Abstract

CePt$_3$Si is a novel ternary compound exhibiting antiferromagnetic order at $T_N \approx 2.2$ K and superconductivity (SC) at $T_c \approx 0.75$ K. Large values of $H_{c2} \approx -8.5$ T/K and $H_{c2}(0) \approx 5$ T indicate Cooper pairs formed out of heavy quasiparticles. The mass enhancement originates from Kondo interaction with a characteristic temperature $T_K \approx 8$ K. NMR and μSR measurements evidence coexistence of SC and long-range magnetic order on a microscopic scale. Moreover, CePt$_3$Si is the first heavy fermion SC without an inversion symmetry. This gives rise to a novel type of NMR relaxation rate $1/T_1$ which is very unique and never reported before for other heavy fermion superconductors. Studies of Si/Ge substitution allow us to establish a phase diagram.

PACS: 74.70.Tx; 71.27.+a; 75.30.Mb

Keywords: CePt$_3$Si; Superconductivity; Antiferromagnetism

1. Introduction

Strongly correlated electron systems have been one of the most interesting topics in condensed
matter physics. The key importance in such research is undoubtedly the discovery of unexpected features and new phases of metals, intermetallics and oxides at low temperatures. Among the topics, quantum phase transitions and related quantum critical phenomena are of particular importance. Quantum critical fluctuations can lead to strong renormalization of normal metallic properties as well as to novel exotic phases emerging from these strongly fluctuating environments. One of the most exciting features in this context is the occurrence of superconductivity (SC).

A recently discovered example is tetragonal CePt$_3$Si [1], the first heavy fermion SC without a centre of inversion. This implies that the electron bands are non-degenerate, except along some high-symmetry lines in the Brillouin zone [2]. Reduced degeneracy, however, weakens or even suppresses SC. Superconductivity with spin-triplet pairings should require inversion symmetry to obtain the necessary degenerate electron states [3]. Thus, it became a widespread view that a material lacking an inversion centre would be an unlikely candidate for spin-triplet pairing [4]. Nevertheless, the extreme large value of the upper critical field $H_{c2}(0) \approx 5$ T of CePt$_3$Si is inconsistent with spin-singlet Cooper-pairs, hinting at some novel features of the SC order parameter.

The aim of this paper is to provide a review of current research on CePt$_3$Si and to locate the system in the standard generic phase diagram of heavy fermion compounds through both substitution and pressure experiments. The paper is organized as follows: After a discussion of normal state properties of CePt$_3$Si, the SC features of CePt$_3$Si are examined before reporting the evolution of magnetism and SC in CePt$_3$(Si,Ge).

2. Normal state properties

Physical properties of ternary CePt$_3$Si are dominated by long range magnetic order below $T_N \approx 2.2$ K and SC below $T_c = 0.75$ K. Crystal electric field (CEF) splitting and Kondo interaction substantially modify Hund’s $J = \frac{3}{2}$ ground state of the Ce ion. The response of the system associated with the mutual interplay of these phenomena will be highlighted below.

Fig. 1 displays $\Delta C_p/T$ vs. $T$ of CePt$_3$Si, where $\Delta C_p$ is defined by the difference between the $C_p(T)$ data of CePt$_3$Si and LaPt$_3$Si, i.e. $C_{mag} \sim \Delta C_p$. This plot exhibits three distinct features: (i) the SC transition of CePt$_3$Si at $T_c = 0.75$ K (see below), (ii) a magnetic transition at $T_N \approx 2.2$ K and (iii) an almost logarithmic tail of $\Delta C_p/T$ above $T_N$, stretching roughly up to 10 K. Well above 10 K, Schottky contributions dominate in the specific heat. The integrated entropy up to 20 K is nearly $R \ln 2$, and the entropy of 8.7 J/mol K integrated up to 100 K is slightly less than $R \ln 4 = 11.53$ J/mol K. These results clearly indicate that the ground state of Ce$^{3+}$ ions is a doublet with the first excited level above 100 K. The logarithmic temperature dependence observed just above the magnetic transition may be considered as hint of non-Fermi liquid behaviour. Therefore, it is a unique observation that non-Fermi liquid behaviour, magnetic ordering and eventually a SC transition consecutively arises on the same sample upon lowering temperature.

In order to analyse in more detail the magnetically ordered region of the system, a model by Continentino [5] is applied with the following
analytic expression for the specific heat well below $T_{mag}$:

\[ C_{mag} = g^2 A_{SW}^{3/2} T^{1/2} \exp(-A_{SW}/T) \times \left[ 1 + \frac{39}{20} \left( \frac{T}{A_{SW}} \right) + \frac{51}{32} \left( \frac{T}{A_{SW}} \right)^2 \right]. \] (1)

This expression is based on antiferromagnetic magnons with a dispersion relation given by $\omega = \sqrt{A_{SW}^2 + D^2 k^2}$, where $A_{SW}$ is the spin-wave gap and $D$ is the spin-wave velocity; $g \propto 1/D^3 \propto 1/\Gamma^3$, and $\Gamma$ is an effective magnetic coupling between Ce ions. A least-squares fit of Eq. (1) to the data below $T_N$ (solid line, Fig. 1) reveals $A_{SW} \approx 2.7$ K, a reasonable gap value with respect to the ordering temperature. Another model calculation with simple antiferromagnetic spin waves with $C_{mag} \propto T^3$ gives reasonable agreement with the data, too. A recent neutron diffraction study on CePt$_3$Si reveals antiferromagnetic ordering below $T_N \approx 2.2$ K with a wave vector $\mathbf{k} = (0, 0, \frac{1}{2})$, i.e. doubling of the magnetic unit cell along $c$-direction [6]. Using both models, we estimate a Sommerfeld coefficient of 0.41 and 0.39 J/mol K$^2$ for the former and latter models, respectively. These figures are in good agreement with an extrapolation of high-field specific heat data where SC is suppressed by applying magnetic fields.

Considering Kondo type interactions to be responsible for the significant renormalization of electrons in CePt$_3$Si as evidenced by the Sommerfeld value $\gamma$, the magnetic entropy allows to estimate the Kondo temperature $T_K$. Taking the results derived in Ref. [7] yields $T_K \approx 7.2$ K. A second possible estimate $T_K$ follows from the competition of the RKKY interaction and the Kondo effect, which leads to a significant reduction of the specific heat jump at $T = T_N$. Following the procedure developed in Ref. [8] gives $T_K \approx 9$ K, in reasonable agreement with the previous estimate.

For better understanding of the magnetic ground state and expected localized character of Ce 4f electrons, inelastic neutron scattering experiments at the HET spectrometer of ISIS, UK, were carried out. In order to accurately and reliably determine magnetic scattering from the magnetic moments of Ce, both CePt$_3$Si and LaPt$_3$Si were investigated in powder form under identical conditions. For phonon subtraction, we used two well-established methods [9], with almost the same results. Our main finding is that there are strong and clear features from 10 to 30 meV. As shown in Fig. 2 scattering intensity ought to be of magnetic origin as the phonon contributions have been subtracted. In order to explain the data, we used the CEF Hamiltonian for Ce$^{3+}$ with $C_{4v}$ point symmetry: $H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4$. With $B_2^0 = -0.4972$ meV, $B_4^0 = 0.0418$ meV, and $B_4^4 = 0.2314$ meV, the observed magnetic scattering is reasonably well explained (solid line, Fig. 2). Keeping the CEF parameters unchanged, we could also explain the data obtained at 94 K equally well. Moreover, the two CEF excitations centred at 13 and 20 meV are also consistent with the heat capacity data as discussed above. We furthermore studied low-energy excitations using lower incident energy to find a weak feature around 1.4 meV. The dispersion of that intensity at $T = 5$ K, particularly around $Q = 0.8$ Å$^{-1}$ is a signature for the development of short-ranged magnetic correlations and explains the anomalous behaviour of the specific heat above magnetic ordering. At higher

![Fig. 2. Magnetic scattering obtained at 6.4 K with the incident energy of 35 meV. The dashed line is for the elastic component with FWHM = 2.4 meV while the short-dashed line represents the quasi-elastic component with FWHM = 0.8 meV. The dashed-dotted line is for the sum of two Lorentzian components centred at 13 and 20 meV with FWHM = 10.0 meV.](image)
temperatures \((T \approx 30\,\text{K})\) scattering becomes \(Q\)-independent. This feature is completely absent in non-magnetic LaPt_3Si. We note that a recent inelastic neutron scattering experiment [6] reported two CEF peaks at 1.0 and 24 meV. However, our data show that their second excitation is most likely to be mistaken.

3. Superconducting properties of CePt_3Si

Signs of bulk SC of CePt_3Si below \(T_c = 0.75\,\text{K}\) are numerous: zero resistivity, diamagnetic signal in the susceptibility, a jump in the specific heat and NMR relaxation rate at \(T_c\). Here, we show in Fig. 3(a) the field-dependent specific heat at low temperatures and at various external magnetic fields. Sommerfeld coefficient \(\gamma_n \approx 0.39\,\text{J/mol K}^2\) of CePt_3Si at zero field can be obtained from a careful extrapolation of the normal state invoking the \(T^3\) dependence associated with antiferromagnetic ordering. This extrapolation also satisfies the basic requirement of an entropy balance between the SC and normal state regions.

The application of magnetic fields reduces \(T_c\), giving rise to a rather large change of \(dH_{c2}/dT \equiv H'_{c2} \approx -8.5\,\text{T/K}\), in good agreement with the conclusion drawn from electrical resistivity [see Fig. 3(b)]. An extrapolation of \(T_c(H)\) towards zero yields \(H_{c2}(0) \approx 5\,\text{T}\), well above the Pauli–Clogston limiting field \([1]\). Furthermore, an estimation of the Sommerfeld coefficient from the high field data gives 0.36 J/mol K², in fair agreement with the value obtained from an extrapolation of the normal state in the zero field data (see Fig. 3). The upturn of \(C_p/T\) at lowest temperatures that gets stronger with increasing magnetic fields is most likely due to the nuclear contribution of \(^{195}\text{Pt}\).

The jump in the specific heat \(\Delta C_p/T\big|_{T_c} \approx 0.1\,\text{J/mol K}^2\), leads to \(\Delta C_p/(\gamma_n T_c) \approx 0.25\), which is much smaller than expected from the BCS theory \((\Delta C_p/(\gamma T_c)) \approx 1.43\). Even using the electronic specific heat coefficient in the SC state, \(\gamma_s \approx 0.18(1)\,\text{J/mol K}^2\), we obtained \(\Delta C_p/(\gamma_s T_c) \approx 0.55\) that is still below the BCS value.

We can think of two scenarios that may well explain such a substantial reduction of \(\Delta C_p/(\gamma T_c)\) with respect to the BCS value; (i) spin triplet SC’s like Sr_2RuO_4 exhibit a similarly reduced magnitude of \(\Delta C_p/(\gamma T_c)\) \([10]\) and (ii) not all electrons condense into Cooper pairs; thus, only a fraction of the carriers mediate the super-current. It implies that electrons responsible for normal state features, like antiferromagnetic order, coexist with those forming the Cooper pairs. In fact, the finite value of \(\gamma_s \approx 0.18\,\text{J/mol K}^2\) provides evidence that even at \(T = 0\,\text{K}\) a significant portion of the Fermi surface is still not involved in the SC condensate.

Microscopic evidence for the latter conclusion can be found from zero-field \(\mu\)SR spectroscopy.
data obtained in the magnetic phase below and above $T_c$ in the magnetic phase. (Fig. 4). At temperatures much above $T_N$, the $\mu$SR signal is characteristic of a paramagnetic state with a depolarization solely arising from nuclear moments. Below $T_N$ the $\mu$SR signal indicates that the full sample volume orders magnetically. High statistic runs performed above and below $T_c$ did not show any change of the magnetic signal, supporting the view of a microscopic coexistence between magnetism and SC. This points to a novel state for SC Ce-based heavy-fermion systems at ambient pressure, for which, to date, magnetism was found to be either absent [11] or strongly competing against SC [12]. The observed coexistence is reminiscent of the situation observed in UPd$_2$Al$_3$ [13], where a model of two independent electron subsets, localized or itinerant, was proposed in view of similar microscopic data [14].

Another microscopic information about the SC state can be obtained from the temperature dependent $^{195}$Pt nuclear spin-relaxation rate $1/T_1$ [15]. Results are shown as $(1/T_1 T)_{SC}/(1/T_1 T)_N$ vs. $T/T_c$ plot in Fig. 5 for 8.9 and 18.1 MHz. The relaxation behaviour $1/T_1 T$ of CePt$_3$Si is characterized by a kind of the Hebel–Slichter anomaly [16] indicating coherence effects as in conventional BCS SC. The peak height, however, is significantly smaller than that observed for conventional BCS SC and, additionally, shows no field dependence at the 8.9 MHz ($H \sim 1$ T) and 18.1 MHz ($H \sim 2$ T) run.

$(1/T_1 T)$ at $H \sim 2$ T seems to saturate at low temperature, which can be attributed to the presence of vortex cores where the normal-state region is introduced; $1/T_1 T$ at 8.9 MHz ($H \sim 1$ T), however, continues to decrease down to $T = 0.2$ K, the lowest measured temperature. Neither an exponential law nor a $T^3$ behaviour is observed for the data down to $T = 0.2$ K. Therefore, CePt$_3$Si is the first HF SC that exhibits a peak in $1/T_1 T$ just below $T_c$ and, moreover, does not follow the $T^3$ law reported for most of the unconventional HF SC (see e.g. Ref. [17] and references therein).

To account for the relaxation behaviour below $T_c$ in non-centrosymmetric CePt$_3$Si, three models were adopted for a description of the temperature dependence of $1/T_1$ at $H \sim 1$ T. The dashed line in Fig. 5 represents a fit according to the Balian–Werthamer model (isotropic spin-triplet SC state) with a value of $2\Delta/k_B T_c = 3.9$ [18], while the dashed-dotted line is a fit using a line-node model with $2\Delta/k_B T_c = 5.1$. The dotted line refers to a point-node model with $2\Delta/k_B T_c = 3.6$. The models used, however, failed to give satisfactory description of the observed temperature dependence of $1/T_1$ over the entire temperature range. While the line-node model gives a reasonable agreement with the data at lowest temperatures, the BW model describes reasonably well the data just below $T_c$. The peak in $1/T_1 T$ would indicate the presence of an isotropic energy gap, even though a coherence effect—inherent for the isotropic spin-singlet s-wave pairing state—is absent.

In almost all previous studies on either conventional and unconventional SC, it was assumed that the crystal has an inversion centre, which allows separate consideration of the even (spin-singlet) and odd (spin-triplet) components of the SC order parameter. In CePt$_3$Si, however, a centre of symmetry is absent. Therefore, the novel relaxation behaviour found below $T_c$ hints at a possibly new class of a SC state being realized in non-centrosymmetric CePt$_3$Si.

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**Fig. 5.** A plot of $(1/T_1 T)/(1/T_1 T)_N$ vs. $T/T_c$ at 8.9 MHz ($H \sim 1$ T) and 18.1 MHz ($H \sim 2$ T). The dashed line is for the Balian–Werthamer model (BW isotropic triplet SC state) with a value of $2\Delta/k_B T_c = 4$. The dotted line assumes a point-node model with $2\Delta/k_B T_c = 3.6$ and the dashed-dotted line represents a fit by a line-node gap model with $2\Delta/k_B T_c = 5.1$. 

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Gorkov and Rashba [19] demonstrated that in the absence of inversion symmetry the order parameter becomes a mixture of spin-singlet and spin-triplet components, which leads, for instance, to the Knight shift attaining a non-zero value at $T = 0\,\text{K}$. A novel idea with respect to the order parameter of systems without inversion symmetry was put forward very recently by Saxena and Monthoux [20]. In their model for the case of broken inversion symmetry, the spins might rotate in the momentum space around the surface.

4. Evolution of magnetism and superconductivity in CePt$_3$(Si, Ge)

In order to follow the evolution of physical properties upon Si/Ge substitution, we prepared several alloys. Guinier X-ray powder intensity profiles of the alloys from the series CePt$_3$ (Si$_{1-x}$Ge$_x$) with $x = 0.02, 0.03, 0.06, 0.10, 0.15$ and $0.20$ were all indexed completely on the basis of a primitive tetragonal unit cell, confirming isotypism with the structure type of CePt$_3$Si [21] with a random substitution of the Si/Ge atoms in the 1a sites of space group P4/mmm. Small secondary peaks arise beyond $x \approx 0.2$ indicating the limit of the CePt$_3$B type phase region. Fig. 6 shows the concentration-dependent lattice parameters $a$ and $c$ as a function of Si/Ge substitution, together with the unit cell volume. The monotonic increase of both $a$ and $c$ parameters yields a growing unit cell volume upon substitution. The general increase of the unit cell volumes reduces chemical pressure on the Ce atoms leading to a decrease of hybridization.

The temperature dependent electrical resistivity $\rho$ of CePt$_3$(Si$_{1-x}$Ge$_x$) is shown for several concentrations $x$ in Fig. 7 for temperatures below about 4 K. The overall $\rho(T)$ values increase due to increasing substitutional disorder on the 1a site. Samples investigated are characterized by a concentration dependent onset of SC, where the Si/Ge substitution suppresses the SC roughly above $x = 0.1$. At somewhat elevated temperatures, $\rho(T)$ exhibits a pronounced curvature which can be taken as a signature for long range magnetic order, in agreement with specific heat measurements. A magnetic instability is evidenced from the resistivity data in terms of a $d\rho/dT$ plot (lines, Fig. 7, right axis). $d\rho/dT$ shows pronounced anomalies, referring to broadened magnetic phase transitions; the respective temperatures increase continuously with increasing Ge content.

The magnetic contribution to the specific heat of CePt$_3$(Si$_{1-x}$Ge$_x$) is plotted in Fig. 8 as $C_{\text{mag}}/T$ vs. $T$ for several compositions up to $x = 0.2$ from 1.8 to 20 K. $C_{\text{mag}}$ is derived as in Fig. 1 using the measured data of isostructural non-magnetic LaPt$_3$Si. A common feature in all the data sets is a mean-field-like anomaly, which is associated with magnetic order of the cerium sublattice. $T_N$
rises with increasing Ge content and, simultaneously, the phase transitions appear to be broadened, in agreement with the observation made from $d\rho/dT$. While for $x = 0$, the logarithmic behaviour well above $T_N$ is quite pronounced and obvious, its temperature range becomes narrower with increasing Ge content as a consequence of increasing magnetic interactions, driving a magnetic instability at much higher temperatures. The double-peak feature for $x = 0.2$ is most likely due to a secondary phase as indicated by our XRD analysis.

The phase diagram shown in Fig. 9 summarizes characteristic temperatures deduced for CePt$_3$(Si$_{1-x}$Ge$_x$) at ambient pressure, as well as data derived from resistivity studies on CePt$_3$Si under hydrostatic pressure up to about 15 kbar [22]. In order to make comparison between substitution and pressure, Murnaghan’s equation of state is adopted, with a bulk modulus $B_0 = 1000$ kbar. Pressure of 15 kbar corresponds then to a reduction of the unit cell volume of about 1%. The phase diagram thus deduced resembles very well those characteristics, which determine the standard generic phase diagram associated with a quantum phase transition. The increase of the unit cell volume by the Si/Ge substitution is, in a first-order approximation, responsible for a decrease of hybridization. This has two consequences: (i) the Kondo interaction decreases and (ii) magnetic interaction strengthens, causing the observed increase of the magnetic transition temperature. Concomitantly, the SC transition temperature becomes suppressed and finally, SC vanishes beyond $x > 0.1$. Increasing hydrostatic pressure is responsible for a decrease of both $T_N$ and $T_c$. Ternary CePt$_3$Si thus appears to be, by chance, situated at the maximum position of the “superconducting dome”. Whether or not this SC dome is constrained within the magnetic phase is still unknown. Depending on the particular choice of $B_0$, i.e. smaller or larger than $B_0 = 1000$ kbar the volume below $V/V_0 = 1$ becomes stretched or narrower. In any case, $T_c^{\text{max}}$ is well below the magnetic phase line, being a signature that Cooper pairing may be mediated by magnetic fluctuations rather than by the standard phonon mechanism.

We summarize that non-centrosymmetric CePt$_3$Si is a heavy fermion SC with $T_c = 0.75$ K that orders magnetically at $T_N = 2.2$ K. The NMR relaxation rate $1/T_1$ shows unexpected features which were found before neither in conventional nor in heavy fermion SC, indicative of very unusual shapes of the SC order parameter. In fact, a number of theoretical scenarios support these observations. The Si/Ge substitution simply drives a volume expansion, thus magnetism is stabilized and SC finally ceases to exist.
Acknowledgements

This work is supported by the Austrian FWF P16370, P15066 and by the DFG, SFB 484 (Augsburg). The Austrian–Russian exchange within project I.18/4 is acknowledged. JGP and WYS acknowledge financial support by the CSCMR of Seoul National University.

References

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