Single crystals of the heavy fermion system $CeCu_2Si_2$ grown from the primary solidification field

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Abstract. A systematic investigation of the ternary phase diagram of Ce–Cu–Si to determine the primary solidification area of the heavy fermion system CeCu$_2$Si$_2$ is presented. We examine the liquidus surface by differential scanning calorimetric analysis using a special crucible system. Crystal growth experiments are performed from a levitated melt using the Nacken Kyropoulos technique. The starting compositions are chosen within the primary solidification area. We obtain high quality single crystals of CeCu$_2$Si$_2$ with dimensions up to 7 mm.

1. Introduction

CeCu$_2$Si$_2$ is a heavy fermion system with a complex B–T phase diagram below 1 K [1]. It shows superconductivity [2] with a critical temperature T_c of about 0.7 K.

The physical properties at low temperatures are strongly sample dependent. In earlier investigations Ishikawa *et al* [3] found a correspondence of T_c and the starting composition of polycrystalline material. Also the so called A- and B-phases of the B–T diagram are not observed in all investigations [4, 5]. These phases depend strongly on the initial melt composition. In addition the low temperature properties in CeCu$_2$Si$_2$ single crystals are influenced by the growth parameters [6, 7].

The investigations of Braun *et al* [8] pointed out the peritectic reaction of Ce$_2$CuSi$_3$ and liquid to CeCu$_2$Si$_2$. Only three isothermal sections at 400, 600 and 750 °C of the phase diagram of Ce–Cu–Si are known [8, 9]. This peritectic solidification can lead to strained and low quality single crystals with properitectic inclusions. In order to find the region of the primary crystallization field of the compound CeCu$_2$Si$_2$, we systematically study the ternary phase diagram. This knowledge enables us to grow crystals, which are not built up from a peritectic reaction. Such crystals are more homogeneous because they have no properitectic inclusions.

2. The phase diagram of Ce–Cu–Si

In this section we report on the investigation of the liquidus surface of the ternary phase diagram of the Ce–Cu–Si system to determine the primary crystallization field of CeCu$_2$Si$_2$. For metallographic studies samples with different compositions in the vicinity of the compound CeCu$_2$Si$_2$ are prereacted in an argon arc furnace. For better homogenization the samples are molten by high frequency absorption (HF) in a Hukin type [10] cold crucible. Thereafter the samples are quenched at the water cooled copper fingers by rapidly reducing the HF power. The

quenched material is characterized by scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and x-ray powder diffraction (XRD).

Figure 1 shows the solidification morphology of a sample with a average composition of (Ce:Cu:Si) 1:2.1:2. The bright phase is identified as the Ce_2CuSi_3 phase which is embedded in the $CeCu_2Si_2$ phase (grey). The black material is a residual Cu–Si phase. The observed structure is typical for a peritectic reaction with the properitectic phase Ce_2CuSi_3.
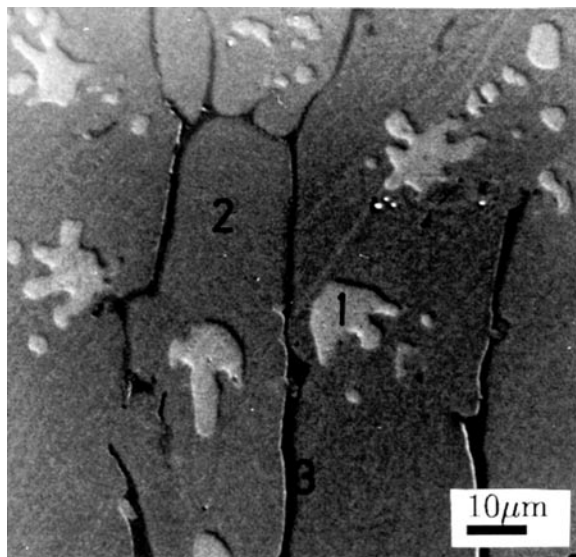

Figure 1. SEM image (backscattered electrons) of cross sections of quenched samples with starting compositions (Ce:Cu:Si) 1:2.1:2. (1) Ce_2CuSi_3, (2) $CeCu_2Si_2$, (3) binary Cu–Si phase.

To determine the liquidus surface of the interesting part of the ternary phase diagram more than 50 samples of different composition are investigated using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), energy-dispersive x-ray analysis (EDX) and x-ray diffraction. For the DSC measurements a special crucible system is developed consisting of an outer Ta crucible and an inner Al_2O_3 crucible. The figure 2 shows the sealed Ta crucible with the Al_2O_3 crucible inserted. Ta itself is heavily attacked by the melt, the Al_2O_3 inset permits at least short time experiments only. Due to the wetting behaviour, small quantities of $Ce_xCu_ySi_z$ are forming stable pellets, and do not react with the Al_2O_3. In order to avoid material loss by evaporation during the investigation the crucible is sealed under an Ar atmosphere of 100 mbar using a home made press. The sample is heated and cooled with a rate of 10 K min^{-1} during DSC measurements. A detailed description of this DSC crucible system is given in the following references [12, 13].

A part of the sample is polished in order to analyse the solidification morphology with SEM and EDX. To determine the structure of the phases the residual material is powdered for XRD examination. It is possible to correlate each DSC peak with the solidification of a certain phase.

Four quasibinary sections of the phase diagram are investigated. In the ternary phase diagram in figure 3 the sections are marked with dotted lines and letters B, C, D and E.

Figure 4(a) shows the (DSC) cooling curves of three different sample stoichiometries belonging to the section $CeCu_2Si_{2(1+y)}$ from $CeCu_2Si_2$ to pure Si (D line). The first curve belongs to a Ce:Cu:Si ratio 1:2:2 showing a peak sequence typical for peritectic solidification. In the second curve ($y = 0.23$) the first peak—indicating the formation of the properitectic phase—is
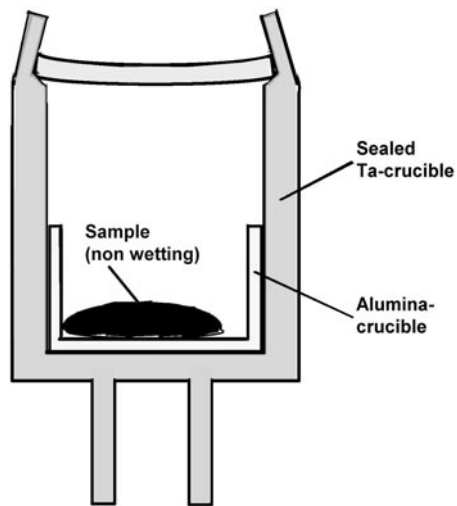
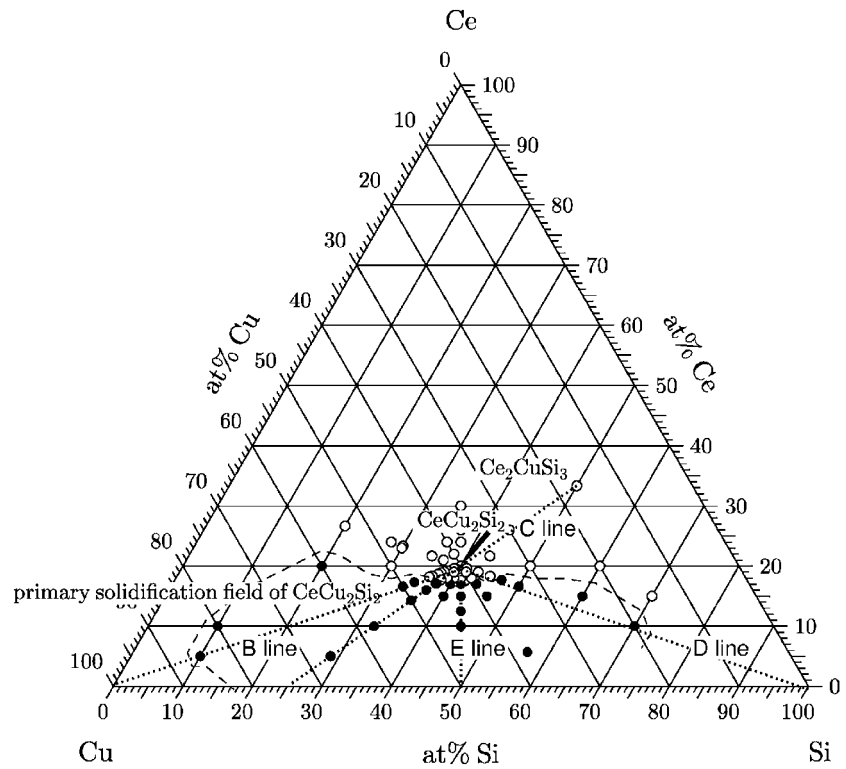**Figure 2.** DSC crucible system, the crucible diameter of the Ta crucible is 8 mm.
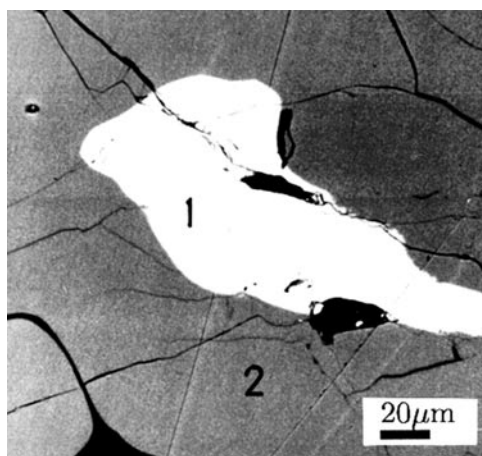

Figure 3. Ternary phase diagram with compositions inside (●) and outside (○) the primary solidification area of CeCu₂Si₂ based on DSC measurements and metallographic investigations.
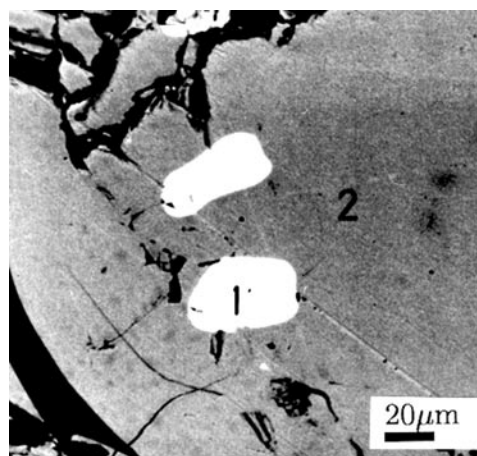
smaller and is shifted to lower temperatures. For even higher silicon content ($y = 0.5$) this peak has vanished completely indicating that CeCu₂Si₂ is formed as the primary solid phase.
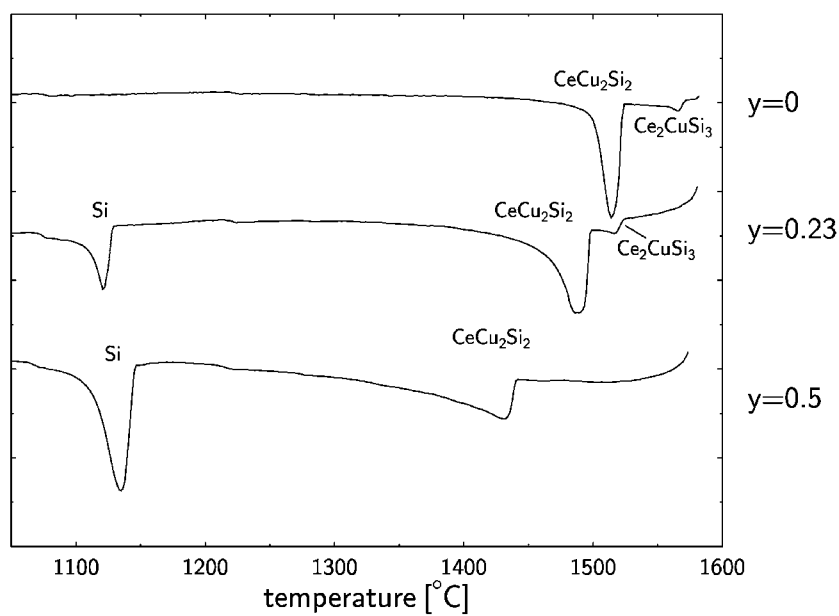
(a)

(b)

(c)

Figure 4. DSC cooling curves $CeCu_2Si_{2(1+y)}$ for starting compositions in the section from $CeCu_2Si_2$ to pure Si (a) and SEM images of DSC investigations of the compositions (Ce:Cu:Si) 1:2:2 (b) and 1:2:2.23 (c).

The figures 4(b) and 4(c) show two SEM images of the samples with $y = 0$ and $y = 0.23$. With higher Si content the amount of the properitectic phase Ce_2CuSi_3 decreases. The properitectic phase is not observed in the sample with $y = 0.5$ where $CeCu_2Si_2$ solidifies as the first (primary) phase. This composition is therefore inside the primary solidification field of $CeCu_2Si_2$.

The DSC curves of samples with starting compositions belonging to the section with equal Cu–Si ratio (E line) can be seen in figure 5(a). In this region of the phase diagram Ce–Cu–Si, $CeCu_2Si_2$ phase solidifies peritectically from the nominal composition up to a Ce:Cu:Si ratio

of 17:41.5:41.5. SEM and EDX investigations of a sample with the latter composition do not show the Ce$_2$CuSi$_3$ phase. In figure 5(b) we show the solidification temperatures of the first solidified phase marking the liquidus line for this section.

The liquidus line of the section Ce$_2$CuSi$_3$ to CeCu$_2$Si$_2$ (C line, figure 5(c)) looks quite similar. Within this section primary solidification of the phase CeCu$_2$Si$_2$ takes place at a content of less than 17.41 at.% Ce.

To determine the complete extension of the primary solidification field of CeCu$_2$Si$_2$, several other compositions are investigated. Each point in the ternary diagram (figure 3) denotes a complete DSC investigation/quench experiment with a complete characterization. Open circles are located outside and full circles within the primary solidification field. The primary solidification field starts approximately with 17.5 at.% Ce and ends near the binary Si–Cu edge. At high Cu content we observe two different eutectics. One eutectic consists of CeCu$_2$Si$_2$ and a Cu-rich binary phase and the other of a ternary phase with a low Si content and a Cu-rich binary phase. In the Si-rich side of the phase diagram we find a eutectic point with Si and two Si-rich phases. At a Ce content higher than 20 at.% we always find the solidification of the Ce$_2$CuSi$_3$ compound.

3. Crystal growth

The investigations of the ternary phase diagram provide the basis for the choice of an appropriate starting composition for crystal growth. In order to achieve large high-quality CeCu$_2$Si$_2$ crystals growth directly from the melt is favourable. On the other hand the starting composition should be near the stoichiometric composition to avoid strong segregation at the growth front. Thus a melt composition should be used that is located within the primary solidification field not too far from the 'peritectic line'. Starting compositions (Ce:Cu:Si) 16.6:50:33.3 (K6), 17:41.5:41.5 (K7) and 16:47:37 (K8) are chosen. For comparison we carry out growth experiments with starting compositions outside the primary solidification field where CeCu$_2$Si$_2$ is formed peritectically.

Crystal growth of CeCu$_2$Si$_2$ is complicated because of the high vapour pressure of Cu and Si at the melting temperature (about 1510 °C) and a lack of inert crucible material. To avoid these problems the Nacken Kyropoulos method in combination with a levitating melt has been used. The solidification takes place inside the melt volume and therefore we have less evaporation at the growth front. This allows low growth rates (approximately 0.1 mm h^{-1}) that are favourable to reduce impurities caused by segregation.

For the growth experiments a water cooled tungsten rod is lowered into a melt, levitating in the cold crucible system. After dipping the melt with the tungsten rod the RF generator power is reduced very slowly and seeding takes place at the tip of the rod. The pulling rod is not rotated in our experiments. The studies of the crystal growth with this method is described in the reference [11]. Figure 6 shows a schematic set-up of the Nacken Kyropoulos crystal growth experiment.

Figure 7 compares x-ray powder diffraction diagrams of samples with starting compositions outside and inside the primary crystallization field. In samples of a growth experiment with a starting composition outside the primary solidification of CeCu$_2$Si$_2$ we find in material close to the seed the Ce$_2$CuSi$_3$ phase (curve 1). This phase is not observed in samples (curve 2 and 3) taken from a growth batch with a starting composition inside the primary solidification field ((Ce:Cu:Si) 16.6:50:33.3). The curve 2 belongs to material close to the seed, curve 3 to material of the middle of the batch. CeCu$_2$Si$_2$ solidifies directly from the melt in the last growth experiment. Due to the low growth rate tungsten oxide impurities are found near the tungsten seed.
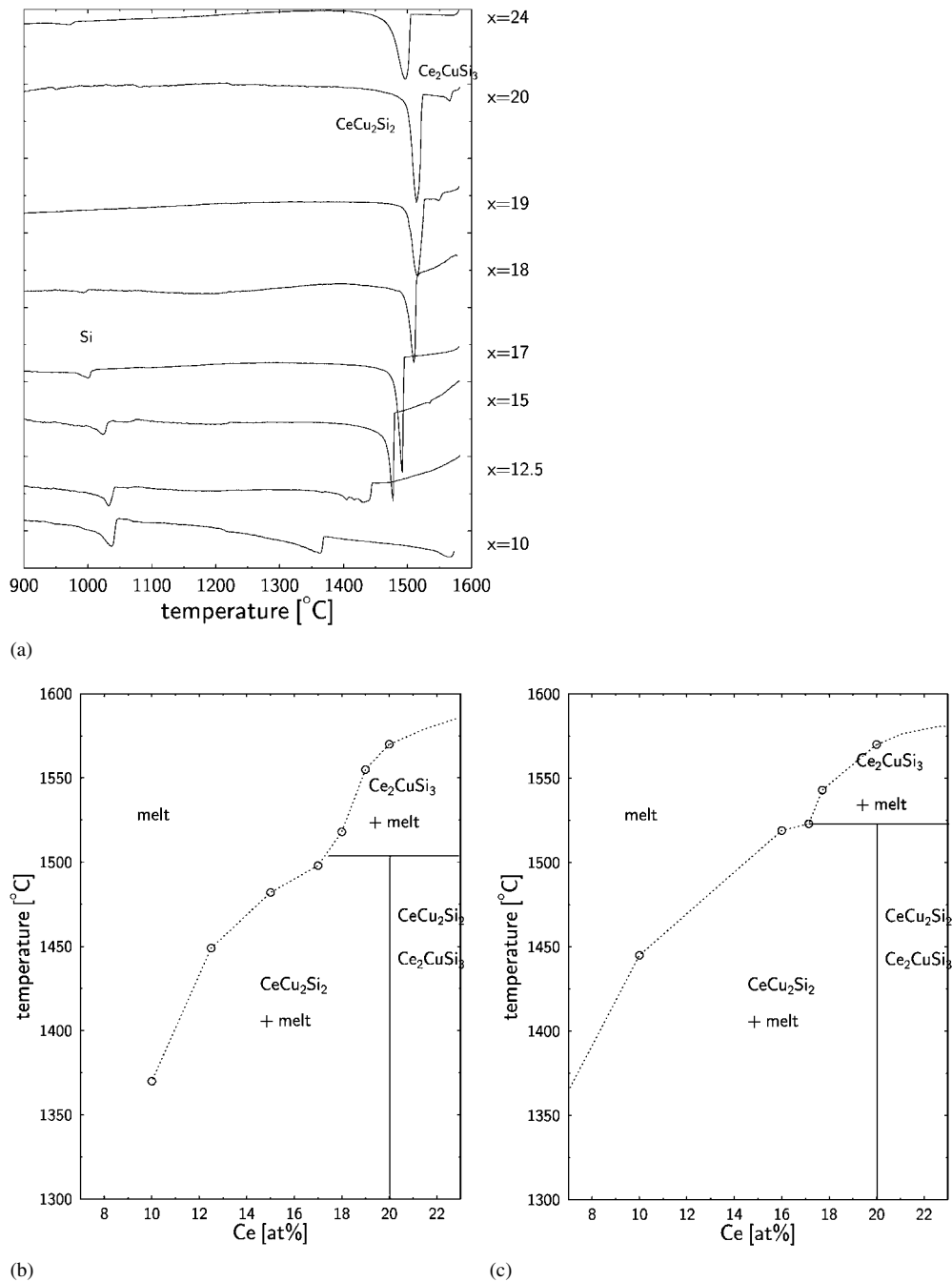
Figure 5. DSC cooling curves $Ce_xCu_{50-x/2}Si_{50-x/2}$ of compositions located in section from Ce to $CeCu_2Si_2$ (a), quasibinary section of the same part (b), a part of the quasibinary section from Ce_2CuSi_3 to $CeCu_2Si_2$ (c).

Near the tip of the tungsten rod we find polycrystalline material. Large single grain samples of $CeCu_2Si_2$ crystals up to cm scale can be prepared from the middle of the growth
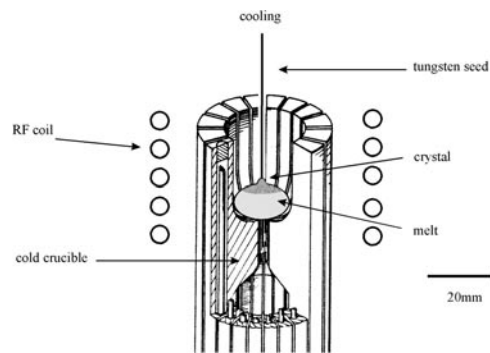
Figure 6. Schematic set-up of the Nacken Kyropoulos crystal growth experiment.
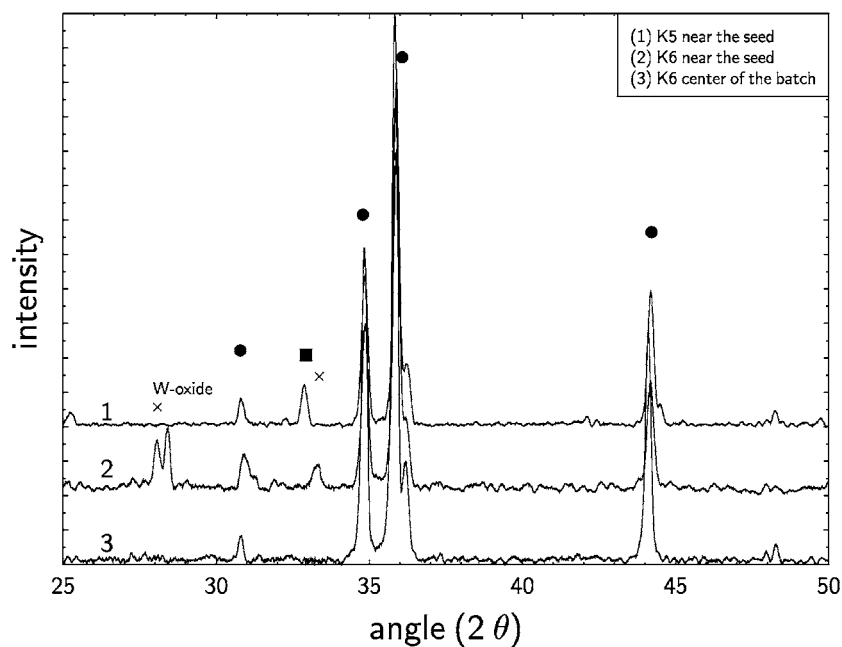

Figure 7. XRD spectra of material near the seed (starting composition outside the primary solidification area) (1), of material near the seed (starting composition inside the primary solidification area) (2) and material of the centre of the batch. Symbol (●) indicates CeC$_2$Si$_2$ peaks, the symbol (■) the Ce$_2$CuSi$_3$ peak and the symbol (×) W oxide.

batch using starting compositions inside the primary crystallization field. Figure 8 shows a single crystal on a mm scale with a length of 7 mm.

We investigate the compositions which are used in growth experiments as starting compositions. All these samples solidify in a typical peritectic manner.

We investigate with wavelength dispersive x-ray analysis (WDX) the composition of several CeCu$_2$Si$_2$ single crystals using CeCu$_2$ and Si as standards. The compositions of the different crystals are shown in table 1. Only a small variation can be observed. The compositions of the crystals grown with a starting composition within the primary

Figure 8. Single crystal of $CeCu_2Si_2$ over a mm scale.

Table 1. WDX investigation of several $CeCu_2Si_2$ single crystals. The growth experiment K5 has a starting composition outside the primary solidification field and the growth experiments K7 and K8 have a starting composition within the primary solidification field.

Growth experiment	Starting composition (at.%)	Composition of prepared crystals (WDX analysis) (at.%)
K5	Ce 19.34	Ce 19.75
	Cu 41.59	Cu 39.18
	Si 39.07	Si 41.08
K6	Ce 16.666	Ce 19.64
	Cu 50	Cu 39.63
	Si 33.333	Si 40.73
K7	Ce 17	Ce 19.94
	Cu 41.5	Cu 38.95
	Si 41.5	Si 41.11

crystallization field (K6, K7) are nearly the same as the composition of the peritecticaly grown crystal (K5).

Low temperature measurements of the grown single crystals are in progress.

4. Conclusions and discussion

In this paper we report on the determination of the primary crystallization field of the heavy fermion compound $CeCu_2Si_2$. With respect to the nominal composition the primary crystallization field is shifted to lower cerium content and starts approximately with 18% Ce. We present crystal growth experiments using the Nacken Kyropoulos method in combination with levitating melt. We can obtain single crystals of $CeCu_2Si_2$ with dimensions up to 7 mm. With the knowledge of the phase diagram we understand the solidification past of the $CeCu_2Si_2$ phase in different growth experiments.

For the first time it is possible to grow crystals directly from the melt and not through a peritectic reaction. From this we obtain the following advantages: in such crystals no properitectic phase impurities are found, neither near the tungsten seed nor in the peripheral zone of the growth batch where evaporation of Si or Cu takes place. $CeCu_2Si_2$ is formed as a homogenous and stable phase.

In crystals grown with starting compositions outside the primary solidification field the properitectic phase inclusions Ce_2CuSi_3 had to be converted into $CeCu_2Si_2$ during an annealing

process. This process leads to heavily stressed crystals because Ce_2CuSi_3 and $CeCu_2Si_2$ have a very different cell volume. Stressed crystals can avoided by crystal growth with starting compositions inside the primary solidification field.

Acknowledgment

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