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SUPERCONDUCTIVITY IN $CeCu_2Si_2$: DEPENDENCE OF T_c ON ALLOYING AND STOICHIOMETRY[*]

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Abstract

We have determined the transition temperatures of the alloy systems $(Ce,M)Cu_2Si_2$ with M = La,Y,Sc, $Ce(Cu,T)_2Si_2$ with T = Ag,Au,Mn,Ru,Rh,Pd and $CeCu_2(Si,Ge)_2$ as well as of $CeCu_2Si_2$ samples with varying stoichiometry. In each case, alloying is found to depress T_c, the critical concentrations necessary to destroy superconductivity ranging between < 1 at % and 10 at %. Off-stoichiometry samples with a Cu- or Ce-deficiency of a few at % are not superconducting, while samples prepared with a comparable excess of Cu or Ce show sharp transitions at $T_c \gtrsim 600$ mK. We infer that stoichiometric $CeCu_2Si_2$ contains substantial concentrations of Cu- and Ce-vacancies, which hinder superconductivity. First results on $CeCu_2Si_2$ single crystals, which exhibit bulk superconductivity, are also reported.

1. "Heavy-Fermion" Superconductivity in $CeCu_2Si_2$

The tetragonal compound $CeCu_2Si_2$ belongs to the interesting class of "Kondo-lattice" systems which can be distinguished from both dilute Kondo alloys and mixed-valence systems (1). Measurements of bulk properties (2), magnetic neutron scattering (3) and NMR (4) reveal that the valence of the Ce ions in $CeCu_2Si_2$ is close to three. The J = 5/2 multiplet of Ce^{3+} was found to be split by the crystal field into three doublets with excitation energies $k_B \cdot 140$ K and $k_B \cdot 364$ K (3). A gradual disappearence of the effective magnetic Ce-moment below T ≃ 10 K was inferred from (i) a cross-over from a high-temperature

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Curie-Weiss law to a low-temperature Pauli-like susceptibility and (ii) a removal of local magnetic entropies (2) as well as from (iii) a finite halfwidth of the quasi-elastic neutron peak (as $T \to 0$), $\Gamma_o/2k_B \simeq 10$ K $= T^*$, the spin fluctuation temperature of the Ce's (3).

In its low-temperature state ($T < 1$ K), $CeCu_2Si_2$ behaves non-magnetically in that it shows simple power laws in the temperature dependences of various bulk properties, e.g. $\chi = \chi_o T^o$, $C = \gamma T$, and $\rho - \rho_o = AT^2$ (ρ_o : residual resistivity). Herein the coefficients are very much larger than those found for simple metals : $\chi_o \simeq 6.5 \cdot 10^{-3}$ emu/mol, $\gamma \simeq 1$ J/mol K^2 and $A \simeq 10$ $\mu\Omega$cm/K^2 (2). Very similar effects have been reported before (5) for the hexagonal Kondo-lattice system $CeAl_3$ and attributed to the formation of fermion quasi-particles with extremely large effective mass ("heavy fermions").

In polycrystalline $CeCu_2Si_2$ samples, the afore-mentioned features were found to disappear below $T_c \simeq 0.5$ K because of the onset of superconductivity (6). This phase transition is interesting for several reasons : (i) The homolog $LaCu_2Si_2$, lacking "heavy-fermion" effects, does not superconduct (7), (ii) the specific-heat-jump height at T_c, ΔC, scales for most of the samples studied with the gigantic specific heat in the normal state, γT_c (6,8,2), and (iii) the absolute slope of the upper-critical-field curve at T_c, B'_{c2}, is as large as or even larger than that of Chevrel-phase superconductors (9) and scales, in the "pure limit", with $\gamma^2 T_c$ (10). Analyzing these results reveals parameters for the system of "heavy fermions" in $CeCu_2Si_2$, which differ from the corresponding parameters in simple metals by more than two orders of magnitude, i.e. $m^* \simeq 220\ m_o$ and $v_F \simeq 8.5 \cdot 10^5$ cm/s (10).

2. Influence of Sample Quality on Superconducting Properties : Earlier Results

$CeCu_2Si_2$ appears to be an inhomogeneous type-II superconductor (6,2), with a Ginzburg-Landau parameter $\kappa \geqslant 10$ (10).

Performing DC-magnetization experiments on unannealed bulk samples, i.e. by cooling them in a finite B-field to $T < T_c$, we have found a Meissner effect corresponding to typically only a few percent of the volume, while Meissner signals corresponding to $\leqslant 65$ vol % were observed after the same samples had been annealed and powdered (2,7). These large Meissner signals, along with the also large ΔC-values, prove that superconductivity is intrinsic to $CeCu_2Si_2$ and can, by no means, be attributed to spurious phases, grain-boundary superconductivity, etc.

Nevertheless, there exists a substantial sensitivity of superconducting properties on sample quality. This is best documented by two recent observations :

(i) The transition temperatures of annealed polycrystalline $CeCu_2Si_2$ samples investigated in our laboratory show a wide scatter, i.e. between 0.11 K and 0.66 K (11). Other authors did not observe superconductivity for $T \geqslant 60$ mK at all (12). Although we could not explain this T_c-scatter, we have been able to increase initially low T_c's, by means of improved heat treatment, to usual values, i.e. $\overline{T}_c = (0.55 \pm 0.15)$K (11). Striking correlations exist between T_c and other physical properties : decreasing T_c was found to be accompanied by a slight reduction of the spin fluctuation temperature T^* (taken to be proportional to both the temperature T_ρ of the low-lying peak in the $\rho(T)$ curve and the inverse of the specific-heat coefficient γ^{-1}) and by the disappearence of the gap in the excitation spectrum ("gapless superconductivity") (11).

(ii) Aliev et al. (13) did not find superconductivity in $CeCu_2Si_2$ single crystals at ambient pressure ($p \simeq 0$) down to $T = 50$ mK. This was confirmed, down to $T = 20$ mK, in our laboratory with single crystals grown from stoichiometric starting material (11). In both cases (13,14), $T_\rho \simeq 6$ K was found, while it is of the order of 20 K for polycrystalline samples with $T_c \simeq 0.6$ K (2). Most surprisingly, superconductivity occured if an external pressure $p \geqslant 1$ kbar was applied. $T_c(p)$ reaches a maximum of $T_c \simeq 0.5$ K at $p \simeq 4$ kbar, while $T_\rho(p)$ increases steadily to $T_\rho = 11.5$ K at $p = 12$ kbar (13). Structure-factor

measurements (at p ≃ 0) on such a non-superconducting single crystal have revealed an astonishingly large deficiency (≃ 20 at %) in the occupation of Cu sites (11). This may be considered a possible reason for the quite large residual resistivity, $\rho_o \simeq 100\ \mu\Omega cm$, as found for $CeCu_2Si_2$ single crystals (13, 14).

In the following sections, we will report new results on the transition temperature of polycrystalline $CeCu_2Si_2$ samples in which we have changed the composition either by controlled alloying or by systematically varying the stoichiometry. This will enable us to propose a way how to prepare superconducting single crystals of $CeCu_2Si_2$. Our data on the off-stoichiometry samples can be compared with those by Ishikawa et al. (15).

3. T_c - Depression by Controlled Alloying

Fig. 1,3a,b show the transition temperature as function of the impurity concentration for various quasi-binary alloy systems of the types $(Ce_{1-x}M_x)Cu_2Si_2$, $Ce(Cu_{1-y}T_y)_2Si_2$ and $CeCu_2(Si_{1-z}Ge_z)_2$. T_c was determined by low-field (0.05 G), AC-(119 Hz) susceptibility from the midpoint of the transition. The samples have been prepared by argon-arc melting (eight times each). They have been annealed in a high vacuum at T = 1300 K for four days. After a time span, which varied between 2 weeks and 8 months, the $(Ce_{1-x}M_x)Cu_2Si_2$ alloy samples, either in bulk or powder form, have been annealed for a second time under the afore-mentioned conditions. Weight losses caused by sample preparation were typically 0.6 % (corresponding to a loss of, e.g., Cu of 1.5 at %). Data points plotted in the figures were taken subsequently after annealing. The salient features of these experiments are : (i) Substitution of Ce by trivalent transition-metal atoms reveals a positive curvature for all $(Ce_{1-x}M_x)Cu_2Si_2$ alloys studied. The critical concentration, x_{cr}, at which $T_c \to 0$, varies strongly with the nature of the doping atoms. One might be tempted to correlate x_{cr} with their volume. To illustrate this, in Fig. 2 is plotted x_{cr} vs. a_{20}, the lattice parameter a of the respective $(Ce_{0.8}M_{0.2})Cu_2Si_2$ alloys (used instead of the MCu_2Si_2

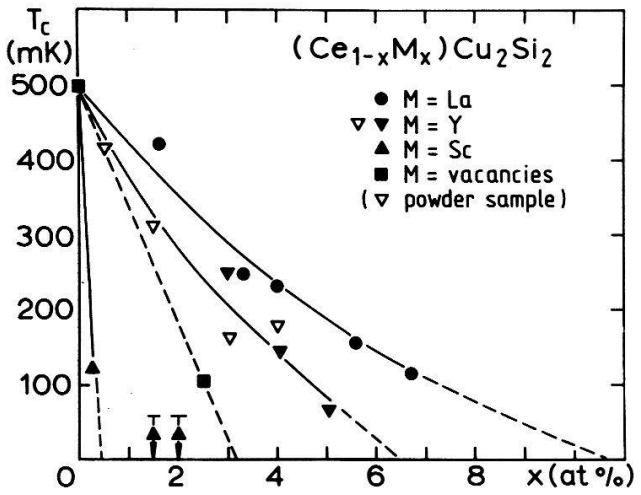

Fig. 1. Transition temperature of $(Ce_{1-x}M_x)Cu_2Si_2$ as function of concentration x.x (vacancies) as defined in Fig. 4b. Critical concentrations $x_{cr} = x(T_c \to 0)$ deviate from those reported in Ref. 11. This is caused by the additional heat treatment used in the present work (16).

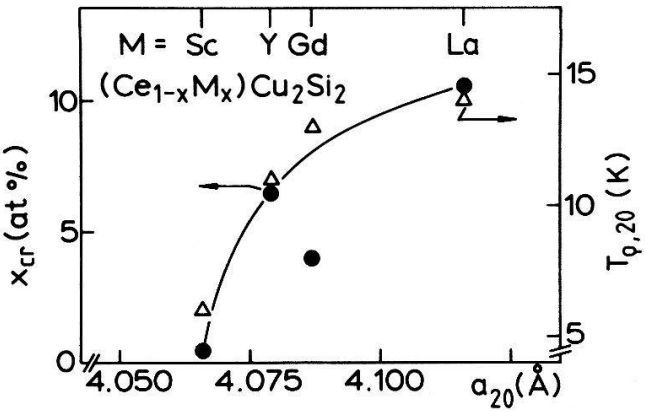

Fig. 2. Critical concentration x_{cr} (at which $T_c \to 0$) of different alloys $(Ce_{1-x}M_x)Cu_2Si_2$ (left scale) and temperature $T_{\rho,20}$ (= position of $\rho(T)$-peak, see text) of corresponding alloys with x = 20 at % (right scale) as function of the lattice parameter a_{20} of the x = 20 at % alloys.

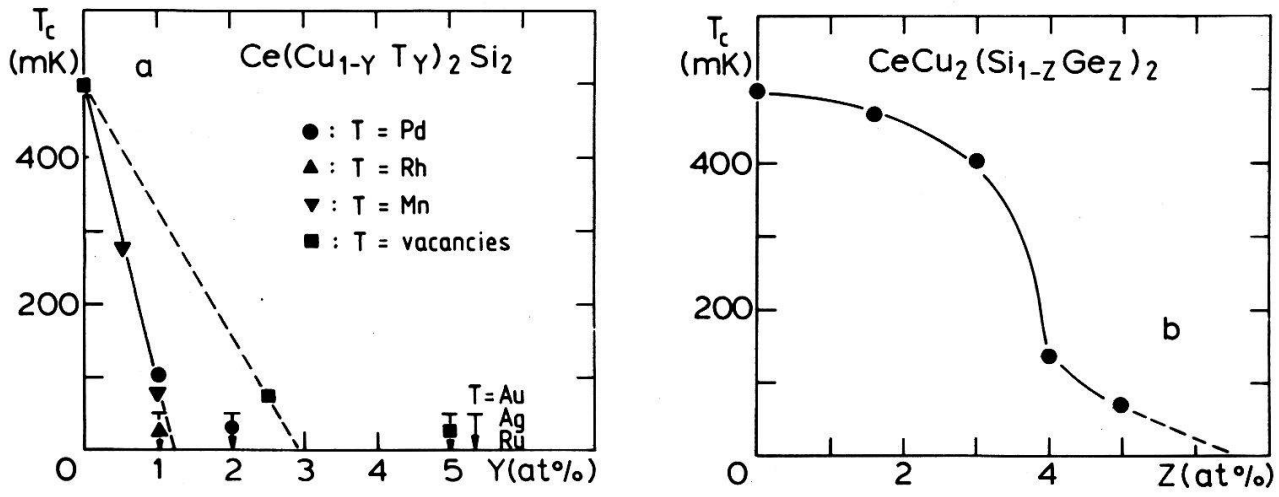

Fig. 3. T_c of different $Ce(Cu_{1-y}T_y)_2Si_2$ alloys (a) and of $CeCu_2(Si_{1-z}Ge_z)_2$ (b) as function of respective concentrations, y and z. y (vacancies) as defined in Fig. 4b.

compounds, since $ScCu_2Si_2$ could not be prepared in single phase). The critical concentration tracks the behavior in $T_{\rho,20}$, the temperature of the low-lying peak in the $\rho(T)$ curve of these $x = 20$ at % alloys. It is found that superconductivity tends to disappear for $T_{\rho,20} < 5$ K. We wish to note, however, that the "volume dependence" of T_ρ as inferred from these alloying experiments has the opposite sign than what was found for $CeCu_2Si_2$ single crystals under external pressure (13). In Fig. 2 is also included the value $x_{cr} \simeq 4$ at % for M = Gd. This is only about half the value expected from the"volume dependence"and demonstrates the additional pair-breaking effect of the Gd-spin.
(ii) Substitution of Cu by noble-metal or transition-metal atoms has a strong,destructive effect on superconductivity. From Fig.3a, we find the following critical concentrations : $y_{cr} < 1$ at % for T = Rh, $\simeq 1.5$ at % (Pd, Mn), < 5 at % (Au, Ag, Ru). We cannot resolve any substantial contribution of the Mn-spin to the T_c-depression. No systematic variation of T_c (or x_{cr}) with T_ρ is found in these alloys. (iii) For $CeCu_2(Si_{1-z}Ge_z)_2$ we read off Fig. 3b $z_{cr} \simeq 6.5$ at %. For low Ge-concentration d^2T_c/dz^2 is negative, but changes sign near z = 4 at %.

4. Dependence of T_c on Stoichiometry

In Fig. 4a, the transition temperatures are displayed for several polycrystalline samples with different Ce-Cu-Si composition. Sample preparation was the same as for the alloy systems discussed in the preceding section, save the second annealing process. Weight losses are comparable to those in Sect.3. All samples were measured in bulk form. Most results of Fig. 4a, in which it is assumed that no vacancies exist in the lattice, agree with those obtained in Ref. 15 ; the exception being some samples prepared with either an excess of Si or a deficiency of Ce (i.e., samples no.8, 14 and 15 in Ref. 15).

For the stoichiometric $CeCu_2Si_2$ composition $T_c \simeq 500$ mK was found from the average over a large number of samples. It is also obtained by extrapolating impurity concentrations to zero in

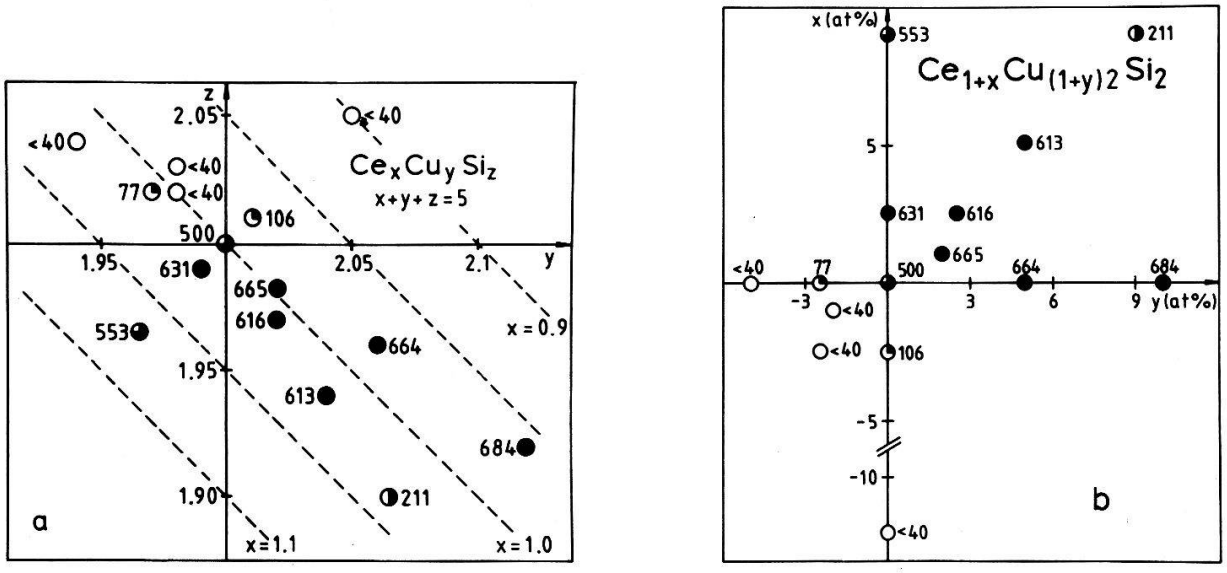

Fig. 4. T_c of $CeCu_2Si_2$ and several off-stoichiometry samples displayed in the composition plane under the assumption that either each lattice-site is occupied (a) or each Si-site is occupied by Si(b). ● : $T_c \geqslant 600$ mK ; ◕ : 400 mK $\leqslant T_c <$ 600 mK ; ◑ : 200 mK $\leqslant T_c <$ 400 mK ; ◔ : 40 mK $\leqslant T_c <$ 200 mK ; O : $T_c <$ 40 mK.

the alloy systems of Sect.3 (see Fig. 1,3 a,b).

Obviously, we observe the highest T_c's at the Cu- and Ce-rich sides, while T_c drops rapidly at the Cu- and Ce-poor sides. On the other hand, excess of Si seems to strongly disfavor superconductivity, while a Si-deficiency results in a T_c-increase. This suggests that a possible homogeneity range must be rather narrow (< 1 at %) ; for, it would not be plausible that Cu- or Ce-atoms on Si-sites ("Si-deficiency") would result in a substantial rise of T_c, while substitution of Si by Ge atoms leads to a depression of T_c (Fig. 3b). Neglecting such a narrow homogeneity range we may assume, because of the above T_c-results, that the number of Si atoms weighed in determines the number of lattice cells. In this way, we consider each Si site to be occupied by a Si atom and allow for deviations from stoichiometry on Ce- and Cu-sites only.

Our results are re-plotted under this assumption in Fig. 4b. The maximum T_c (= 684 mK) is obtained for a nominal

Cu-excess of 10 at %, whereas at higher Cu-concentration T_c slightly decreases again(16). For a nominal Cu-deficiency ("Cu-vacancies") of about 3 at %, superconductivity appears to be completely destroyed. A similar, albeit less pronounced, effect is observed when the nominal Ce concentration is varied. As shown in Fig. 1 and 3b, the critical concentrations of Ce- and Cu-vacancies, x_{cr} and y_{cr}, extrapolated from Fig. 4b for $T_c \to 0$, are quite comparable to those of the respective M- and T-doping atoms.

If we would assume that in stoichiometric $CeCu_2Si_2$ the occupation of lattice sites were, in fact, regular (as determined by thermal equilibrium), excess atoms of Cu and Ce, then, had to reside on interstitial sites in order to be able to strongly influence T_c as found. However, the respective interstices seem to be not available in the lattice with $ThCr_2Si_2$ structure . Therefore,we propose that even stoichiometric $CeCu_2Si_2$ contains a rather large concentration ($\geqslant$ 10 at %) of Cu-vacancies and possibly also a moderate concentration ($\simeq$ 3 at %) of Ce vacancies ; a corresponding number of Cu and Ce atoms presumably being dispersed in grain-boundaries, strain-fields near dislocations, etc. This view is consistent with our lattice-parameter results taken from Guinier-de-Wolff photographs, which do not show any systematic variations among the large number of off-stoichiometry samples discussed here (16). It is interesting to note that Ce-vacancies of similar concentration presumably also exist in stoichiometric $CePd_3$, a mixed-valence compound with Cu_3Au structure. Here, samples with a Ce-excess of a few at% have to be prepared in order to obtain a very low residual resistivity, indicating a rather regular lattice (17). In the $CeCu_2Si_2$ system, we infer from the observed increase of T_c that the number of vacancies becomes reduced by an excess of both Cu and Ce. In addition, for stoichiometric samples T_c should increase after both aging and annealing, i.e. due to a reduction of the vacancy concentration. This has, in fact, been observed (6,2,11).

In summary, we propose that those samples with highest transition temperatures show the smallest deviations from the

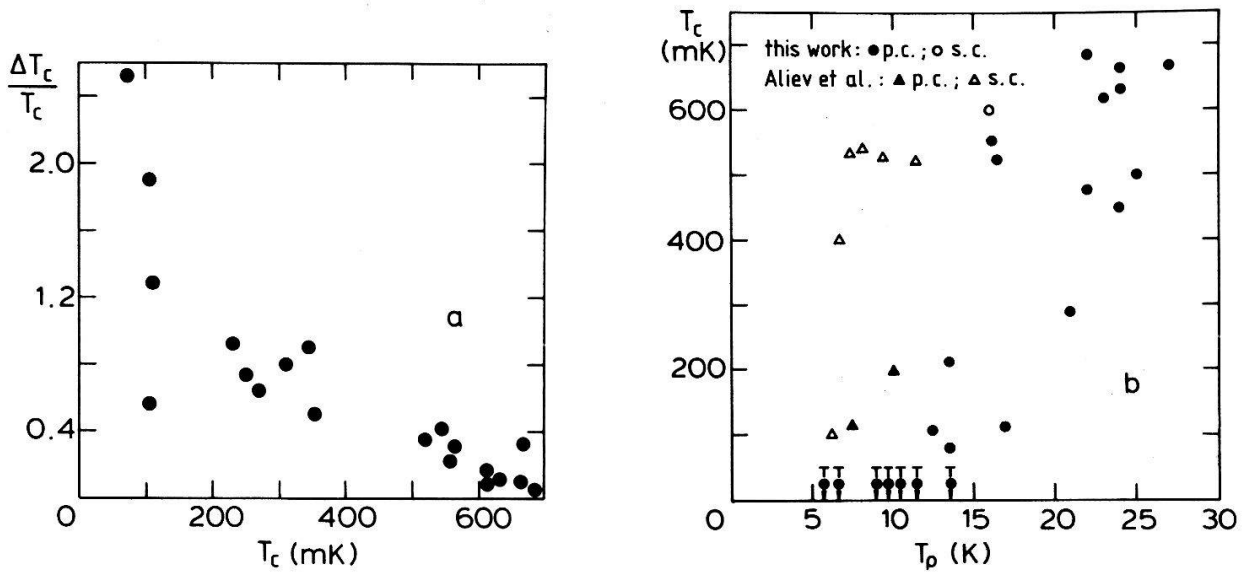

Fig. 5. Relative transition width as function of T_c (a) and T_c as function of resistivity-peak temperature T_ρ (b) for $CeCu_2Si_2$ and several off-stoichiometry samples. ΔT_c was taken between 10 and 90 % points of the transition, T_c and T_ρ were determined with the same samples. In (b) results from Ref. 13 are included.

regular $CeCu_2Si_2$ lattice. In accordance with this, we find that the high-T_c samples exhibit particularly sharp transitions (Fig. 5a). As is displayed in Fig. 5b, for the off-stoichiometry samples studied in this work a correlation exists between T_c and T_ρ, the temperature of the low-lying $\rho(T)$ peak, which is similar to the one previously found for certain stoichiometric samples (11). More specifically, despite considerable scatter of the data points, three regimes may be distinguished in which (i) $T_c < 40$ mK ($T_\rho \lesssim 13$ K), (ii) $T_c \sim \Delta T_\rho$, and (iii) $T_\rho \simeq$ const $\simeq 25$ K ($T_c > 500$ mK). Note that T_ρ is a good empirical measure of the spin-fluctuation temperature T^* (18).

In order to check our above interpretation of the T_c-results on polycristalline samples, in the following, we will compare them with results on $CeCu_2Si_2$ single crystals. As already mentioned in Sect. 2, a single crystal grown from stoichiometric starting material was found to be not superconducting and to contain a concentration of Cu-vacancies of the order of 10-20 at % (11). The fact that this single crystal behaved differently from

stoichiometric polycrystalline samples has presumably to be attributed to the different procedures of sample preparation and shall not be discussed here. In the same type of reasoning as before, however, we expect to observe superconductivity in single crystals grown from starting material, which contains a sufficiently large excess of Cu.

Such single crystals have recently been prepared by M. Herrmann and W. Assmus (University of Frankfurt) using a Cu-excess of 27 at %. In fact, we have found for them a superconducting transition around T_c 600 mK, as is shown by the $X_{AC}(T)$

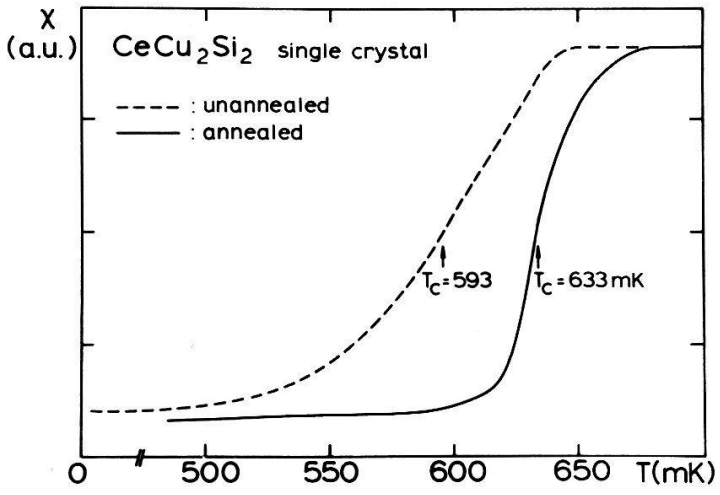

Fig. 6. Signal of AC-susceptibility, in arbitrary units, as function of temperature, demonstrating the superconducting transition of single crystals grown from starting material of composition $CeCu_{2.5}Si_2$. Data were taken on one crystal, which was unannealed, and on another one, which had been annealed (1300 K, 4 days).

result in Fig. 6. The height of the signal change between $T > T_c$ and $T < T_c$ is comparable to that taken on a Cd sample of comparable cross-section (19). A DC-magnetization experiment, made on an unannealed crystal, has revealed a Meissner effect corresponding to 25 % of the volume. Comparing this with typical Meissner signals of bulk polycrystalline samples (a few vol %) strongly suggests that it is, in fact, the whole volume of these single crystals which becomes superconducting. In addition, resistivity

measurements performed on one of them revealed that the $\rho(T)$ peak occurs at $T_\rho \simeq 16$ K (14) and, therefore, meets the general $T_c(T_\rho)$ trend displayed in Fig. 5b for our polycrystalline samples, while the data points by Aliev et al. (13) for both single crystals (measured under applied pressure) and polycrystalline samples deviate considerably from ours (see Fig. 5b). Preliminary results of a total lattice-structure analysis, performed with one of the new superconducting single crystals, indicate (20) that the occupation of Cu sites is, in agreement with our expectation, substantially higher than in the non-superconducting one, though not yet complete. More detailed information about $CeCu_2Si_2$ single crystals will be communicated elsewhere.

5. Concluding Remarks

We have shown that substitution of any constituent of $CeCu_2Si_2$ by doping atoms leads to a reduction of the superconducting transition temperature ; most pronounced being the effect of transition-metal or noble-metal impurities replacing Cu. Additional evidence that the Cu atoms might play a particularly important role with respect to the novel superconducting ground state of $CeCu_2Si_2$ can be derived from recent results of resonant X-ray photoemission spectroscopy : for the isostructural Kondo-lattice systems CeT_2Si_2 (T = Cu,Ag,Au,Pd), hybridization between localized 4f-states and conduction-band states, a key parameter to understand the (Kondo-) screening of Ce moments at low temperature, was found to be dominated by the T-derived d-density of states at the Fermi level (21).

Next, by comparing the T_c's of the substitutional alloys with the T_c's of both stoichiometric $CeCu_2Si_2$ and a large number of off-stoichiometry samples, we have inferred considerable vacancy concentrations on the Cu- and Ce-sublattices. The existence of such vacancies, which seem to hinder superconductivity, can help to explain both the previously discovered, distinct effect of annealing on the T_c's of polycrystalline, stoichiometric samples (11) and the absence of superconductivity in single

crystals, grown from stoichiometric starting material (13,11). Utilizing the above results, $CeCu_2Si_2$ single crystals could be prepared which exhibit bulk superconductivity below $T_c \simeq 600$ mK.

Acknowledgments

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