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Impurities in heavy fermion superconductors

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In honor of Martin Peter's 60th birthday.

Abstract. Stimulated by the unusual phase diagram of the superconducting states in $U_{1-x}Th_xBe_{13}$ which furnished a renewed debate about the nature of the heavy-fermion superconducting order parameter (conventionally anisotropic *vs.* unconventional), we have initiated a study of the effect of impurities on the superconducting state of $CeCu_2Si_2$. We conclude a 'diamagnetic' pair-breaking effect by the non-magnetic impurities La and Y and an additional "paramagnetic" one by Gd. Comparison with low-temperature resistivity results in the normal state leads to the assumption that the T_c – depression for vanishing dopant concentration is determined by a highly anisotropic scattering of the heavy quasiparticles off these impurities.

1. Heavy-fermion superconductivity: retrospect

The relationship between magnetism and superconductivity has been a subject of much interest in solid-state physics during the past three decades, beginning with early investigations on the pair-breaking effect of magnetic impurities in host superconductors [1, 2] and ending up in the recent discovery of high- T_c superconductivity in ceramic Cu-oxides [3]. In contrast to the so-called 'magnetic superconductors' [4–6] where magnetism and superconductivity originate from quite different type of electrons (localized *d*- or *f*-electrons and delocalized conduction-electrons), in 'heavy-fermion superconductors' the *f*-electrons are responsible for both magnetic and superconducting phenomena. Because of this rather unexpected [7] situation, first indications of superconductivity in UBe_{13} [8] as well as $CeCu_2Si_2$ [9] were discarded as a bulk effect and ascribed to some secondary phases.

In fact, the $CeCu_2Si_2$ samples used for the transport measurements by Franz et al. [9] contained strange phases at the 10% level. Since at this time we were interested to learn whether, in the absence of 'spurious superconductivity', the same kind of enhanced Fermi-liquid effects as discovered before for $CeAl_3$ [10] can be seen in $CeCu_2Si_2$ too, near single-phase material was prepared in collaboration with Herbert Schäfer (E. Zintl-Institut, TH Darmstadt). Although

these more thoroughly prepared CeCu_2Si_2 samples showed several similarities to CeAl_3 below $T = 1$ K, notably a dominating 'heavy-fermion' derived specific heat contribution γT with $\gamma \approx 1 \text{ J/K}^2$ mole, pronounced superconducting phase-transition anomalies were detected at $T_c \approx 0.6$ K [11, 12]: A gigantic specific heat jump ΔC and a substantial Meissner effect [13, 14] proved that superconductivity was a bulk property of CeCu_2Si_2 , in contrast to the conjecture in [9].

The size of ΔC , which scaled with the giant normal-state specific heat γT_c , along with a steep slope of the upper critical field curve at T_c ($\approx -20T/\text{K}$) [15], revealed the existence of Cooper pairs that are formed by the same heavy-mass quasiparticles causing the exciting Fermi-liquid effects in the normal state. The phenomenon of 'heavy-fermion superconductivity', though enthusiastically welcomed by most theorists, was not accepted by the majority of the experimentalists. The counter argument most frequently offered involved the disastrous pair-breaking capability of dilute Ce^{3+} ions when dissolved in classical superconductors. For example, much less than $x = 1$ at % doping suffices to suppress superconductivity completely in $(\text{La}_{1-x}\text{Ce}_x)\text{Al}_2$ [16].

Because of phenomenological similarities of CeCu_2Si_2 with liquid ^3He [14], speculations came up rather early about exotic superconducting states, notably triplet pairing [17]. This view appeared to be supported by strikingly unusual properties of the two U-based heavy-fermion superconductors UBe_{13} [18] and UPt_3 [19]. In particular, a T^3 -dependence of the specific heat of UBe_{13} [20] and the presence of 'paramagnons' in UPt_3 [19, 21, 22] were considered strong hints for triplet (or more generally: odd parity) superconductivity; for an early review, see Stewart [23]. On the other hand, the dominating effect of Pauli paramagnetic limiting on $B_{c2}(T)$ [24, 25, 26] and, in particular, the observation of a large DC Josephson effect [27, 28] ruled out the possibility of odd-parity pairing in this material. After a substantial body of work on heavy-fermion superconductors during the past years [29], it is fair to state that at the present time the nature of their order parameter Δ is still not understood [30]: Despite an increasing contention [29] that Δ is highly anisotropic and of even parity (corresponding to singlet pairing), with gap zeros along lines on the Fermi surface, the main question remains as yet unanswered: Is the order parameter a conventional one, in that it exhibits the symmetry of the Fermi surface [31], or is it of the unconventional type, with a symmetry lower than that of the Fermi surface [32]?

2. Conventional vs. unconventional pairing: coexistence of two superconducting order parameters in $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$

Any anisotropic superconducting order parameter, regardless of whether it is of the conventional or unconventional type, should be seriously affected by impurities: Already ordinary potential scattering should lead to 'diamagnetic' pair breaking, i.e. depairing of the orbital state of the Cooper pairs [33, 34]. In fact, a strong depression of T_c upon alloying in the at% range has been observed for both CeCu_2Si_2 [35] and UBe_{13} [36, 37]. As an interesting by-product of these

investigations, the initial T_c -depression by Gd in UBe_{13} was found to cause no resolvable contribution of ‘paramagnetic’ pair breaking via the Gd-spin [36]. This was taken another indication for a potential odd-parity-pairing state. On the other hand, the size of the critical Gd-concentration, $x_{cr}(T_c \rightarrow 0)$, *did* suggest such an extra contribution to be present in the case of $\text{Ce}_{1-x}\text{Gd}_x\text{Cu}_2\text{Si}_2$ [35].

Recent activities in this branch of heavy-fermion research derived from the surprising discovery by Ott et al. [38] of a double-peak structure, at T_{ca} and T_{cb} , in the specific heat of UBe_{13} doped with 2–5 at% Th. Several attempts to explain these experimental observations have been made: In analogy to the phase diagram of superfluid ^3He , the lower transition at T_{cb} was ascribed to a complete transformation of one unconventional superconducting phase into a second one [39]. Alternatively a ‘superconducting glass transition’ [40] and an antiferromagnetic transition within the superconducting state [41] have been proposed. The latter proposal was based upon the observation of a giant anomaly in the ultrasound attenuation and seemed to gain additional support by very recent μSR -results that indicate the formation of an extremely small ordered magnetic moment ($\approx 10^{-3} \mu_B$) below T_{cb} [42]. However, a discontinuous increase in the slope of the lower critical field, B_{c1} vs T , at T_{cb} found [43] for a 3 at% Th sample, makes an antiferromagnetic transition unlikely: Our $B_{c1}(T)$ results indicate a stabilization of superconductivity [44], cf. Figs 1a and 1b. The height of the specific-heat discontinuity at T_{cb} , ΔC_b , is explained exclusively by the increase in superconducting condensation energy, i.e. any (additional) antiferromagnetic transition would not contribute measurably to ΔC_b . In [44] it is also argued that the lower critical field data can be understood only, if one assumes a second order parameter Δ_b to add, at T_{cb} , to the first order parameter Δ_a , already formed at

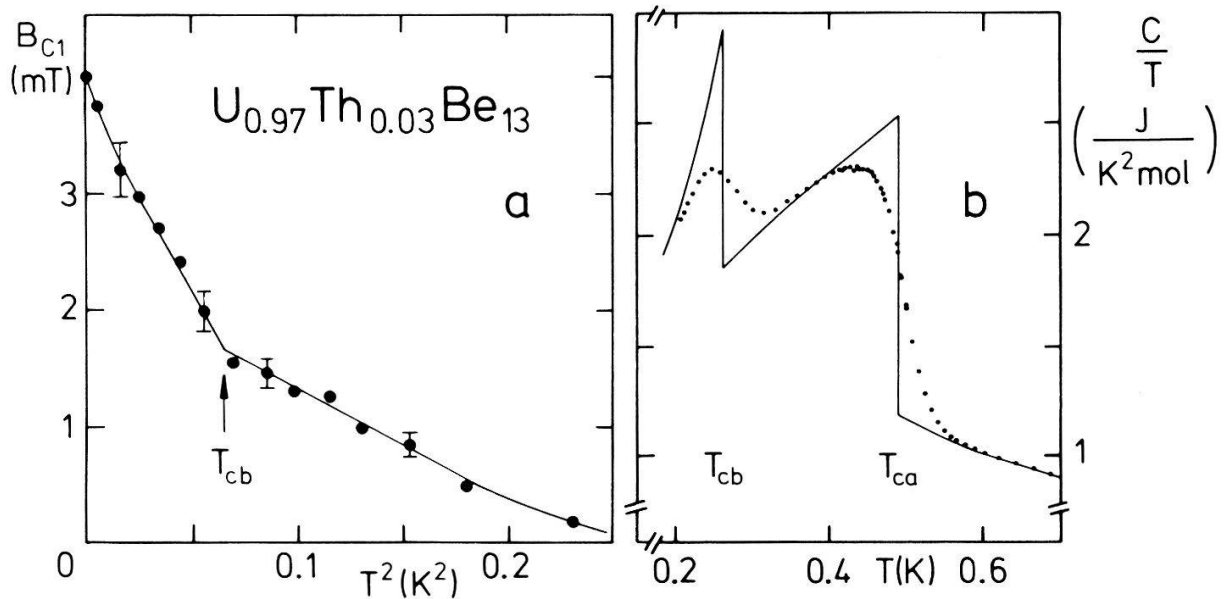


Figure 1

a: Lower Critical magnetic field of $\text{U}_{0.97}\text{Th}_{0.03}\text{Be}_{13}$ in a plot B_{c1} vs T^2 . Solid line is a guide to the eye [43]. b: Specific heat of the same sample. Solid line is a schematic replacement of the data by two sharp transitions [45].

T_{ca} . Since at the lower transition temperature not the slightest anomaly can be resolved in the diamagnetic response of the sample [45], it has moreover to be conjectured that Δ_a and Δ_b coexist on different parts of the Fermi surface, rather than in different parts of real space [44].

The most straightforward conclusion from such a scenario would invoke two order parameters of *different* symmetries, at least one of which being necessarily of the unconventional type. In fact, Kumar and Wölfle [46] recently proposed the coexistence of an *s*-wave and a *d*-wave order parameter. On the other hand, in [44] we emphasized the possibility that both Δ_a and Δ_b may have the symmetry of the renormalized Fermi surface, i.e. are conventional order parameters. Such a situation can, however, only exist if the coupling between the Fermi-surface sheets carrying the two different order parameters is extremely weak. Thus, the scattering rate due to Th impurities in UBe_{13} *between* those sheets, τ_{inter}^{-1} , has to be small compared to τ_{intra}^{-1} , describing the scattering events *within* the respective sheets. In this picture, Th gives rise to a highly anisotropic scattering rate. On the other hand, La- and Lu-impurities seem to act less anisotropically in that they are causing τ_{inter}^{-1} to be closer to τ_{intra}^{-1} : In the presence of these scattering centers, a second superconducting order parameter does not form [37]. From the results on $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ one infers a need to understand better the role of impurities in the heavy-fermion superconducting state. Such an investigation has been initiated recently with $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ quasi-binary alloys [47].

3. 'Superconducting spectroscopy' of impurities in $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$

The aim of our investigation of the effect of non-magnetic impurities (La and Y) on the superconducting properties of $\text{CeCu}_{2.2}\text{Si}_2$ [48] was threefold: (1) Does impurity scattering cause 'pair-breaking' (rather than 'pair weakening') as expected for anisotropic superconductors [33, 34]? (2) Is the impurity-induced disturbance of the coherent normal state related to that of the superconducting state? (3) Are there significant differences in the effects due to La-impurities, with the same valence-electron configuration ($6s^25d^1$) as Ce on the one hand, and due to Y-impurities ($5s^24d^1$) on the other? The preliminary answers to these questions given in [47] will be briefly reviewed in the following. In addition, we shall discuss new results on Gd-doped $\text{CeCu}_{2.2}\text{Si}_2$ which point to the importance of paramagnetic pair breaking in heavy-fermion superconductors.

Before focussing on the issues listed above, we should mention the most obvious influence of impurities on the properties of a Kondo system, i.e. due to the different atomic sizes of Ce on the one hand and the respective dopant on the other. This results in a change of the mean lattice parameter and, thus, of the characteristic single-ion energy $k_B T^*$ (Kondo energy) which determines to a good degree the thermodynamics of a Kondo system. In any single-ion model, T^* is inversely proportional to the Pauli spin susceptibility, χ_0 , and to $\gamma_0 = C_{el}/T$, the Sommerfeld coefficient of the electronic specific heat as $T \rightarrow 0$. According to pressure work on Ce systems [49], we expect that replacement of Ce by the

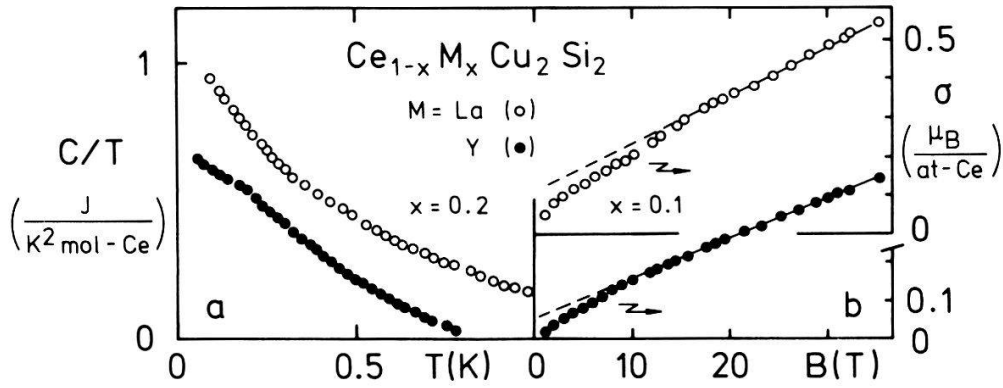


Figure 2

a: Sommerfeld coefficient $\gamma = C/T$ vs T (at $B = 0$) for 20 at% alloys $Ce_{1-x}M_xCu_2Si_2$ with $M = La$ and $M = Y$ [50]. b: High-field magnetization vs B measured at $T = 1.4$ K for the corresponding 10 at% alloys [51].

smaller Y atom (average compression of the lattice) should lead to a T^* -increase, whereas doping with La (slightly bigger than Ce) should give rise to a T^* -reduction. In fact, the corresponding quasi-binary alloys based on stoichiometric $CeCu_2Si_2$ -material demonstrate the expected difference in T^* via low-temperature specific heat [50] and high-field magnetization results [51] (Figs 2a and 2b). Both γ_0 and χ_0 (which equals the slope of $\sigma(B)$ above 15T) reveal that T^* for La-doped $CeCu_2Si_2$ is about 15% lower than for the Y-doped system: $T_{La}^* < T_Y^*$. The same tendency is recognized in the specific heat of $Ce_{1-x}M_xCu_{2.2}Si_2$ in Figs 3a and 3b, i.e. when comparing the $x = 0.03$ data for $M = La$ with those for $M = Y$.

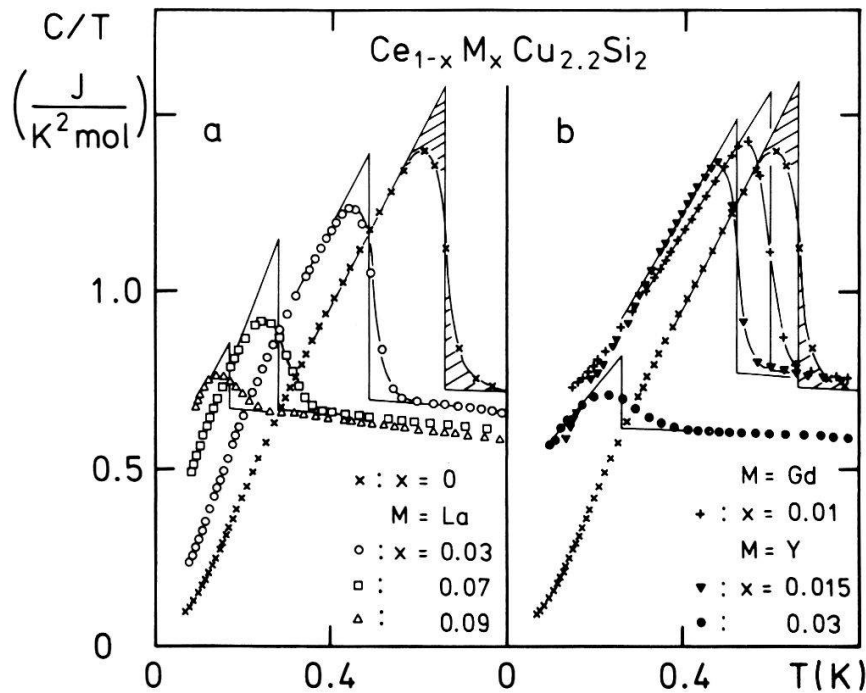


Figure 3

Specific heat as C/T vs T for quasibinary systems $Ce_{1-x}M_xCu_{2.2}Si_2$ with $M = La, Gd$ and Y . For the sake of clarity, units are per mole of the actual alloy, rather than per mole of Ce. Lines through data points are intended as guides to the eye. Thin solid lines and hatched areas mark idealized specific-heat jumps.

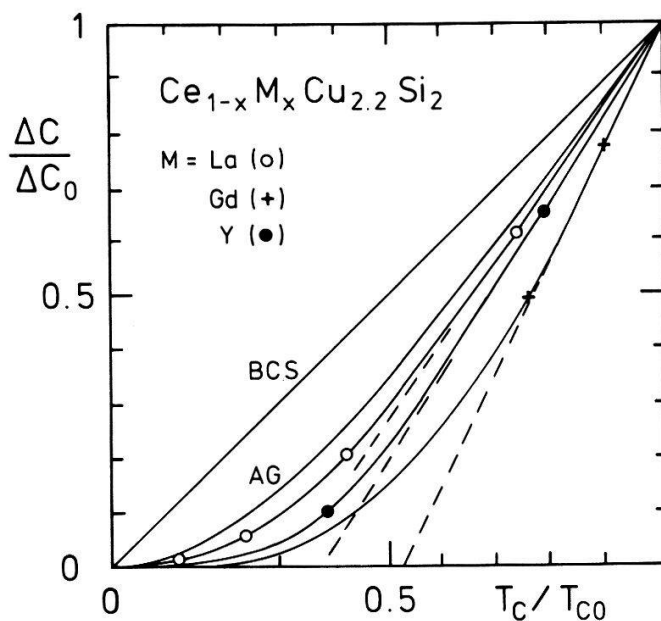


Figure 4
 $\Delta C/\Delta C_0$ vs T_c/T_{c0} for $Ce_{1-x}M_xCu_{2.2}Si_2$ with $M = La, Gd$ and Y . Solid lines through data points are guides to the eye. Dashed lines indicate initial slopes. Also shown are results of the Abrikosov-Gor'kov (AG) theory [54] and the BCS 'law of corresponding states'.

The salient features in Figs 3a and 3b are:

- (1) For a given dopant, the specific-heat jump height ΔC , as derived from the measured data in a straightforward way, is depressed upon increasing dopant concentration x more strongly than the transition temperature T_c .
- (2) Compared with the host superconductor $CeCu_{2.2}Si_2$, for which only a small, if any, residual linear term $\gamma_s T$ exists in the specific heat, increasing dopant concentration gives rise to the development of a substantial γ_s .
- (3) Compared with La-doping, Y-doping causes T_c and ΔC to drop more strongly (cf. $x = 0.03$ data).

It was emphasized in [47] that the data on both La- and Y-doped $CeCu_{2.2}Si_2$ are formally similar to those of so-called 'Kondo superconductors' i.e. superconducting Kondo alloys like $(La_{1-x}Ce_x)Al_2$ [52, 53]. This is shown in Fig. 4 where the depression of ΔC is compared with that of T_c for the different dopants. Such a representation of $\Delta C/\Delta C_0$ vs T_c/T_{c0} (ΔC_0 and T_{c0} referring to the host superconductor) has frequently been used for a 'superconducting spectroscopy' of the magnetic state of impurities in classical superconductors: 'Nearly magnetic' impurities like U in Th [52] give rise to pair weakening and obey the BCS 'law of corresponding states'. Rare-earth ions with stable magnetic moments like Gd^{3+} in $LaAl_2$ [52] rather cause pair breaking and yield $\Delta C/\Delta C_0$ vs T_c/T_{c0} data following the universal result of the Abrikosov-Gor'kov (AG) theory [54]. Even stronger relative ΔC -depressions can originate from the particularly efficient pair-breaking mechanism introduced by a Kondo ion [52, 53]. Applying the theory of Müller-Hartmann and Zittartz [55] to the initial slopes we found that both La- and Y-impurities in the Kondo lattice $CeCu_{2.2}Si_2$, though not carrying

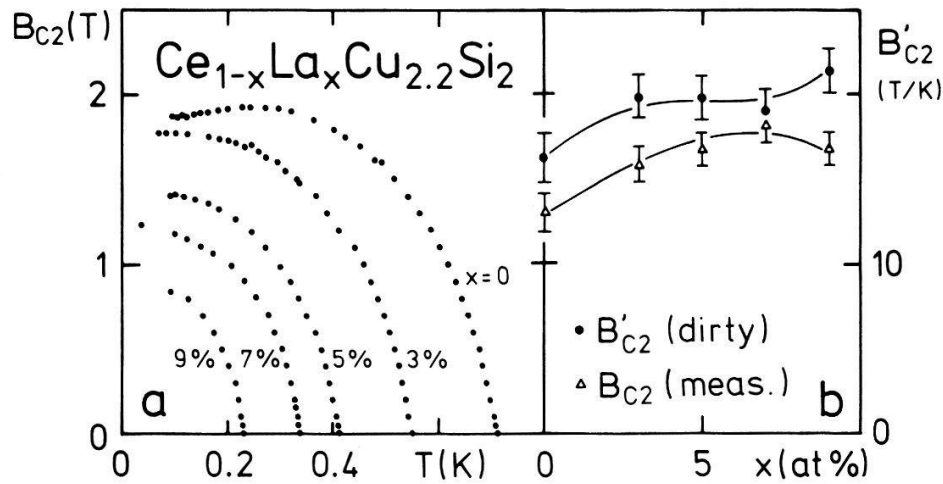


Figure 5

a: Upper critical magnetic field, $B_{c2}(T)$, for $\text{Ce}_{1-x}\text{La}_x\text{Cu}_{2.2}\text{Si}_2$ alloys with varying La-concentration. b: Initial slope, B'_{c2} , as measured and as calculated for the dirty limit (see text) vs. La-concentration in $\text{Ce}_{1-x}\text{La}_x\text{Cu}_{2.2}\text{Si}_2$.

magnetic moments, act formally like Kondo ions of spin 1/2 with characteristic temperatures $T_{h,La} \approx 350$ K and $T_{h,Y} \approx 95$ K [56]. Thus, there exists an anticorrelation to the characteristic single-ion temperatures T^* , for which $T_{La}^* < T_Y^*$. Here, instead of the Kondo temperature T_K characterizing, e.g. a Ce^{3+} ion in LaAl_2 , we prefer to use the label T_h in order to indicate that a non-magnetic impurity replacing Ce in a Kondo lattice may be considered a ‘Kondo hole’.

The pronounced depression of the specific-heat-jump height relative to the T_c -depression confirms the anticipated pair-breaking capability of non-magnetic (ie. La and Y) impurities in a Kondo lattice. This, in turn, may be taken as a strong indication for an anisotropic superconducting order parameter in CeCu_2Si_2 . Further support for La-induced pair-breaking stems from an analysis of upper critical field data: In Fig. 5a we show the resistively determined $B_{c2}(T)$ -curves for the investigated La-doped samples. For $x = 0$ one observes a broad maximum in $B_{c2}(T)$ near 0.2 K which has been reported before [26] and ascribed to the coherent nature of the ground state of stoichiometric CeCu_2Si_2 . Consequently, doping destroys this coherence effect. Figure 5b shows the initial slopes $B'_{c2} = -(\delta B_{c2}/\delta T)_{T=T_c}$ of the critical field curves as a function of La-concentration x . The measured data are compared with the ‘dirty-limit slope’ calculated from $B'_{c2}(\text{dirty}) = 4490 (Tm^2K/\Omega J) \cdot \gamma \cdot \rho_0$ [57]. $B'_{c2}(\text{dirty})$ represents the critical-field slope of a conventional s -wave superconductor in the dirty limit. For small doping, $B'_{c2}(\text{measured})$ increases with increasing $B'_{c2}(\text{dirty})$ as expected from the equation given above. For $x = 0.09$, however, we observe a decrease of the measured slope, while $B'_{c2}(\text{dirty})$ further increases. This result is at least consistent with a La-induced pair-breaking effect.

There are different potential reasons for the observed pair breaking by ‘Kondo holes’ [47]: Firstly, since Kondo holes act as nearly resonant scatterers [58, 59], the formation of localized excited states (LES) near E_F efficiently fills up the gap (‘gapless superconductivity’) as predicted [60, 61] and, in fact, observed

[53] for Kondo impurities in non-Kondo lattice superconductors. In case of our $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ quasibinaries, the presence of LES appears to be well documented by the linear $\gamma_s T$ -contribution to the low-temperature specific heat. Secondly, scattering into ‘normal channels’ appears to be relevant: Earlier results on $B_{c2}(T)$ [43] and the thermal conductivity [62] of CeCu_2Si_2 suggest that for this compound part of the reconstructed Fermi surface (for $T \ll T^*$) contains states with light effective masses and an only very small, if any, superconducting order parameter. Scattering of Cooper pairs into these “normal” states constitutes a pair-breaking process. If this mechanism is the dominant one, it follows from the stronger pair-breaking strength of Y compared to La that the former impurity gives rise to a more efficient scattering between the superconducting and ‘normal’ portions of the Fermi surface, i.e. $\tau_{\text{inter}}^{-1}/\tau_{\text{intra}}^{-1}$ is larger for Y- than La-impurities.

Turning now to the effect of Gd, we recognize a surprisingly marked initial ΔC -depression: Whereas Gd-impurities in non-Kondo lattice superconductors cause a pair breaking in agreement with AG theory, implying $m_{\Delta C} = -(\Delta C/\Delta C_0)/(T_c/T_{c0})_{T \rightarrow T_c} \approx 1.43$ [54], the corresponding number for Gd-doped $\text{CeCu}_{2.2}\text{Si}_2$ (2.13) exceeds those for $M = \text{La}$ (1.45) and $M = \text{Y}$ (1.6) distinctly. We take this as an indication for an extra pair-breaking mechanism originating from the Gd-spin and acting on the spin state of the Cooper pairs.

In Fig. 6a we show the concentration dependence of T_c for the three $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ systems. Whereas a rather linear $T_c(x)$ curve is found in the presence of non-magnetic La-impurities, the data for $M = \text{Gd}$ follow well the prediction of AG theory [63]. This is a convincing proof for our conclusion that the Gd-spin breaks up the spin pairing of the Cooper pairs, i.e. leads to an increase of the spin susceptibility. Like the Josephson effect [27, 28] and the Pauli

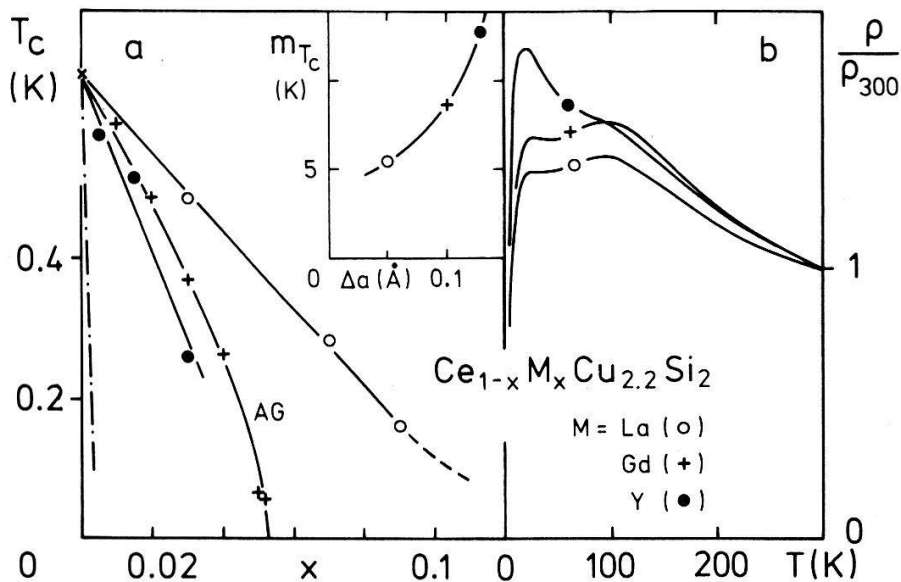


Figure 6

a: Concentration dependence of T_c for $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ alloys with $M = \text{La}$, Gd and Y. Dash-dotted line represents earlier data on $\text{Ce}_{1-x}\text{Sc}_x\text{Cu}_2\text{Si}_2$ [35]. Inset shows initial slope $m_{T_c} = -(\delta T_c/\delta x)_{x \rightarrow 0}$ as a function of lattice-parameter mismatch $\Delta a = |a_{\text{Ce}_1\text{Si}_2} - a_{\text{M}\text{Cu}_{2.2}\text{Si}_2}|$. b: Temperature dependence of the electrical resistivity normalized to the 300 K value for $x = 3$ at% alloys $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ with $M = \text{La}$, Gd and Y.

limiting in $B_{c2}(T)$ [25, 26], this result points to an even-parity rather than odd-parity pairing state in CeCu_2Si_2 .

If we compare the initial $T_c(x)$ slopes $m_{T_c} = -(\delta T_c / \delta x)_{x \rightarrow 0}$ in Fig. 6a, we find a monotonous increase on going from $M = \text{La}$ to Gd and further to Y . It confirms earlier results on stoichiometric CeCu_2Si_2 containing the respective dopants [35] as well as $M = \text{Sc}$. For the latter, a dramatic depression of T_c was found, cf. dash-dotted curve in Fig. 6a.

Following [47], we wish to relate the systematic change in m_{T_c} to an also systematic change in the normal-state, low-temperature resistivity (Fig. 6b): Y-impurities appear to be the most efficient scatterers, whereas Gd- and, notably, La-impurities give rise to much less incoherent scattering. One might be tempted to explain these observations by tracing back [35] the differences in scattering strength to differences in the atomic size of the respective dopants relative to that of Ce, cf. inset of Fig. 6a. This would imply that the scattering is dominated by the strain fields around the impurity. However, with the (plausible) assumption that this is a dominantly isotropic scattering process one estimates m_{T_c} values (corresponding to the measured resistivity changes) which exceed the observed ones by up to three orders of magnitude [64]. Therefore, *we have to conclude a highly anisotropic scattering* ($\tau_{\text{intra}}^{-1} / \tau_{\text{inter}}^{-1} \gg 1$, cf. Sect. 3): In this case, T_c of the anisotropic superconductor $\text{CeCu}_{2.2}\text{Si}_2$ is conceivably insensitive against replacement of Ce by La impurities, similar to what is found when U in UBe_{13} is substituted by Th impurities (cf. Sect. 3). We have suggested in [47] that the more pronounced pair-breaking capability of Y-impurities is related to its valence-electron configuration ($5s^2 4d^1$) which differs from that of Ce and La ($6s^2 5d^1$). In the same kind of reasoning one understands the relatively weak initial T_c – depression due to Gd-impurities on the one hand and the precipitous drop of T_c in the presence of Sc-impurities ($4s^2 3d^1$) on the other.

We wish to note that in $\text{Ce}_{1-x}\text{Gd}_x\text{Cu}_{2.2}\text{Si}_2$, the paramagnetic pair-breaking effect inferred from the AG-type concentration dependence of $T_c(x)$ (and from the ΔC depression, Fig. 4) must contribute to the observed initial T_c -depression, too. Assuming that m_{T_c} is dominated by the valence-electron configuration rather than by the size mismatch, we obtain an *upper limit* for the paramagnetic contribution via $m_{T_c, \text{para}} \cong m_{T_c}(\text{Gd}) - m_{T_c}(\text{La}) \approx 3 \text{ K}$. This is substantially smaller than what we expect from the concentration dependence of the ‘spin-glass temperature’ T_G of higher concentrated $\text{Ce}_{1-x}\text{Gd}_x\text{Cu}_{2.2}\text{Si}_2$ systems [65]. The apparent discrepancy between $T_G(x)$ and the T_c depression could possibly be resolved in the following way: T_G is determined by the RKKY interaction which samples features of the entire conduction band, whereas $m_{T_c, \text{para}}$ tracks the density of states in the vicinity of the Fermi level. In view of the smallness of this effect – which, depending on the assumptions made, may even be considered negligible [36] – we would like to stress again, however, that the pair-breaking effect due to the Gd-spin is clearly demonstrated if one compares the critical concentrations $x_{cr}(T_c \rightarrow 0)$ rather than the initial $T_c(x)$ -slopes for the different $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ systems (fig. 6a), in agreement with the finding by Spille et al. [35].

4. Perspective

The following observations were discussed in this paper:

1. Non-magnetic substitutes for Ce in $\text{CeCu}_{2.2}\text{Si}_2$ give rise to true pair breaking as concluded from a pronounced depression of the specific heat jump in proportion to the depression of T_c .
2. Compared with La-impurities, Y-impurities are more efficient pair breakers.
3. Owing to the ΔC -depression and to the concentration dependence of T_c , which follows the AG result, an additional, spin-derived contribution to the pair breaking exists for Gd-impurities.
4. The absolute values of the initial $T_c(x)$ -slopes increase continuously with increasing mismatch between the size of Ce and that of the respective dopants.
5. Whereas La- and Gd-impurities are relatively harmless scatters, Y-impurities cause enormous incoherent scattering in the low-temperature, normal phase of $\text{CeCu}_{2.2}\text{Si}_2$.

We would like to emphasize that the data of this work are preliminary and have to be completed by further experiments. They allow us, however, to derive the following hypotheses to be checked by future investigations:

- (i) The initial T_c -depression in the quasibinary $\text{Ce}_{1-x}\text{M}_x\text{Cu}_{2.2}\text{Si}_2$ alloys is related to impurity-induced, highly anisotropic scattering processes. The difference in the anisotropy of the scattering potential of these impurities originates in the difference of their valence-electron configurations when compared with that of Ce.
- (ii) Non-magnetic impurities act on the orbital state of the Cooper pairs. The strength of this 'diamagnetic pair breaking' tracks the strength of incoherent scattering in the low- T , normal phase.
- (iii) The additional 'paramagnetic pair-breaking' mechanism introduced by the local Gd-spin supports a superconducting order parameter of even rather than of odd parity.

The existence of a pronounced diamagnetic pair-breaking effect via the formation of LES and scattering into 'normal channels', that is caused by non-magnetic impurities in the Kondo-lattice system CeCu_2Si_2 , supports the existence of a highly anisotropic superconducting order parameter Δk . Although it is presently not clear whether the symmetry of Δk is the same as or lower than that of the reconstructed Fermi surface (for $T \ll T^*$), which has the symmetry of the lattice, we feel that the type of alloying experiments described here will help to solve the issue of conventional *vs* unconventional pairing in heavy-fermion superconductors. For this purpose a thorough treatment of impurities in terms of phase shifts has to be included into the modern calculations of quasiparticle bands in heavy-fermion systems [66–68].

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