onset of superconductivity, there is a distinct change of the slope in $\rho(T)$ around 2 K, which becomes more evident from a $d\rho/dT$ plot [right axis, Fig. 2(b)]. In the context of specific heat data (see below), this anomaly is interpreted as a signature of an initiation of long range magnetic order. A least squares fit according to $\rho = \rho_0 + AT^2$ reveals the residual resistivity $\rho_0 = 5.2$ $\mu\Omega$ cm and a material dependent constant $A = 2.35$ $\mu\Omega\,cm/K^2$.

Corroboration of bulk superconductivity can be read off from specific heat measurements, $C_p(T)$. Results are shown in Fig. 3 as C_p/T vs $\ln T$. Data of $LaPt_3Si$ are added for comparison. Standard analysis for the latter yields $\gamma = 9$ mJ/mol K^2, and $\theta_D^{LT} = 255$ K. Two different features are obvious for $CePt_3Si$ (from higher to lower temperatures): (i) a distinct λ-like anomaly at about 2 K and (ii) a jump of the specific heat around 0.7 K.

The λ-like anomaly of the specific heat at 2.2 K signifies the onset of long range magnetic order. A T^3 dependence of $C_p(T)$ well below the transition may characterize antiferromagnetic ordering (solid line, Fig. 3). Antiferromagnetic order also follows from a field driven shift of the λ-like anomaly towards lower temperatures and is confirmed by the absence of spontaneous magnetization. Above T_N, C_p/T of $CePt_3Si$ exhibits an extended—almost logarithmic—tail, indicative of

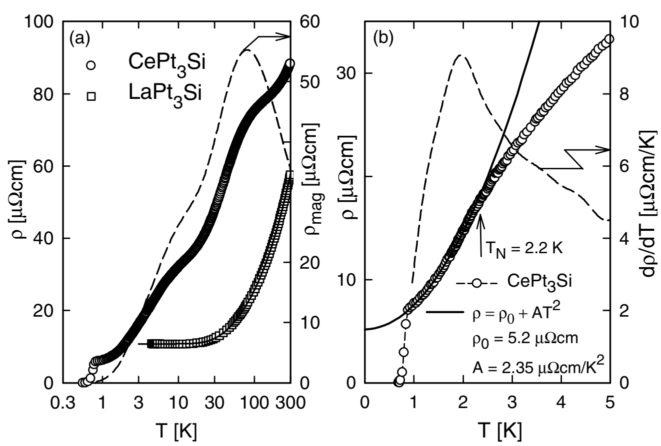

FIG. 2. (a) Temperature dependent electrical resistivity ρ of $CePt_3Si$ and $LaPt_3Si$ plotted on a logarithmic temperature scale. The magnetic contribution $\rho_{mag}(T)$ (dashed line) refers to the right axis. (b) Low temperature details of $\rho(T)$ of $CePt_3Si$. The solid line is a least squares fit (see text) and the dashed line shows $d\rho(T)/dT$.

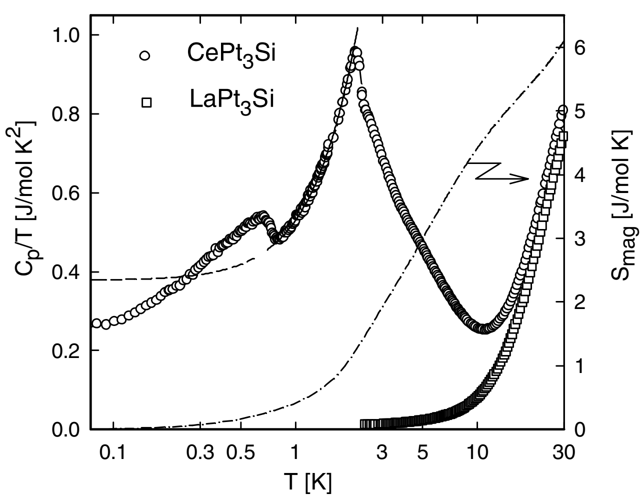

FIG. 3. Temperature dependent specific heat C_p of $CePt_3Si$ and $LaPt_3Si$ plotted as C_p/T vs $\ln T$. The solid and dashed lines are least squares fits (see text). Right axis: temperature dependent magnetic entropy S_{mag} of $CePt_3Si$ (dash-dotted line).

pronounced spin fluctuations in the paramagnetic state. The anisotropy of the crystal structure ($c/a \simeq 1.34$) is supposed to be an additional cause for such enhanced short range magnetic correlations.

The magnetic entropy $S(T)$ was derived from a comparison of $C_p(T)$ of both $CePt_3Si$ and $LaPt_3Si$. Results are shown as a dash-dotted line in Fig. 3. The entropy gain of about $0.22R\ln 2$ at $T = T_N$ is well below that associated with the lifting of the degeneracy of the ground state doublet and suggests ordering with substantially reduced magnetic moments. Involving Kondo-type interactions as a possible mechanism for the above observation would reflect a characteristic temperature T_K of about 10 to 15 K. $R\ln 2$ is reached around 25 K only.

The most interesting feature, the anomaly around 0.7 K, indicates the transition into a superconducting phase, in agreement with the above $\rho(T)$ data. In order to accurately determine T_c, the standard procedure with an idealized jump at T_c is applied, yielding $T_c = 0.75$ K. Some estimation of the normal state Sommerfeld value γ_n may be obtained from an extrapolation of the T^3 dependence (dashed line, Fig. 3), arriving at $\gamma_n \approx 0.39$ J/mol K^2. This extrapolation primely satisfies the basic requirement of entropy balance between the superconducting and the normal state. The jump of the specific heat $\Delta C_p/T_c \approx 0.1$ J/mol K^2 allows calculation of the parameter $\Delta C_p/(\gamma_n T_c) \approx 0.25$, which is well below the figure expected from BCS theory [$\Delta C_p/(\gamma T_c) \approx 1.43$]. Assessing the electronic specific heat coefficient in the superconducting state, $\gamma_s \approx 0.18(1)$ J/mol K^2, from the difference between data derived from the T^3 extrapolation and those estimated at low temperature and zero field yields $\Delta C_p/(\gamma_s T_c) \approx 0.55$, which is still under the BCS value. It should be noted that, e.g., $\Delta C_p/(\gamma T_c)$ of the spin-triplet superconductor Sr_2RuO_4 is similarily downsized [15].

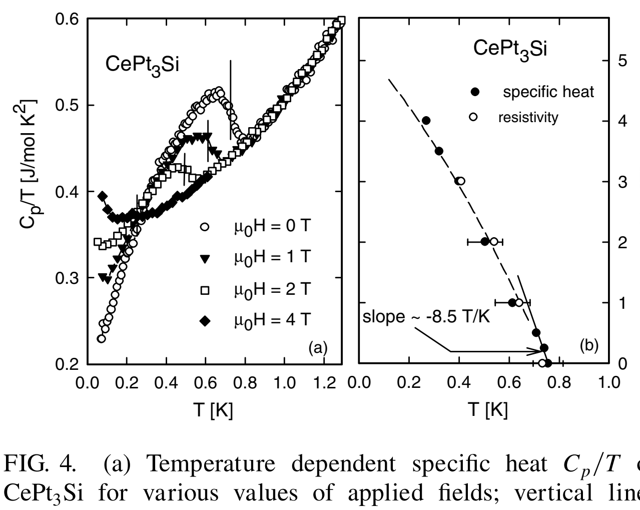

FIG. 4. (a) Temperature dependent specific heat C_p/T of $CePt_3Si$ for various values of applied fields; vertical lines indicate the SC transition. (b) Temperature dependence of the upper critical field H_{c2} deduced from specific heat and resistivity measurements. The solid straight line yields $H'_{c2} \approx -8.5$ T/K, and the dashed line is a guide to the eyes.

The specific heat of $CePt_3Si$ for various external fields is plotted in Fig. 4(a). The application of magnetic fields reduces T_c, giving rise to a rather large change of $dH_{c2}/dT \equiv H'_{c2} \approx -8.5$ T/K, in excellent agreement with the respective data from electrical resistivity [see Fig. 4(b)]. Extrapolation of the field dependent transition temperatures towards zero yields $H_{c2}(0) \approx 5$ T. Furthermore, an estimation of the Sommerfeld coefficient for high fields results in 0.36 J/mol K^2, in fair agreement with the value gained from an extrapolation of normal state, zero field data (see Fig. 3). The upturn of C_p/T at lowest temperatures, reenforcing in magnetic fields, is primarily associated with the nuclear contribution of ^{195}Pt.

By analogy to commonly employed practice concerning heavy fermion superconductors, we estimate in the following a number of parameters from an analysis of superconducting and normal state properties in terms of the BCS theory [16,17] assuming a spherical Fermi surface and incorporating clean and dirty limit terms. Starting parameters are $\gamma_s = 0.18(2)$ J/mol K^2 (as a lower limit), $H'_{c2} = -8.5$ T/K, and $\rho_0 = 5.2$ $\mu\Omega$ cm. Although deviations from a spherical Fermi surface are expected for tetragonal $CePt_3Si$, reasonable physical parameters can be anticipated (compare, e.g., Refs. [17,18]).

The effective Fermi surface S_s is computed [Eq. (2) in Ref. [17]] as $S_s^{\rm cl} \simeq 3.7 \times 10^{20}$ m^{-2} within the clean limit and $S_s^{\rm dl} \simeq 3.5 \times 10^{20}$ m^{-2} for the dirty limit. Considering the dirty limit only, $H'_{c2}(\text{calc}) = -0.77$ T/K, a value rather low with respect to the experimentally derived slope $H'_{c2} = -8.5$ T/K. This indicates that $CePt_3Si$ is not a typical dirty limit superconductor. Irrespective of all the shortcomings present, further calculations are carried out using clean limit parameters.

Combining the Fermi surface with γ_s gives the Fermi velocity $v_F \simeq 5300$ m/s and in the context of the residual resistivity, $\rho_0 = 5.2$ $\mu\Omega$ cm, a mean free path $l_{tr} \simeq 8 \times 10^{-8}$ m can be derived. The coherence length ξ_0 for $T \to 0$ was obtained from two independent relations. One follows from the BCS equation, $\xi_0 = 0.18\hbar v_F/(k_B T_c) \simeq 9.7 \times 10^{-9}$ m. A second expression stems from the well-known formula $\mu_0 H_{c2} = \Phi_0/(2\pi\xi_0^2)$, yielding $\xi_0 \simeq 8.1 \times 10^{-9}$ m, in reasonable agreement with the former. Evaluation of the Ginzburg-Landau parameter $\kappa_{\rm GL} = \lambda/\xi$ requires the knowledge of the thermodynamic critical field $\mu_0 H_c(0) \simeq 26(2)$ mT, which is calculated from the free energy difference between the superconducting and the normal state: $\Delta F(T) = F_n - F_s = \mu_0 H_c^2(T)/2 = \int_{T_c}^{T}\int_{T_c}^{T'} \frac{(C_s - C_n)}{T''} dT'' dT'$. C_s is obtained from the zero field specific heat and C_n is taken from the T^3 extrapolation as indicated by the dashed line in Fig. 3. With $H_{c2}(0) \approx 5$ T one derives a value for $\kappa_{\rm GL} = H_{c2}(0)/(\sqrt{2}H_c) \simeq 140$ which, in turn, determines the London penetration depth $\lambda_L(T \to 0) \simeq 1.1 \times 10^{-6}$ m.

Evaluating Eq. (A.13) of Ref. [17] with $\rho_{\rm max} \approx 100$ $\mu\Omega$ cm yields $S_{hT} \simeq 3.1 \times 10^{21}$ m^{-2}, the Fermi surface at elevated temperatures. The discrepancy between S_s

and S_{hT} suggests that only a minor part of the Fermi surface is involved in forming Cooper pairs while the major part engages in normal state magnetic correlations. This finding seems to be convincingly supported from the lessened value of $\Delta C_p/(\gamma T_c)$. In terms of the coexistence of both superconductivity ($T_c = 0.75$ K) and long range magnetic order ($T_N = 2.2$ K), the downsized specific heat jump at T_c may explain, at least partly, that the Fermi surface is likely to be subdivided into a superconducting part (related to γ_s) and a normal state region.

To classify the behavior of $CePt_3Si$ within a wider framework, we adopt a generic phase diagram which has been observed for various Ce-based systems as well as for $3d$ systems such as MnSi [19]. With an external control parameter δ, such as doping or pressure, the system may be shifted towards $T_{mag} = 0$, defining the quantum critical point (QCP) of magnetic order. In several cases a dome of superconductivity has been discovered in a region around a QCP, e.g., in $CeIn_3$ [2] or $CePd_2Si_2$ [5]. The superconducting instability occurs on the background of fluctuation-induced non-Fermi-liquid behavior. From this point of view we would place $CePt_3Si$ slightly away from the QCP towards the magnetically ordered region. On cooling, the system undergoes successive phase transitions to magnetic order and superconductivity.

The discussion of pairing symmetry in $CePt_3Si$ raises an interesting problem. Here superconductivity occurs within a magnetically ordered phase. This coexistence alone does not imply unconventional pairing. The strong electron correlation effects, however, give very likely rise to pairing with a higher angular momentum. An important aspect of $CePt_3Si$ is the lack of an inversion center in the crystal structure. It is believed that this excludes spin-triplet pairing, since in the absence of inversion symmetry the necessary set of degenerate electron states cannot be provided for this type of pairing [20]. This argument was used to explain the absence of superconductivity close to the quantum critical point in weakly ferromagnetic MnSi [21], although this material exists as an ultrapure single crystal excluding pair breaking scattering [19]. The upper critical field $H_{c2}(0)$ in $CePt_3Si$ is surprisingly high and exceeds the Pauli-Clogston limiting field, which in a simple-minded approach is given by $H_p \approx \Delta/(\sqrt{2}\mu_B) \sim 1.5\,[\mathrm{T/K}]\,T_c \approx 1\ \mathrm{T} < H_{c2}(0)$, implying per definition an effective electron g factor of 2. If this rough estimate holds for $CePt_3Si$, the high $H_{c2}(0)$ would then be incompatible with spin-singlet pairing and rather signals spin-triplet superconductivity. The apparent conflict may be resolved by noticing that the lack of inversion symmetry is not excluding spin-triplet pairing completely. In our case the space group $P4mm$ involves the absence of the mirror plane $z \rightarrow -z$ which yields a Rashba-type spin orbit coupling and leaves the triplet (equal-spin) pairing state $\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}}k_y - \hat{\mathbf{y}}k_x$ (irreducible representation A_{2u} of D_{4h}) as a possible pairing state [22,23].

In summary, $CePt_3Si$ is a heavy fermion compound undergoing both a magnetic transition at $T_N = 2.2$ K and a superconducting transition at $T_c = 0.75$ K. The ratio $l_{tr}/\xi_0 \simeq 8$ is indicative of a clean limit superconductor. Thermodynamic data derived for $CePt_3Si$ suggest that the Cooper pairs are formed of heavy quasiparticles. The pairing is likely affected by the absence of an inversion center. Relatively large H_{c2} might be a hint for the presence of spin-triplet pairing. While still speculative, the prospect of spin-triplet pairing in a system without inversion symmetry is an exciting issue for future studies.

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