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Pair breaking by nonmagnetic impurities in the noncentrosymmetric superconductor $CePt_3Si$

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We have studied the effect of Ge substitution and pressure on the heavy-fermion superconductor $CePt_3Si$. Ge substitution on the Si site acts as negative chemical pressure leading to an increase in the unit-cell volume but also introduces chemical disorder. We carried out electrical resistivity and ac heat-capacity experiments under hydrostatic pressure on $CePt_3Si_{1-x}Ge_x$ ($x=0,0.06$). Our experiments show that the suppression of superconductivity in $CePt_3Si_{1-x}Ge_x$ is mainly caused by the scattering potential, rather than volume expansion, introduced by the Ge dopants. 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 noncentrosymmetric heavy-fermion (HF) superconductor $CePt_3Si$,[1] 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 noncentrosymmetric 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.[2–4] For strong spin-orbit coupling, i.e., 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 nondegenerate band. This scenario is presumably realized in $CePt_3Si$, 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.[1,3] 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. Rewriting 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 $CePt_3Si$ orders antiferromagnetically at $T_N=2.2$ K while superconductivity appears below $T_c=0.75$ K.[1,5] High-quality single crystals, in contrast, are SC below ~0.5 K, while T_N stays unchanged.[6] Previous pressure studies of $CePt_3Si$ revealed a suppression of T_N with increasing pressure as frequently observed in Ce-based HF metals.[7–10] However, the signature of T_N in electrical resistivity (ρ) 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 $CePt_3Si_{1-x}Ge_x$ increasing Ge concentration leads to a monotonic increase in the average values of both the a-axis and the c-axis lattice parameter without changing the anisotropy significantly.[11] Therefore, in a first approximation, the effect of doping could be thought of as negative chemical pressure causing a decrease in the hybridization between the $4f$ and the conduction electrons. Thus, the Kondo interaction should decrease and the magnetic Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction increase, in agreement with the observed linear increase in T_N with increasing Ge concentration.[11] In contrast, T_c decreases immediately on Ge substitution.[11] Thus, $CePt_3Si$ 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 nonmagnetic impurities on the SC state by $\rho(T)$ and $C(T)$ experiments under hydrostatic pressure.

High-quality polycrystalline material was prepared by high-frequency melting and subsequent annealing.[1] 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 $^3He/^4He$ 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 $CePt_3Si$ and $CePt_3Si_{0.94}Ge_{0.06}$ 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,[12] with shoulders around 10 K and 70 K, respectively. The lower shoulder is due to Kondo scattering off the CEF ground-state doublet, consistent with the Kondo temperature $T_K\approx 10$ K,[1] while scattering off the fully degenerate $j=5/2$ multiplet of Ce^{3+} leads to the second shoulder at

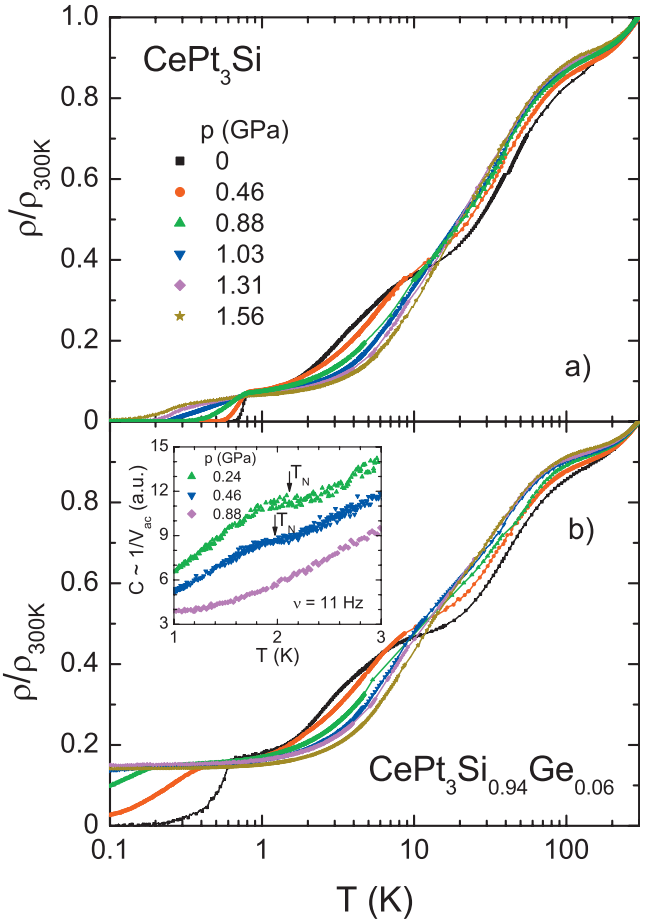

FIG. 1. (Color) $\rho(T)$ normalized by $\rho_{300\ \mathrm{K}}$ of (a) $CePt_3Si$ and (b) $CePt_3Si_{0.94}Ge_{0.06}$ on a logarithmic temperature scale for different pressures. Inset of (b): heat capacity of $CePt_3Si_{0.94}Ge_{0.06}$ plotted as $C \propto 1/V_{ac}$ vs T for $p=0.24$, 0.46, and 0.88 GPa. T_N, determined by an equal entropy approximation, is indicated by arrows.

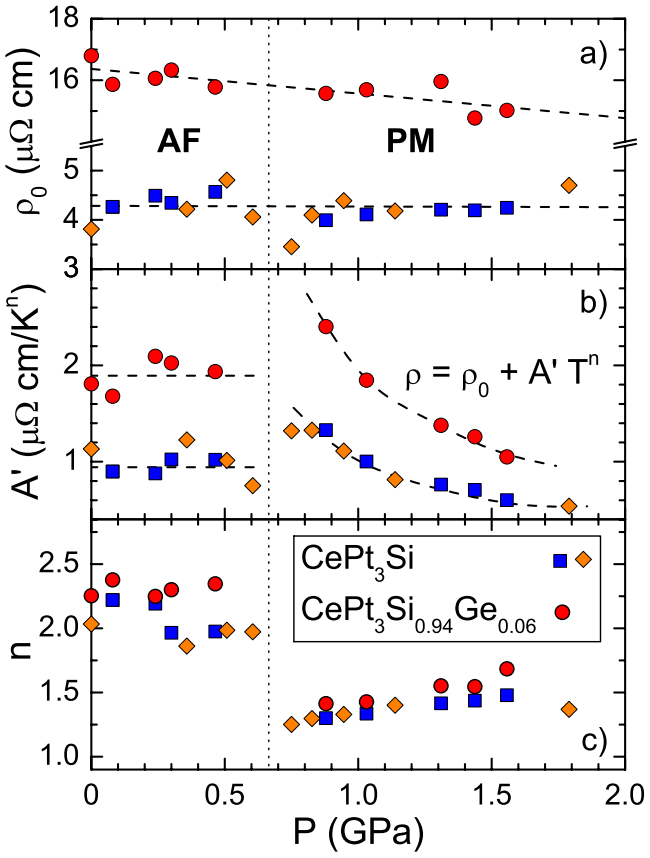

FIG. 2. (Color online) Fit parameters, (a) ρ_0, (b) A', and (c) n obtained by fitting the low-temperature normal-state resistivity using $\rho(T)=\rho_0+A'T^n$. In addition to the results from this work, for $CePt_3Si$ data from Ref. 8 has been analyzed (diamonds). The vertical dotted line delineates the border between the AF and the PM regions. Dashed lines are guides to the eye.

high temperatures. The position of the high-T shoulder is nearly independent of pressure, which indicates that the overall CEF splitting is not changing significantly in the pressure range up to 2 GPa. On the other hand, the low-T shoulder shifts strongly to higher temperature with increasing pressure and finally merges with the high-T shoulder. This behavior is typical for Ce-based Kondo-lattice compounds where T_K generally increases with pressure. Although, the overall pressure and temperature dependence of the resistivity is similar for both, pure and Ge-substituted $CePt_3Si$, the low-T shoulder depends much stronger on pressure in case of $CePt_3Si_{0.94}Ge_{0.06}$. At 1.31 GPa, a clear local shoulder at low temperatures is still apparent in the Ge-substituted compound, while in the case of pure $CePt_3Si$ it has already merged with the high-T shoulder. Thus the pressure response of T_K in $CePt_3Si_{0.94}Ge_{0.06}$ exceeds the one in $CePt_3Si$.

At $p=0$, $CePt_3Si$ and $CePt_3Si_{0.94}Ge_{0.06}$ order antiferromagnetically at $T_N=2.2$ and 2.8 K, before becoming SC at $T_c=0.75$ K and 0.29 K, respectively.[1,11] 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(b)]. 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 $CePt_3Si$ similar results have been reported previously.[9,10] 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 ($T_c \le T \le \min\{T_N, 4\ \mathrm{K}\}$). As expected, the alloying-induced disorder causes an increase in the residual resistivity, ρ_0, by a factor of about 4 from $CePt_3Si$ to $CePt_3Si_{0.94}Ge_{0.06}$. 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 ρ 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^*

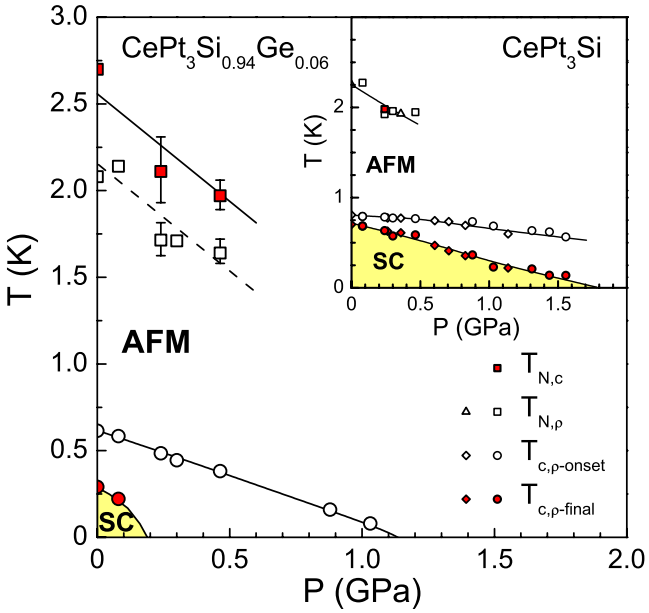

FIG. 3. (Color online) T-p phase diagram of $CePt_3Si_{0.94}Ge_{0.06}$ (main panel) and $CePt_3Si$ (inset). In case of $CePt_3Si$, additional data from Ref. 8 (triangles and diamonds) have been included.

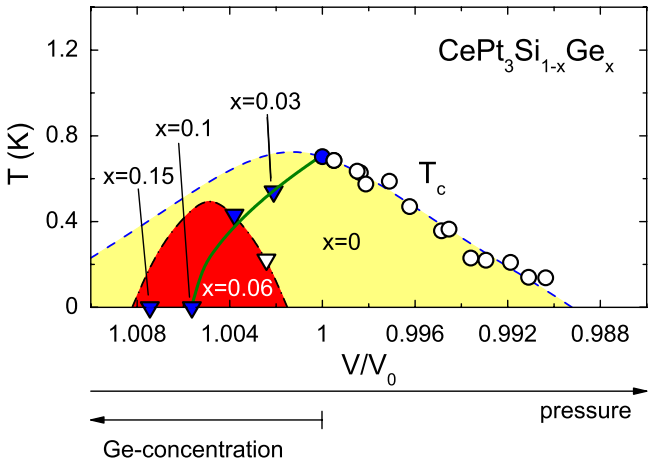

FIG. 4. (Color online) Phase diagram of $CePt_3Si_{1-x}Ge_x$ as function of the reduced unit-cell volume (V/V_0) with V_0 the unit-cell volume of $CePt_3Si$ (Ref. 17). Triangles correspond to T_c of Ge-substituted samples while circles present T_c of $CePt_3Si$. Ambient pressure data is indicated by filled symbols while data under applied pressure by open symbols. T_c of the Ge-substituted samples at $p=0$ is taken from Ref. 11. The solid line represents a fit to the data according to the AG function. The dashed and dashed-dotted lines are suggesting the shape of the SC dome for $CePt_3Si$ and $CePt_3Si_{0.94}Ge_{0.06}$, respectively, for the case that the SC behavior would be only governed by volume effects. See text for details.

≈ 0.6 GPa to ≈ 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 quasiparticle-quasiparticle (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 in $\rho_0(p)$ 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. $T_{c,\rho\ \mathrm{onset}}$ and $T_{c,\rho\ \mathrm{final}}$ are taken as the temperatures where the resistivity is reduced to 90% and 10% of its value in the normal state, respectively. In $CePt_3Si$, $T_{c,\rho\ \mathrm{final}}$ 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 $\Delta T = T_{c,\rho\ \mathrm{onset}} - T_{c,\rho\ \mathrm{final}} = 105$ mK at 0 GPa to $\Delta T = 420$ mK at 1.56 GPa. Compared with $CePt_3Si$ the SC state in $CePt_3Si_{0.94}Ge_{0.06}$ 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 1.03 GPa. No surprise, for the alloy, the resistive transition at ambient pressure is found to be already rather broad, $\Delta T = 325$ mK. A recent neutron Lamor-diffraction study on high-quality single-crystalline $CePt_3Si$ evidenced a wide distribution of lattice constants of $\approx 10^{-3}$, which might be interpreted as a wide range of effective pressures across the sample volume. Consequently, a substantial width of ΔT is already observed in $CePt_3Si$.[13]

Considering the domelike shape of the SC phase often observed in a T-p phase diagram in HF superconductors, $CePt_3Si$ seems to be situated close to the T_c maximum which occurs at a hypothetical minor negative pressure.[11] 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.[11]

Doping with 6% Ge leads to an increase in the unit-cell volume, V, of $\approx 0.38\%$ compared with the stoichiometric compound. Using the bulk modulus $B=162$ GPa,[14] this corresponds to the application of a hypothetical negative pressure of $\Delta p = -0.6$ GPa, resulting in a reduction in T_c and an increase in 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 nonmagnetic impurity in a noncentrosymmetric superconductor is far from being obvious. Theoretical analysis shows that adding nonmagnetic impurities results,[15] for weak disorder, in the suppression of T_c for *both* conventional as well as unconventional Cooper pairing. Moreover, for the conventional Cooper pairing, nonmagnetic impurities yield a decrease in 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.[11] Thus, the latter observation points toward an unconventional symmetry of the Cooper pairing in $CePt_3Si$, involving lines of nodes. The particular symmetry of the order parameter is not yet known in $CePt_3Si$, however, line nodes occur for any of the A_2, B_1, or B_2 of the C_{4v} group. Then, for all types of unconventional pairing, the suppression of T_c is described by the universal Abrikosov-Gor'kov (AG) function,[16] $\ln[\frac{T_c}{T_{c0}}]=\Psi(\frac{1}{2})-\Psi(\frac{1}{2}+\frac{\alpha}{2\pi k_B T_c})$, where T_{c0} is the SC transition temperature without impurities and $\alpha=\frac{\hbar}{2\tau}$ is the pair-breaking parameter. Here, $\tau^{-1}=2\pi n_{imp}N(0)I^2$ is the inverse collision time resulting for the impurity potential with n_{imp} being the impurity 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 $CePt_3Si$ which is destroyed by nonmagnetic 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 $CePt_3Si_{0.94}Ge_{0.06}$ 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 $CePt_3Si$. 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 $p=0$ results on $CePt_3Si_{1-x}Ge_x$ and the pressure studies on $CePt_3Si$ in a T-V phase diagram (see also Fig. 4).[11] Our results, however, suggest that the effect of nonmagnetic impurities on the superconductivity cannot be neglected.

In conclusion, our results show that the suppression of T_c on Ge substitution in $CePt_3Si$ is basically not due to a volume effect but is caused by scattering processes on nonmagnetic impurities introduced by the Ge substitution. We have argued that the peculiar effect of nonmagnetic impurities in noncentrosymmetric superconductors plays an important role in destroying superconductivity in $CePt_3Si$. In addition, we have shown that the SC state in the Ge-substituted sample is much more sensitive to pressure than in $CePt_3Si$.

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