Pair breaking by non-magnetic impurities in the non-centrosymmetric superconductor CePt$_3$Si

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We have studied the effect of Ge-substitution and pressure on the heavy-fermion superconductor CePt$_3$Si. Ge-substitution on the Si-site acts as negative chemical pressure leading to an increase of the unit-cell volume, but also introduces chemical disorder. We carried out electrical resistivity and AC heat-capacity experiments under hydrostatic pressure on CePt$_3$Si$_{1-x}$Ge$_x$ ($x = 0, 0.06$). Our experiments show that the suppression of superconductivity in CePt$_3$Si$_{1-x}$Ge$_x$ is mainly caused by the scattering potential, rather than volume expansion, introduced by the Ge dopands. The antiferromagnetic order is essentially not affected by the chemical disorder.

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The physics of unconventional superconductivity in materials without inversion symmetry like the non-centrosymmetric heavy-fermion (HF) superconductor CePt$_3$Si has recently become a subject of growing interest. The lack of inversion symmetry - one of the key symmetries for Cooper pairing - is responsible for a number of novel properties. In particular, a specific property of the non-centrosymmetric superconductors is that the spin-orbit coupling qualitatively changes the nature of single-electron states involved in the Cooper pairing by lifting their spin degeneracy and splitting the conduction bands. For strong spin-orbit coupling, when the band splitting exceeds the superconducting (SC) energy scales, Cooper pairing between electrons with opposite momenta occurs only, if they are from the same non-degenerate band. This scenario is presumably realized in CePt$_3$Si, since, here, band-structure calculations yield an energy of the spin-orbit coupling, $E_{SO} \approx 1000$ K, which is much larger than the SC critical temperature $T_c \approx 0.75$ K. In the band picture, the SC order parameter is given by a set of complex wave functions, one for each band, which are coupled due to interband Cooper-pair scattering. The overall structure of the gap equations resembles those of multiband superconductors, except that the pairing symmetry is more peculiar. While each order parameter is an odd function of the momentum, the gap symmetry and the positions of the nodes are determined by one of the even representations of the point group of the crystal. Re-writing this in the spin representation, one finds the order parameter to become a mixture of singlet and triplet components, and the latter appears without any spin-triplet term in the underlying pairing interaction. This is a consequence of the band splitting as well as the difference between the gap magnitude and the density of states in the different bands.

Polycrystalline CePt$_3$Si orders antiferromagnetically at $T_N = 2.2$ K, while superconductivity appears below $T_c = 0.75$ K. High quality single crystals, in contrast, are SC below $\sim 0.5$ K, while $T_N$ stays unchanged. Previous pressure studies of CePt$_3$Si revealed a suppression of $T_N$ with increasing pressure as frequently observed in Ce-based HF metals. However, the signature of $T_N$ in electrical resistivity ($\rho$) and specific heat ($C$) is lost for pressures above $p^* \approx 0.6$ GPa, indicating a sudden suppression of $T_N$. $T_c$ decreases monotonically with application of pressure and becomes $T_c = 0$ at a critical pressure $p_c \approx 1.8$ GPa. On the other hand, the crystal lattice can be expanded, e.g., by isoelectronic substitution of Si by Ge. In CePt$_3$Si$_{1-x}$Ge$_x$ increasing Ge concentration leads to a monotonic increase of the average values of both the $a$ and the $c$ axis lattice parameter without changing the anisotropy significantly. Therefore, in a first approximation, the effect of doping could be thought of as negative chemical pressure causing a decrease of the hybridization between the $4f$ and the conduction electrons. Thus, the Kondo interaction should decrease and the magnetic RKKY interaction increase, in agreement with the observed linear increase of $T_N$ with increasing Ge concentration. In contrast, $T_c$ decreases immediately on Ge substitution. Thus, CePt$_3$Si appears to be situated right at the position where $T_c$ attains its maximum in the temperature-pressure ($T-p$) phase diagram.

We will address the interplay of antiferromagnetism and superconductivity in CePt$_3$(Si,Ge) and the effect of non-magnetic impurities on the SC state by $\rho(T)$ and $C(T)$ experiments under hydrostatic pressure.

High quality poly-crystalline material was prepared by high-frequency melting and subsequent annealing. Pressures up to 1.85 GPa were generated in a Cu-Be clamp-type cell using Flourinert FC-75 as the pressure-transmitting medium. High purity Sn served as pressure gauge. Temperatures down to 50 mK could be reached in a $^3$He/$^4$He dilution cryostat. The resistivity was measured by a conventional four-probe AC technique using an LR-700 resistance bridge. In addition, AC specific-heat measurements were conducted using a Au/AuFe...
thermocouple as thermometer and a ruthenium-oxide resistance as heater utilizing a digital lock-in amplifier.

Figure 1 shows $\rho(T)$ of CePt$_3$Si and CePt$_3$Si$_{0.94}$Ge$_{0.06}$ for selected pressures. At low-$p$ $\rho(T)$ exhibits, for both compounds, the typical features of a Kondo-lattice system in the presence of a strong crystalline electric-field (CEF) splitting, with shoulders around 10 and 70 K, respectively. The lower shoulder is due to Kondo scattering off the CEF ground-state doublet, consistent with the stronger pressure dependence of the Kondo temperature $T_K$ of the CePt$_3$Si$_{0.94}$Ge$_{0.06}$ compound, while in the case of pure CePt$_3$Si it has already merged with the high-$T$ shoulder. Thus the pressure response of $T_K$ in CePt$_3$Si$_{0.94}$Ge$_{0.06}$ exceeds the one in CePt$_3$Si.

At $p = 0$, CePt$_3$Si and CePt$_3$Si$_{0.94}$Ge$_{0.06}$ order antiferromagnetically at $T_N = 2.2$ and 2.8 K, before becoming SC at $T_c = 0.75$ and 0.29 K, respectively. A smooth change in the curvature indicates the onset of antiferromagnetic (AF) order in $\rho(T)$. The inflection point of $\rho(T)$ agrees well with $T_N$ obtained from specific-heat data (cf. inset of Fig. 1). In the following we define $T_N$ from the inflection point in $\rho(T)$. $T_N(p)$ is suppressed with increasing pressure. Above $p^* \approx 0.6$ GPa, no signature of the AF transition is observed anymore in either $\rho(T)$ or $C(T)$ data, suggesting a sudden suppression of $T_N(p)$ in both materials. For CePt$_3$Si similar results have been reported previously. Consistent with the stronger pressure dependence of $T_K$ in the Ge-substituted system, the absolute value of its slope $|dT_N(p)/dp|_{p=0}$ is larger than that of the stoichiometric compound $|dT_N(p)/dp|_{p=0} = -1.2$ K/GPa and $-0.94$ K/GPa, respectively.

Figure 2 shows the results of a fit of $\rho(T) = \rho_0 + A'T^n$ to the low-$T$ resistivity data ($T \leq T \leq \min(T_N, 4K)$). As expected, the alloying-induced disorder causes an increase of the residual resistivity, $\rho_0$, by a factor of about 4 from CePt$_3$Si to CePt$_3$Si$_{0.94}$Ge$_{0.06}$. For both samples $\rho_0(p)$ is nearly pressure independent; only a weak decrease is observed for the Ge-substituted sample. Especially, there is no feature in $\rho_0(p)$ at $p^*$ where the AF order disappears. $\rho(T)$ follows a $T^2$ behavior inside the AF state. Simultaneously with the loss of the signature of the Néel transition in resistivity and heat capacity, the temperature dependence of $\rho$ changes drastically for both compounds in that the pressure dependence of resistivity exponent $n(p)$ exhibits a sharp step from $n \approx 2$ below $p^* \approx 0.6$ GPa to $n \approx 1.3$ at higher pressure. Therefore, the heavy Fermi-liquid (FL) phase ($n = 2$) at low pressure becomes unstable against a non-Fermi liquid phase ($n < 2$), which exists in the whole pressure range $p^* < p \leq 1.88$ GPa, the highest pressure in our experiment. In the FL phase $A'$ is a measure of the effective quasi-particle – quasi-particle (QP–QP) scattering cross section. $A'$ stays constant in the AF phase and, therefore, the QP – QP scattering cross section does not change. In particular, there is no divergence of the QP – QP scattering rate or a strong increase of $\rho_0(p)$ as it might be expected on approaching a quantum critical point.

The results of our experiments are summarized in the phase diagram displayed in Fig. 3. $T_{c,\rho_{onset}}$ and $T_{c,\rho_{final}}$ are taken as the temperatures where the resistivity is reduced to 90% and 10% of its value in the normal state, respectively. In CePt$_3$Si, $T_{c,\rho_{final}}$ extrapolates to $T = 0$ at about $p \approx 1.8$ GPa. Whereas $T_c$ is suppressed upon increasing pressure, the resistive transition successively broadens, i.e. from $\Delta T = T_{c,\rho_{onset}} - T_{c,\rho_{final}} = 105$ mK
at 0 GPa to $\Delta T = 420$ mK at 1.56 GPa. Compared with CePt$_3$Si the SC state in CePt$_3$Si$_{0.94}$Ge$_{0.06}$ responds more sensitively to external pressure. At 0.24 GPa, no $\rho = 0$ state is observed any more, but the onset of the SC transition in resistivity is still visible up to 1 GPa. A recent neutron Laue-diffraction study on high-quality single crystalline CePt$_3$Si evidenced a wide distribution of lattice constants of $\approx 10^{-3}$, which might be interpreted as a wide range of effective pressures across the the sample volume. Consequently, a substantial width of $\Delta T$ is already observed in CePt$_3$Si.$^{15}$

Considering the dome-like shape of the SC phase often observed in a $T-p$ phase diagram in HF superconductors, CePt$_3$Si seems to be situated close to the $T_c$-maximum which occurs at a hypothetical minor negative pressure.$^{10}$ The small initial slope of $T_c(p)$ suggests that the maximum $T_c$ exceeds $T_c$ at ambient pressure only slightly. It is important to note that substituting Si by isoelectronic Ge expands the unit-cell volume without changing the electronic structure significantly.$^{10}$

Doping with 6% Ge leads to an increase of the unit-cell volume, $V$, of $\approx 0.38\%$ compared with the stoichiometric compound. Using the bulk modulus $B = 162$ GPa,$^{16}$ this corresponds to the application of a hypothetical negative pressure of $\Delta p = -0.6$ GPa, resulting in a reduction of $T_c$ and an increase of $T_N$. Since the volume expansion reduces the 4f-conduction electron hybridization and, this way, strengthens the RKKY interaction (while weakening the Kondo effect), the observed dependence of $T_N$ on the unit-cell volume can be easily explained. Since the partial Ge-substitution for Si should have no significant effect on the local environment of the Ce$^{3+}$ ions, it can be expected that disorder has only a minor influence on the magnetic properties in this material.

The consequence of adding a non-magnetic impurity in a non-centrosymmetric superconductor is far from being obvious. Theoretical analysis shows that adding non-magnetic impurities results$^{12}$ for weak disorder, in the suppression of $T_c$ for both conventional as well as unconventional Cooper pairing. Moreover, for the conventional Cooper pairing, non-magnetic impurities yield a decrease of $T_c$: superconductivity, however, will not be destroyed completely. This is because the origin of the suppression of $T_c$ is interband impurity scattering which tends to reduce the difference between the gap magnitudes in the two bands. This costs energy and thus suppresses $T_c$. However, once both gaps have become equal, adding further impurities should be harmless for superconductivity, which is in striking contrast to our observation that superconductivity is completely suppressed for a doped sample of 10% Ge.$^{10}$ Thus, the latter observation points toward an unconventional symmetry of the Cooper pairing in CePt$_3$Si, involving lines of nodes. The particular symmetry of the order parameter is not yet known in CePt$_3$Si, however, line nodes occur for any of the $A_2$, $B_1$, or $B_2$ of the $C_{4v}$ group. Then, for all
physically concentration, $N(0)$ is the density of states at the Fermi level, and $I$ is the scattering potential.

The solid line in Fig. 4 shows the fit of the AG function to our experimental results as a function of $n_{imp}$ and assuming $N(0)I^2 \sim 1.6 \times 10^{-4}$ eV. The agreement between our experimental data and the AG theory clearly points toward the unconventional symmetry of the SC order parameter in CePt$_3$Si which is destroyed by non-magnetic impurities. In addition, we find that the strength of the potential scattering off the Ge dopants, rather than the Ge-induced expansion of the average unit-cell volume, more strongly affects $T_c$, quite opposite to the response of $T_N$ to these parameters.

On applying pressure the SC state in CePt$_3$Si$_{0.94}$Ge$_{0.06}$ is suppressed already at a small pressure of only 0.2 GPa. The pressure dependence of $T_c$ is much stronger than in the case of CePt$_3$Si. Especially, $T_c(p)$ does not exhibit an initial increase as one would expect it in the simple picture which was first suggested by combining the results on CePt$_3$Si$_{1-x}$Ge$_x$ and the pressure studies on CePt$_3$Si in a $T-V$ phase diagram (see also Fig. 4). Our results, however, suggest that the effect of non-magnetic impurities on the superconductivity cannot be neglected.

In conclusion, our results show that the suppression of $T_c$ on substitution of CePt$_3$Si is basically not due to a volume effect, but is caused by scattering processes on non-magnetic impurities introduced by the Ge-substitution. We have argued that the peculiar effect of non-magnetic impurities in non-centrosymmetric superconductors plays an important role in destroying superconductivity in CePt$_3$Si. In addition, we have shown that the SC state in the Ge-substituted sample is much more sensitive to pressure than in CePt$_3$Si.

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