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Effect of composition on the superconductivity of $CeCu_2Si_2$

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The superconductivity in fifteen off-stoichiometric samples of the compound $CeCu_2Si_2$ was investigated, and a strong dependence of T_c on the concentration of all three constituents was found. The variation of T_c was particularly pronounced for the series of $CeCu_{2\pm\delta}Si_2$; the highest (0.67 K) and the sharpest T_c was found in copper-rich samples, while T_c of the sample containing only 1 at.% less copper was lower than 0.07 K. Metallographic and crystallographic studies, combined with differential thermal analysis on some of these samples allowed us to discuss the limit of the homogeneity range and the type of formation of $CeCu_2Si_2$. Supplementary results on other compounds in the ternary system Ce-Cu-Si are also presented. Superconductivity was not found above 0.07 K in the compounds isostructural to $CeCu_2Si_2$: CeT_2Si_2 (T=Co, Pd, Rh, and Ru) and CeT_2Ge_2 (T=Co and Ni).

I. INTRODUCTION

In our previous publication,[1] we have shown on the basis of the ternary phase diagram and the upper critical-field curve that the superconductivity in $CeCu_2Si_2$ characterized by Steglich *et al.*[2] is an intrinsic property of the compound. However, we therein provided no convincing simple correlation between the superconducting transition temperature T_c and other parameters such as lattice constants or annealing temperatures. Furthermore, we found no sound explanation for a failure of finding bulk superconductivity in samples similarly prepared by others.[3,4] In an attempt to clarify these questions, we further investigated the superconductivity in $CeCu_2Si_2$ by making careful T_c and x-ray measurements on about fifteen off-stoichiometric samples around the compound. In this Rapid Communication, we report the preliminary results which may help in analyzing some contradictory results reported for this interesting material and also provide a guide for preparing better characterized samples. The crystal structure ($ThCr_2Si_2$ type) of $CeCu_2Si_2$ is very common among transition-metal silicides and germanides, but not very favorable for superconductivity. In fact, only a few superconductors with this structure type have been reported so far.[3,5] Nevertheless, it is important to examine similar compounds[6] containing trivalent or nearly trivalent cerium ions, as in $CeCu_2Si_2$.[1] We have tested several cerium compounds with this structure type for superconductivity down to 0.07 K.

II. EXPERIMENTAL AND RESULTS

The samples were prepared from the elements by arc-melting measured amounts of Ce metal (4N, Rare Earth Products, Ltd.), Cu (4N8, Materials Research Corporation), and Si (5N, Goodfellow Metals). Melting losses were in the order of 0.2% of the total sample weight. If the losses are attributed to one single element, the corresponding uncertainties in the composition are smaller than about 0.1, 0.2, and 0.3 at.% in the Ce, Cu, and Si concentrations, respectively. By metallography and x-ray powder diffraction, the samples were characterized in the as-cast state and after annealing in sealed quartz capsules at 900 °C for 6 d. Lattice parameters were determined from Guinier photographs (Cu $K\alpha$ radiation: Si internal standard) by least-squares refinement and in some cases from the high-angle lines of Debye-Scherrer photographs. T_c was determined by an ac inductive technique (f=80.6 Hz and H_{p-p}=200 mOe). Table I summarizes the results of these measurements. The T_c values are defined as 50% of the total signal change and those defined as 10 and 90% of the total signal change are given in parentheses. The first group of the samples (Nos. 1 to 6) in the table are on the Cu-$CeSi_2$ line (hereafter called the line A) in the ternary phase diagram[7] which is shown in Fig. 1. These samples can be denoted by $CeCu_{2\pm\delta}Si_2$. The alloys of the second group (Nos. 7 to 12), denoted by $CeCu_{2\pm\delta}Si_{2\mp\delta}$, are on the 20 at.% Ce line (B). These samples were made by combining previously melted master alloys of $Ce_{20}Cu_{38.5}Si_{41.5}$ and $Ce_{20}Cu_{42.5}Si_{37.5}$ in the desired proportions. The third (Nos. 13 and 14) and the fourth (Nos. 15 and 16) groups are on the Si-$CeCu_2$ (C) and the Ce-"CuSi" line (D), respectively.

It should be noted first that all samples except Nos. 7, 12, 13, and 16 have about the same lattice constants: a=4.102 ±0.001 and c=9.923 ±0.002 Å. If we realize the similar atomic radii for Cu and Si atoms, it is not, however, in contradiction with the

TABLE I. T_c values (midpoint and 10 and 90% of the transition in parentheses) and lattice constants derermined by Guinier method. Those indicated by an asterisk were also checked with Debye-Scherrer method. Numbers in parentheses are the standard deviation on the last digit.

No.	Concentration $Ce_xCu_ySi_z$	T_c (K) $\chi_{ac}^{50\%}$ ($\chi_{ac}^{90\%} \sim \chi_{ac}^{10\%}$)	Lattice constants (Å) a	c
1	$Ce_{18.7}Cu_{44}Si_{37.3}$	0.63 (0.65 ~ 0.58)	4.1034(4)	9.925(1)
2	$Ce_{19.3}Cu_{42}Si_{38.7}$	0.67 (0.68 ~ 0.60)	4.1012(3)	9.925(1)*
3	$Ce_{19.7}Cu_{41}Si_{39.3}$	0.67 (0.68 ~ 0.60)	4.1003(3)	9.920(1)
4	$Ce_{20}Cu_{40}Si_{40}$	0.54 (0.58 ~ 0.44)	4.1004(7)	9.925(3)
5	$Ce_{20.3}Cu_{39}Si_{40.7}$	< 0.07	4.1014(5)	9.923(1)*
6	$Ce_{20.7}Cu_{38}Si_{41.3}$	< 0.07	4.1026(8)	9.923(3)*
7	$Ce_{20}Cu_{38.5}Si_{41.5}$	< 0.07	4.1053(8)	9.934(3)
8	$Ce_{20}Cu_{39.25}Si_{40.75}$	0.22 (0.325 ~ 0.1)	4.1016(6)	9.924(2)
9	$Ce_{20}Cu_{39.75}Si_{40.25}$	0.25 (0.325 ~ 0.1)	4.1010(4)	9.924(2)
10	$Ce_{20}Cu_{40.25}Si_{39.75}$	0.66 (0.675 ~ 0.58)	4.1017(8)	9.923(3)
11	$Ce_{20}Cu_{40.75}Si_{39.25}$	0.64 (0.675 ~ 0.58)	4.1010(6)	9.918(2)
12	$Ce_{20}Cu_{42.5}Si_{37.5}$	0.23 (0.33 ~ 0.14)	4.1106(5)	9.895(2)
13	$Ce_{20.7}Cu_{41.3}Si_{38}$	0.24 (0.39 ~ 0.1)	4.1132(4)	9.891(2)*
14	$Ce_{19.3}Cu_{38.7}Si_{42}$	0.29 (0.37 ~ 0.1)	4.1013(4)	9.923(2)
15	$Ce_{18}Cu_{41}Si_{41}$	0.13 (0.22 ~ 0.07)	4.1026(4)	9.924(2)
16	$Ce_{22.8}Cu_{38.6}Si_{38.6}$	0.45 (0.5 ~ 0.39)	4.1062(4)	9.911(2)

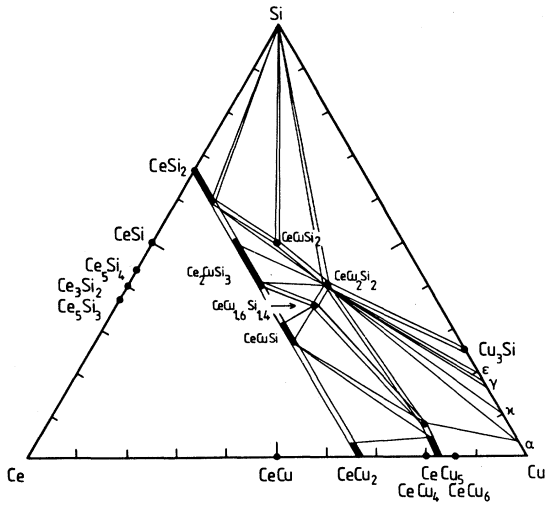

FIG. 1. Partial phase diagram of Ce-Cu-Si by Bodak *et al.* (Ref. 7).

assumption of a homogeneity range, which will be discussed in the following. It is also noted that there is a rapid monotonic variation of T_c with the concentration. No systematic correlation of lattice constants with either T_c or concentration exists. We further note that structure refinement on a single crystal taken from a nominally stoichiometric sample gave no evidence for vacancies or site exchange disorder between Cu and Si sites.

T_c values corresponding to $\chi_{ac}^{50\%}$ are displayed in Fig. 2, where an estimation of the impurity phases present, based on the examination of heavily overexposed Guinier photographs, is also included. One can see that T_c monotonically changes with the concentration of any constituents. The variation of T_c with the copper concentration along the line A, i.e., in $CeCu_{2\pm\delta}Si_2$, is particularly striking: On the copper-rich side, T_c reaches the highest value of 0.67 K at 1 at.% off the stoichiometry and remains constant up to about 2 at.%. In this range, the transition width remains very narrow (see Table I). Further off the stoichiometry, T_c slightly drops and the amount of impurities increases. This degradation may be due to proximity effects or an excess amount of defects.

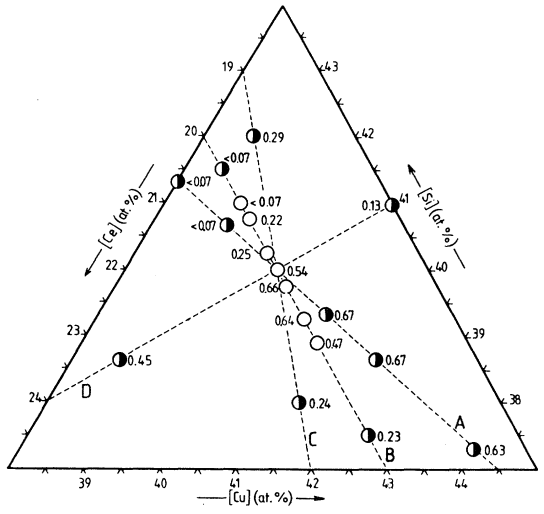

FIG. 2. Inductively determined T_c values (midpoint) of the samples. Half-filled circles indicate two or three phase samples detected on heavily overexposed Guinier films.

On the other hand, T_c drops below 0.07 K already at 1 at.% off the stoichiometry on the copper-poor side. The variation of T_c in the series of $CeCu_{2\pm\delta}Si_{2\mp\delta}$ (the line *B*) is not so abrupt as in $CeCu_{2\pm\delta}Si_2$, but an appreciable decrease on the copper-poor side is nevertheless evident. In the other directions (lines *C* and *D*), we investigated so far only a few samples at about 2 at.% off the stoichiometry and found that their T_c was generally low but above 0.1 K. This may imply either that the homogeneity range in these directions is so narrow that T_c does not change much or that Si and Ce atoms do not influence the superconductivity of $CeCu_2Si_2$ as much as Cu atoms do.

From the variation of T_c along the lines *A* and *B* and x-ray analyses shown in Fig. 2, we may set the upper limit of the homogeneity range of $CeCu_2Si_2$ at about 1 at.% from the stoichiometry. Metallographic studies, however, indicated that the homogeneity range is slightly more extended on the copper-poor side than on the other side. The most straightforward explanation of the strong change of T_c within this narrow homogeneity range may be the effect of composition. Effects of stoichiometry and order were entensively studied in *A*15 compounds.[8] The stoichiometry is attained only with a slight nominal excess of copper and T_c reaches the maximum value with the narrowest transition width. However, the very abrupt change of T_c along the line *A* may also imply that copper atoms significantly modify the electronic structure of the compound, for example, by shifting the *f* level relative to the Fermi level of the conduction electrons. This hypothesis may be checked with a substitution of Cu or Si by another element.

According to our preliminary study with differential thermal analysis (DTA) on several samples along the line *A*, $CeCu_2Si_2$ forms peritectically at 1540 ±15 °C with the liquidus line at about 1550 °C. DTA along other directions in the phase diagram is under way to get more detailed information.

To convince ourselves of the results on $CeCu_2Si_2$, we felt it necessary[1] to examine the neighboring compounds reported in the phase diagram of Bodak *et al.*[7]

In the following, we summarize our supplementary results on several compounds:

(i) Cu_3Si (η phase[9]) is the second and probably the only other superconductor in the phase diagram with T_c higher than 0.07 K ($T_c = 0.27 \sim 0.30$ K, $H_{c2}(0) \simeq 120$ Oe).

(ii) $Cu_{15}Si_4$ (ϵ phase[9]) is not superconducting above 0.07 K.

(iii) Ce_2CuSi_3 (AlB_2 type[7]) is probably the most stable compound in the present phase diagram. From DTA the melting point was found to be 1785 ±15 °C. Ce_2CuSi_3 was frequently detected as a major impurity phase in samples poor in copper and in almost all as-cast alloys. χ_{ac} measurements below 20 K revealed a small cusplike anomaly around 2.5 K.

(iv) $CeCuSi_2$ and $CeCu_{1.6}Si_{1.4}$ ($CeNiSi_2$ type)[7]: No magnetic phase transition was found between 0.07 and 20 K for both compounds. The former is indicated as a stoichiometric compound in the phase diagram of Bodak *et al.*[7], which was established at 600 °C, but its homogeneity range is apparently shifted towards the Si-rich side at 900 °C.

(v) The solubility of Cu in $CeSi_2$ is about 7 at.%, as previously reported.[7] $Ce_{0.33}Si_{0.60}Cu_{0.07}$ (α-$ThSi_2$ type) orders ferromagnetically at 6.5 K.

As mentioned in Sec. I, $CeCu_2Si_2$ is one of the very rare superconductors with the $ThCr_2Si_2$-type structure. We tested for superconductivity several other compounds of this structure type, containing trivalent or nearly trivalent cerium ions[6] as in $CeCu_2Si_2$. CeT_2Si_2 (T = Co, Pd, Rh, and Ru) and CeT_2Ge_2 (T = Co and Ni) showed neither superconductive nor magnetic phase transition between 0.07 and 20 K.

Since the samples of the $ThCr_2Si_2$ type studied in the present work were annealed only at 900 °C, we cannot discuss a possible effect of annealing temperature on T_c and, in particular, an effect of long-range order. A study of this effect is currently under way in our laboratory. But, the present work has clearly demonstrated that if a preferential loss of copper, for example, during melting or a prolonged annealing at a higher temperature takes place, it has a detrimental effect on T_c. Our data thus provide a possible explanation for the failure of finding superconductivity or for a loss of superconductivity after a high-temperature annealing. Our data have also shown that a high-quality sample of $CeCu_2Si_2$ with a sharp superconducting transition and a high T_c can be obtained with a slight nominal excess of copper.

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