

## Cerium – Copper – Silicon

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### Introduction

Although phase relations in the ternary system have been established in form of isothermal sections by several research groups [1965Gla, 1966Bod, 1967Ram, 1969Rie, 1974Bod], the discovery of  $\text{CeCu}_2\text{Si}_2$  as the first superconducting heavy fermion system [1979Ste], made the Ce–Cu–Si system and particularly  $\text{CeCu}_2\text{Si}_2$  the subject of intensive experimental and theoretical investigations because of the unusual interplay between superconducting and magnetic interactions at low temperature [1980Ste]. A summary of the physical properties is given below in section “*Notes on Materials Properties and Applications*”. Most of the ternary compounds in the Ce–Cu–Si system are now well characterized with respect to region of existence and their crystal structures [1965Gla, 1966Bod, 1967Ram, 1969Rie, 1974Bod, 1983Jar, 1983Ian, 1983Kle, 1985Bra, 1985Neu, 1986Gig, 1986Spa, 1987Boe, 1988Neu, 1992Lev, 1996Hwa, 2004Ish]. Information on phase relations, structures and thermodynamics is summarized in Table 1.

### Binary Systems

The Ce–Si system was adopted from a recent investigation by [2002Bul]. There is no doubt about the formation of the phase,  $\text{Ce}_2\text{Si}_{3-x}(\text{CeSi}_{1.34})$ , for which crystal and magnetic structures were determined by [1993Sch]. The Ce–Cu system is accepted from [1994Sub] and [2002Per]. The Cu–Si binary is taken from a recent MSIT assessment [2002Leb]. Crystallographic and melting data pertinent to the compounds of the Ce–Cu–Si system are given in Table 2.

### Solid Phases

Crystallographic data of the binary and ternary compounds are listed in Table 2. Of all compounds the heavy fermion superconductor,  $\text{CeCu}_2\text{Si}_2$  with the  $\text{ThCr}_2\text{Si}_2$  structure type, has attracted most attention. Although unnoticed in earlier studies, it was found to exhibit a small homogeneity range at 750°C, which extends for about 3 at.% in the Cu/Si direction,  $\text{CeCu}_{2-x}\text{Si}_{2+x}$  [1985Bra]. However, the ground state in  $\text{CeCu}_2\text{Si}_2$  depends very delicately on the actual composition. Thus, Cu rich samples exhibit only superconductivity, Si rich show a magnetically ordered phase called A phase, while in stoichiometric samples (A/S type) a complex interaction between superconductivity (S) and magnetic order occurs [2001Ste].

Single-crystals of  $\text{CeCu}_2\text{Si}_2$  have been investigated by [1983Jar]. The temperature dependence of lattice parameters for  $\text{CeCu}_2\text{Si}_2$  was studied by [1985Neu] and pressure dependence of lattice parameters for  $\text{CeCu}_2\text{Si}_2$  was reported by [1985Neu, 1986Spa] and for  $\text{CeCu}_{1.8}\text{Si}_2$  by [1986Spa]. Two samples of  $\text{CeCu}_x\text{Si}_2$  with  $x = 1.8$  (non superconducting) and  $x = 2.2$  (superconducting) have been investigated by neutron powder diffraction [1988Neu]. A crystallographic investigation of two  $\text{CeCu}_x\text{Si}_2$  samples with  $x = 1.8$  and  $x = 2.2$  shows that the  $\text{CeCu}_2\text{Si}_2$  structure is formed in both cases but with some differences in the degree of disorder of Cu and Si as well as in the composition of the impurity phases. [1992Lev] emphasized that  $\text{CeCu}_{2-x}\text{Si}_{2+x}$  is a compound of variable composition with lattice parameters and electronic structure depending on Cu and Si content. Anisotropic vibration is detected for the Cu and Si atoms in both phases showing that the lattice degrees of freedom are important in  $\text{CeCu}_2\text{Si}_2$  [1988Neu]. [2000Lou] found that the local atomic structure for a superconducting sample with  $x = 0.33$  is fundamentally different from a nonsuperconducting sample with  $x = -0.08$ , and that superconducting, magnetic and non-Fermi-liquid-like ground states evolve in  $\text{CeCu}_{2+x}\text{Si}_2$  with small changes in the Ce/Cu ratio that leave the average crystal structure unchanged. The  $\text{CeCu}_2\text{Si}_2$  compound has  $4f^2$  final-state amplitudes with formally  $4f^1$  initial state configurations [1981Bia]. A valence transition would presumably result from transfer of the  $4f^1$  electron to a conduction band state. The proximity of the f-electron to the Fermi level is consistent with the normal and superconducting properties [1986Spa]. The tetragonal ambient pressure



phase was at room temperature found to be stable up to 60 GPa; from the equation of state data a bulk modulus of 112.0(5.1) GPa was derived for  $\text{CeCu}_2\text{Si}_2$  [2005Tsu].

The energy band structures and Fermi surfaces are calculated for  $\text{CeCu}_6$  in [1992Har]. 4f-electrons of Ce in  $\text{CeCu}_2\text{Si}_2$  are well localized and do not affect the Fermi surface significantly in an applied magnetic field [1992Har].

[2004Ish] synthesized a new ternary compound  $\text{Ce}_2\text{Cu}_3\text{Si}_5$  (with orthorhombic  $\text{U}_2\text{Co}_3\text{Si}_5$  structure type), which was not included in the phase triangulation of [1974Bod] at 600°C.

The phases  $\tau_2$  and  $\tau_3$  show a close crystallographic relationship: although unit cell, crystal symmetry and atom sites are identical, both compounds differ with respect to atom occupation. As a consequence the two structures may be considered as type ( $\tau_3$ - $\text{CeCuSi}_2$ ) and inverse type ( $\tau_2$ - $\text{CeCu}_2\text{Si}$ ). It shall be noted that both compounds are not in equilibrium but separated by foreign two phase regions. A similar situation is met with the phases  $\tau_4$  and  $\tau_5$ , which both adopt the  $\text{AlB}_2$  type structure separated by a two-phase field between the two phases. In this case a miscibility gap is conceivable suggesting a critical point at higher temperatures.

### Liquidus Surface

[2000Nue1, 2000Nue2] performed a systematic investigation to determine the primary solidification area of the heavy fermion system  $\text{CeCu}_2\text{Si}_2$  examining the liquidus surface by differential scanning calorimetric analysis in a special crucible system. Using the Nacken-Kyropoulos technique crystal growth experiments from a levitated melt within the primary solidification area yielded high quality single crystals of  $\text{CeCu}_2\text{Si}_2$  with dimensions up to 7 mm [2000Nue2].

### Invariant Equilibria

The phase  $\text{CeCu}_2\text{Si}_2$  with the  $\text{ThCr}_2\text{Si}_2$  structure type forms peritectically at  $(1545 \pm 15)^\circ\text{C}$  without evidence for a high temperature polymorphic transformation:  $\text{L} + \text{Ce}_2\text{CuSi}_3 + \text{CeSi}_2 \rightleftharpoons \text{CeCu}_2\text{Si}_2$  [1984Bra, 1985Bra].

### Isothermal Sections

The isothermal section of the Ce–Cu–Si system at 600°C, as shown in Fig. 1, is based on an early investigation by [1974Bod, 1985Bra] with amendments to comply with the accepted binary systems as well as with the findings concerning the extension of the homogeneity region for  $\text{CeCu}_2\text{Si}_2$  (see details in Fig. 2). The location of the ternary compound  $\text{Ce}_2\text{Cu}_3\text{Si}_5$  found by [2004Ish] is indicated by a filled circle. It may be a high temperature phase. Cerium solubility in copper silicides is generally below ca. 1 at.% Ce. Mutual solubility among cerium silicides and cerium copper phases, however, is significant. The essentially random substitution of the almost equally sized atom species copper and silicon is also reflected in extended homogeneous regions for some ternary compounds such as for  $\tau_4\text{-Ce}(\text{Pt}_x\text{Si}_{1-x})_2$  and  $\tau_5\text{-Ce}(\text{Pt}_{1-x}\text{Si}_x)_2$ .

### Thermodynamics

[1985Bre, 1998Geg] studied the low temperature specific heat and the entropy changes for  $\text{CeCu}_x\text{Si}_2$ ,  $x = 1.9, 2.0, 2.2$ .

### Notes on Materials Properties and Applications

Physical property data are known for  $\text{CeCu}_2\text{Si}_2$ ,  $\text{CeCuSi}$ ,  $\text{CeCu}_{0.5}\text{Si}_{1.5}$ ,  $\text{CeCu}_{0.24}\text{Si}_{1.76}$ ,  $\text{Ce}_2\text{Cu}_3\text{Si}_5$  and are discussed below.

#### *CeCu<sub>2</sub>Si<sub>2</sub>*:

Since the observation of superconductivity in  $\text{CeCu}_2\text{Si}_2$  [1979Ste], much work has been devoted to understand the unusual properties of this prototypical heavy-fermion superconductor. Particularly the unusual type of magnetic order in the so-called “A phase” [1994Bru], discovered about ten years after the superconductivity by NMR [1988Nak] and muon spin rotation (mSR) [1989Uem], has attracted much



interest. From thermodynamic and transport measurements a complex magnetic ( $B, T$ ) phase diagram was constructed with superconducting and magnetically ordered phases and a ground state depending very delicately on the actual stoichiometry [1994Bru]. The ground state was claimed to be (i) the A phase, sometimes coexisting with superconductivity, A+S where superconductivity expels the A phase, or (ii) the superconducting S phase [2001Ste]. Doping experiments (Ge substituting for Si) as well as experiments under hydrostatic pressure indicated that  $\text{CeCu}_2\text{Si}_2$  is near a quantum critical point in line with the disappearance of the A phase. In the vicinity of the quantum critical point Non-Fermi-liquid behavior (in the specific heat and the electrical resistivity) was reported. A detailed investigation of the A phase in order to detect magnetic order by neutron diffraction failed, but measurements of the electrical resistivity revealed a spin-density wave (SDW), with an opening of a gap below the ordering temperature in certain directions [1998Geg], and  $\mu\text{SR}$  experiments gave a rough estimation of the ordered moment of  $\sim 0.1 \mu_B$  [1989Uem]. Below  $T_N \sim 0.8$  K the A phase exhibits long-range antiferromagnetic order derived from neutron diffraction experiments on a magnetically ordered  $\text{CeCu}_2\text{Si}_2$  single crystal (see also Fig. 3) [2004Sto]. The propagation vector,  $\mathbf{T} = (0.215 \ 0.215 \ 0.530)$  at  $T = 50$  mK, of the magnetic order appears to be determined by the topology of the Fermi surface of heavy quasiparticles as indicated by renormalized band-structure calculations. The absence of magnetic Bragg peaks in the superconducting phase gives evidence that antiferromagnetism and superconductivity seem to exclude each other on a microscopic scale. The observed instability of the Fermi liquid was reported to be related to the fact that the Fermi surface exhibits parallel flat parts separated by the measured propagation vector. These results suggest that a spin-density-wave instability is the origin of the quantum critical point observed in  $\text{CeCu}_2\text{Si}_2$ . However, the discrepancy between the small ordered moment and the observed large anomalies in the thermal expansion as well as the elastic constants [1994Bru] demand further examination. The existence of long-range incommensurate antiferromagnetic order in the A phase suggests that the origin of the quantum critical point arises from a spin-density-wave instability. The strong electron correlations in  $\text{CeCu}_2\text{Si}_2$  show up *e.g.* in a huge linear coefficient to the electronic specific heat at low temperatures,  $\gamma = C/T \sim 1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$ , indicative of a largely enhanced effective electron mass (heavy-fermion system).

The description of the physical behavior of  $\text{CeCu}_2\text{Si}_2$  given above is rather short. For detailed information the reader may be transferred to a series of reviews on the subject given in [1980Ste, 1984Bra, 1998Geg, 2001Ish, 2001Ste, 2002Kit, 2004Sto, 2005Ste1, 2005Ste2, 2005Ste3, 2005Sto].

#### *CeCuSi:*

$\text{CeCuSi}$  exhibits a ferromagnetic ordering below  $T_c = 15.5$  K, with a magnetic moment of  $1.25 \mu_B$  at 2.5 K, perpendicular to the  $c$ -axis [1983Kid, 1986Gig]. Neutron scattering measurements on the heavy fermion system  $\text{CeCu}_{0.24}\text{Si}_{1.76}$  confirm a phase transition to ferromagnetic order below  $T_c = 8$  K. The ordered moment  $\mu = 0.62 \pm 0.05 \mu_B$  [1987Boe].

#### *CeCu<sub>0.5</sub>Si<sub>1.5</sub>:*

Temperature dependences of specific heat, electrical resistivity and magnetic susceptibility of  $\text{CeCu}_{0.5}\text{Si}_{1.5}$  with  $\text{AlB}_2$  structure type are reported on polycrystalline samples [1996Hwa] as well as on single crystals [2000Nak] revealing complex magnetic properties with strong anisotropy.  $\text{CeCu}_{0.5}\text{Si}_{1.5}$  orders antiferromagnetically at 2.1 K. The magnetic susceptibility exhibits a maximum at 2 K only along the hexagonal  $c$ -axis at low magnetic fields [2000Nak]. Electrical resistivity shows the typical behavior of a Kondo compound with crystalline electric field effect [1996Hwa].

#### *Ce<sub>2</sub>Cu<sub>3</sub>Si<sub>5</sub>:*

Magnetization measurements up to 30 T at 1.5 K in the temperature range from 2.0 to 300 K showed that  $\text{Ce}_2\text{Cu}_3\text{Si}_5$  undergoes a transition to the antiferromagnetic state at  $T_N = 4.4$  K. The highest magnetization values per Ce atom of  $\text{Ce}_2\text{Cu}_3\text{Si}_5$  is  $0.92 \mu_B$  at  $B = 30$  T [2004Ish].

Microhardness was reported for  $\text{CeCu}_2\text{Si}_2$  (394),  $\text{CeCu}_{1.6}\text{Si}_{1.4}$  (464),  $\text{CeCuSi}_2$  (613),  $\text{CeCu}_{1.19-1.10}\text{Si}_{0.8-0.90}$  (446), and for  $\text{CeCu}_{0.78-0.44}\text{Si}_{1.24-1.56}$  ( $634 \text{ kg}\cdot\text{mm}^{-2}$ ) [1974Bod].



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**Table 1:** Investigations of the Ce-Cu-Si Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Studied
[1965Gla]	X-ray diffraction (XPD)	formation, structure of AlB <sub>2</sub> type Ce(Cu,Si) <sub>2</sub> at 800°C
[1966Bod]	XPD	formation, structure of CeCu <sub>2</sub> Si <sub>2</sub>
[1967Ram]	XPD	formation, structure of AlB <sub>2</sub> type Ce <sub>2</sub> CuSi <sub>3</sub> , Ce <sub>2</sub> Cu <sub>3</sub> Si
[1969Rie]	XPD	formation, structure of CeCu <sub>0.67</sub> Si <sub>1.33</sub> , CeCuSi, CeCu <sub>0.5</sub> Si <sub>1.5</sub> , CeCu <sub>1.5</sub> Si <sub>0.5</sub>
[1974Bod]	XPD; X-ray single crystal photographs	formation, structure of CeCu <sub>1.6</sub> Si <sub>1.4</sub> , CeCuSi <sub>2</sub> , CeCu <sub>0.78-0.44</sub> Si <sub>1.24-1.56</sub>



Reference	Method/Experimental Technique	Temperature/Composition/Phase Studied
[1981Bia]	synchrotron radiation	formation, structure of $\gamma$ -Ce, $\text{CeCu}_2\text{Si}_2$
[1983Jar]	X-ray single-crystal four-circle data	structure of $\text{CeCu}_2\text{Si}_2$
[1983Kid]	XPD	formation, structure of $\text{CeCuSi}$
[1983Kle]	Bridgman single-crystal growth, XPD, X-ray single crystal photographs	structure of $\text{CeCu}_2\text{Si}_2$
[1983Ian]	XPD	formation, structure of $\text{CeCuSi}$
[1984Kit]	nuclear quadrupole resonance	$\text{CeCu}_2\text{Si}_2$
[1984Onu]	Czochralski single-crystal growth, XPD, X-ray single crystal photographs	structure of $\text{CeCu}_2\text{Si}_2$
[1985Neu]	XPD	formation, structure of $\text{CeCu}_2\text{Si}_2$
[1985Bra]	XPD, metallography and differential thermal analysis (DTA), microprobe analysis (EMPA)	partial isothermal section
[1986Gig]	neutron powder diffraction	structure of $\text{CeCuSi}$
[1986Spa]	XPD	formation, structure of $\text{CeCu}_2\text{Si}_2$ , $\text{CeCu}_{1.8}\text{Si}_2$
[1986Lev]	XPD	formation, structure of $\text{CeCu}_2\text{Si}_2$
[1987Boe]	neutron powder diffraction	structure of $\text{CeCu}_{0.24}\text{Si}_{1.76}$
[1988Neu]	neutron powder diffraction	structure of $\text{CeCu}_x\text{Si}_2$ ; $x = 1.8, 2.2$
[1992Lev]	XPD	formation, structure of $\text{CeCu}_{2-x}\text{Si}_{2+x}$ at 1000 K; $x = -0.20, -0.15, -0.10, -0.05, 0.005, 0.10, 0.15, 0.20$
[1996Hwa]	XPD	formation, structure of $\text{Ce}_2\text{CuSi}_3$
[1997Mor]	XPD, DTA	formation, structure of $\text{CeCu}_2\text{Si}_2$
[1997Nue]	Nacken Kyropoulos technique, microscopy	$\text{CeCu}_2\text{Si}_2$
[1998Koy]	scattering technique	900°C; $\text{CeCu}_{2.2}\text{Si}_2$
[1999Ish]	XPD	formation, structure of $\text{CeCu}_{2.05}\text{Si}_2$ , $\text{Ce}_{1.025}\text{Cu}_2\text{Si}_2$ , $\text{Ce}_{0.99}\text{Cu}_{2.02}\text{Si}_2$ , $\text{Ce}_{0.975}\text{Cu}_2\text{Si}_2$
[2000Nue1] [2000Nue2]	DSC measurements, Nacken Kyropoulos technique, scanning electron microscopy (SEM), X-ray analysis (EDX), XPD, metallography	partial isothermal section
[2000Nak]	Czochralski single-crystal growth, XPD, X-ray single crystal photographs	formation, structure of $\text{Ce}_2\text{CuSi}_3$ , 800°C
[2000Lou]	neutron pair density function analysis, (GLAD) of the Intense pulsed neutron source (IPNS), powder diffractometer (GPPD) of IPNS, Rietveld refinement method	formation, structure of $\text{CeCu}_{2+x}\text{Si}_2$ at 900°C, $x = 0.33, 0.08$
[2001Kaw]	Cu-NQR measurements, EPMA	$\text{Ce}_{0.99}\text{Cu}_{2.02}\text{Si}_2$ , $\text{CeCu}_{2.05}\text{Si}_2$



Reference	Method/Experimental Technique	Temperature/Composition/Phase Studied
[2001Ish]	XPD	750°C; samples with 20 different compositions near CeCu <sub>2</sub> Si <sub>2</sub> compound
[2002Ish]	XPD	750°C; samples with 20 different compositions near CeCu <sub>2</sub> Si <sub>2</sub> compound
[2003Tay]	X-ray diffraction	formation, structure of CeCu <sub>2</sub> Si <sub>2</sub>
[2004Ish]	XPD	formation, structure of Ce <sub>2</sub> Cu <sub>3</sub> Si <sub>5</sub> at 900°C

**Table 2:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cu) < 1084.62	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 361.46$	at 25°C [Mas2] 0 to 11.3 at.% Si [Mas2]
( $\delta$ Ce) 798 - 726	<i>cI2</i> <i>Im<math>\bar{3}m</math></i> W	$a = 412$	0 to 0.55 at.% Cu at 708°C [1994Sub] 0 to 2.5 at.% Al at 720°C [2000Oka]
( $\gamma$ Ce) 726 - 61	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 516.10$	0 to 0.37 at.% Cu at 708°C [1994Sub]
( $\beta$ Ce) 61 –(–177)	<i>hP4</i> <i>P6<sub>3</sub>/mm</i> La	$a = 308.10$ $c = 1185.7$	at 24°C [1994Sub]
( $\alpha$ Ce) < –177	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 485$	at –196°C [1994Sub]
(Si) < 1414	<i>cF8</i> <i>Fd<math>\bar{3}m</math></i> C <sub>diam.</sub>	$a = 543.09$	[V-C2] 0-0.002 at.% Cu [Mas2]
CeCu < 516	<i>oP8</i> <i>Pnma</i> FeB	$a = 737.0$ $b = 462.3$ $c = 564.8$	[1994Sub], [2002Per]
CeCu <sub>2–x</sub> Si <sub>x</sub>  CeCu <sub>2</sub> < 817	<i>oI12</i> <i>Imma</i> KHg <sub>2</sub> (CeCu <sub>2</sub> )	$a = 442.9$ $b = 706.1$ $c = 747.4$	$0 < x < 0.15$  at $x = 0$ [1994Sub], [2002Per]
CeCu <sub>4</sub> < 796	<i>oP20</i> <i>Pnnm</i> CeCu <sub>4</sub>	$a = 458$ $b = 810$ $c = 935$	[1994Sub], [2002Per]
CeCu <sub>5–x</sub> Si <sub>x</sub>  CeCu <sub>5</sub> < 798	<i>hP6</i> <i>P6/mmm</i> CaCu <sub>5</sub>	$a = 514.8$ $c = 410.8$	$0 < x < 0.54$  [Mas2, 1994Sub]



Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta$ CeCu <sub>6</sub> 938 - (–43)	<i>oP</i> 28 <i>Pnma</i> $\beta$ CeCu <sub>6</sub>	$a = 810.88$	at 22°C [1990Vrt]
		$b = 510.04$	
		$c = 1016.21$	
		$a = 810.09$ $b = 509.78$ $c = 1015.48$	at –23°C [1990Vrt] [1994Sub], [2002Per]
$\alpha$ CeCu <sub>6</sub> < –43	<i>mP</i> 28 <i>P</i> 2 <sub>1</sub> / <i>c</i> LaCu <sub>6</sub>	$a = 509.5$	at –73°C [1990Vrt]
		$b = 1014.66$	
		$c = 809.31$	
		$\beta = 90.485^\circ$	
		$a = 508.92$ $b = 1013.26$ $c = 807.89$ $\beta = 91.148^\circ$	at –173°C [1990Vrt]
		$a = 508.41$ $b = 1012.79$ $c = 807.31$ $\beta = 91.442^\circ$	at –263°C [1990Vrt] [1994Sub], [2002Per]
Cu <sub>7</sub> Si (K) 842 - 552	<i>hP</i> 2 <i>P</i> 6 <sub>3</sub> / <i>mmc</i> Mg	$a = 256.05$	at 730°C, 12.75 at.% Si [Mas2]
		$c = 418.46$	11.05 to 14.5 at.% Si [1994Ole]
Cu <sub>6</sub> Si ( $\beta$ ) 853 - 787	<i>cI</i> 2 <i>Im</i> $\bar{3}m$ W	$a = 285.4$	14.2 to 16.2 at.% Si [1994Ole] at 14.9 at.% Si [1994Ole]
Cu <sub>5</sub> Si ( $\gamma$ ) < 729	<i>cP</i> 20 <i>P</i> 4 <sub>1</sub> 32 $\beta$ Mn	$a = 619.8$	17.15 to 17.6 at.% Si [1994Ole]
Cu <sub>5</sub> Si ( $\delta$ ) 824 - 711	<i>t</i> **		17.6 to 19.6 at.% Si [1994Ole]
		$a = 881.5$ $c = 790.3$	sample annealed at 700°C [V-C2]
Cu <sub>15</sub> Si <sub>4</sub> ( $\epsilon$ ) < 800	<i>cI</i> 76 <i>I</i> $\bar{4}3d$ Cu <sub>15</sub> Si <sub>4</sub>	$a = 961.5$	21.2 at.% Si [1994Ole, V-C2]
Cu <sub>3</sub> Si ( $\eta$ ) 859 - 558	<i>hR</i> * <i>R</i> $\bar{3}m$	$a = 247$ $\alpha = 109.74^\circ$	23.4 to 24.9 at.% Si [1994Ole]
	or <i>t</i> **	$a = 726.7$ $c = 789.0$	[V-C2, Mas2]
Cu <sub>3</sub> Si ( $\eta'$ ) 620 - 467	<i>hR</i> * <i>R</i> $\bar{3}$	$a = 472$ $\alpha = 95.72^\circ$	23.2 to 25.2 at.% Si [1994Ole]



Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\text{Cu}_3\text{Si}$ ( $\eta''$ ) < 570	$o^{**}$	$a = 676$ $b = 700$ $c = 2194$	23.3 to 24.9 at.% Si [1994Ole]
$\text{Ce}_5\text{Si}_3$ < 1260	$tI32$ $I4/mcm$ $\text{Cr}_5\text{B}_3$	$a = 789$ $c = 1377$  $a = 786.8$ $c = 1373$	[2002Bul]  [V-C2]
$\text{Ce}_3\text{Si}_2$ < 1335	$tP10$ $P4/mbm$ $\text{U}_3\text{Si}_2$	$a = 778.0$ $c = 436.7$	[2002Bul]
$\text{Ce}_5\text{Si}_4$ < 1500	$tP36$ $P4_12_12$ $\text{Zr}_5\text{Si}_4$	$a = 793.6$ $c = 1502.9$	[2002Bul]
$\text{CeSi}$ < 1630	$oP8$ $Pnma$ $\text{FeB}$	$a = 828.8$ $b = 396.4$ $c = 595.2$	[2002Bul]
$\text{CeSi}_{1.34}$	$oC20-x$ $Cmcm$ $\text{V}_2\text{B}_3 (\text{Nd}_2\text{Si}_{3-x})$	$a = 440.35$ $b = 2483.89$ $c = 395.17$	[1993Sch]
$\text{CeSi}_{1.67}$ < 1725	$oI12$ $Imma$ $\text{GdSi}_{2-x}$	$a = 411.3$ $b = 419.0$ $c = 1390.6$  $a = 410.0$ $b = 418.0$ $c = 1382.0$	[2002Bul]  [V-C2]
$\text{CeSi}_{2-y}\text{Cu}_y$	$tI12$ $I4_1/amd$ $\text{ThSi}_2$	$a = 417.1$ $c = 1394$  $a = 415.4$ $c = 1382.2$	$0 < y < 0.27$ [V-C2] at $y = 0.24$ ; [1987Boe]  at $x = 0.214$
$\text{CeSi}_{2-x}$ < 1575		$a = 419.2$ $c = 1391.3$	at $x = 0$ [2002Bul]



Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* $\tau_1$ , CeCu <sub>2</sub> Si <sub>2</sub>	<i>tI</i> 10 <i>I</i> 4/ <i>mmm</i> ThCr <sub>2</sub> Si <sub>2</sub> (CeGa <sub>2</sub> Al <sub>2</sub> ) or BaAl <sub>4</sub>	$a = 419.3$	[1966Bod]
		$c = 998.6$	
		$a = 409.4 \pm 0.1$	[1983Jar]
		$c = 993.0 \pm 0.2$	
		$a = 411.0 \pm 0.1$	[1983Kle]
		$c = 994.8 \pm 0.1$	
		$a = 411.2$	[1983Kle]
		$c = 994.6$	single crystal with an excess of 21.5 mass% Cu
		$a = 409.7$	[1984Onu]
		$c = 991.8$	
		$a = 410.0 \pm 0.1 - 410.8 \pm 0.3$	[1985Bra]
		$c = 992.1 \pm 0.3 - 993.1 \pm 0.6$	
			for “CeCu <sub>1.8</sub> Si <sub>2</sub> ”
		$a = 408.63 \pm 0.01$	at 1.5 K [1988Neu]
		$c = 991.15 \pm 0.01$	
		$a = 408.64 \pm 0.01$	at 10 K [1988Neu]
		$c = 991.15 \pm 0.01$	
		$a = 408.91 \pm 0.01$	at 100 K [1988Neu]
		$c = 991.16 \pm 0.01$	
			for “CeCu <sub>2.2</sub> Si <sub>2</sub> ” at
		$a = 408.25 \pm 0.01$	at 1.5 K [1988Neu]
		$c = 991.03 \pm 0.01$	
		$a = 408.26 \pm 0.01$	at 10 K [1988Neu]
		$c = 991.00 \pm 0.02$	
		$a = 408.56 \pm 0.01$	at 100 K [1988Neu]
		$c = 991.01 \pm 0.02$	



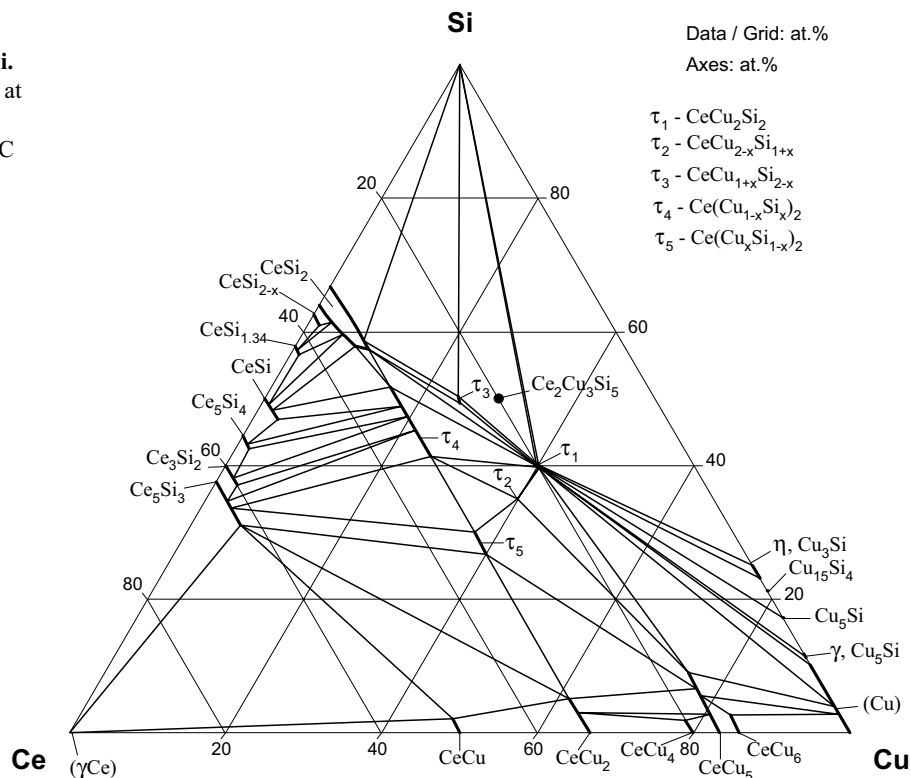
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
CeCu <sub>2-x</sub> Si <sub>2+x</sub>		$a = 409.8 \pm 0.1$ $c = 987.2 \pm 0.3$	at 1000 K $x = -0.20$ [1992Lev]
		$a = 409.4 \pm 0.2$ $c = 986.8 \pm 0.6$	at 1000 K $x = -0.15$ [1992Lev]
		$a = 409.6 \pm 0.2$ $c = 989.0 \pm 0.4$	at 1000 K $x = -0.10$ [1992Lev]
		$a = 410.0 \pm 0.1$ $c = 991.8 \pm 0.3$	at 1000 K $x = -0.05$ [1992Lev]
		$a = 409.3 \pm 0.1$ $c = 990.3 \pm 0.3$	at 1000 K $x = 0.005$ [1992Lev]
		$a = 409.6 \pm 0.1$ $c = 991.2 \pm 0.3$	at 1000 K $x = 0.10$ [1992Lev]
		$a = 409.5 \pm 0.1$ $c = 990.8 \pm 0.3$	at 1000 K $x = 0.15$ [1992Lev]
		$a = 409.6 \pm 0.3$ $c = 990.9 \pm 0.3$	at 1000 K $x = 0.20$ [1992Lev]
		$a = 408.599 \pm 0.013$ $c = 991.49 \pm 0.03$	CeCu <sub>1.92</sub> Si <sub>2</sub> at 20 K [2000Lou]
		$a = 408.441 \pm 0.013$ $c = 990.99 \pm 0.07$	CeCu <sub>2.23</sub> Si <sub>2</sub> at 13 K [2000Lou]
		$a = 410.6 \pm 0.1$ $c = 993.6 \pm 0.9$	CeCu <sub>2</sub> Si <sub>2</sub> [1997Nue]
* $\tau_2$ , CeCu <sub>2-x</sub> Si <sub>1+x</sub>	<i>oS16</i> <i>Cmcm</i> invers CeNiSi <sub>2</sub>	$a = 416$ $b = 1721$ $c = 417$	at $x = 0.4$ [1974Bod]
* $\tau_3$ , CeCu <sub>1+x</sub> Si <sub>2-x</sub>	<i>oS16</i> <i>Cmcm</i> CeNiSi <sub>2</sub>	$a = 412$ $b = 1648$ $c = 416$	at $x = 0$ [1974Bod]



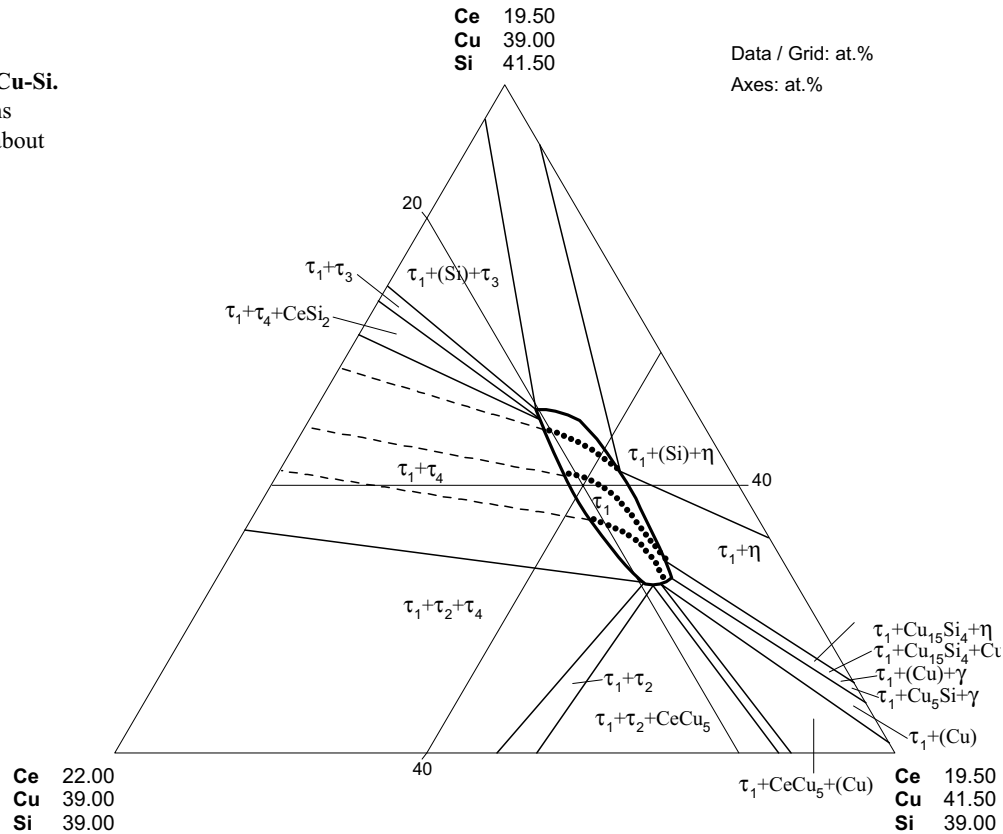
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* $\tau_4$ , Ce(Cu <sub>1-x</sub> Si <sub>x</sub> ) <sub>2</sub>	<i>hP3</i>	$a = 423.1$ to $423.8$	0.405 < $x$ < 0.45 [1974Bod]
	<i>P6/mmm</i>	$c = 398.9$ to $403.0$	
	<i>AlB<sub>2</sub></i>	$a = 423.8$	at $x = 0.25$ [1967Ram]
		$c = 403.0$	
	<i>hP6</i>	$a = 423.3$	at $x = 0.50$ ; 750°C [1986Gig]
	<i>P6<sub>3</sub>/mmc</i>	$c = 798.1$	
	<i>Ni<sub>2</sub>In</i>	$a = 423.9 \pm 0.2$	for $x = 0.50$ [1983Ian]
		$c = 798.0 \pm 0.4$	
* $\tau_5$ , Ce(Cu <sub>x</sub> Si <sub>1-x</sub> ) <sub>2</sub>	<i>hP3</i>	$a = 410.3$ to $407.0$	0.22 < $x$ < 0.38 [1974Bod]
	<i>P6mmm</i>	$c = 424.4$ to $429.1$	
	<i>AlB<sub>2</sub></i>	$a = 405.9 \pm 0.2$	[1996Hwa]
		$c = 429.4 \pm 0.5$	
		$a = 406.5$	CeCu <sub>0.5</sub> Si <sub>1.5</sub> [1967Ram] Si rich
		$c = 430.2$	
		$a = 413.6$	CeCu <sub>0.5</sub> Si <sub>1.5</sub> [1967Ram] Cu rich
		$c = 423.7$	
		$a = 412.4$	at $x = 0.50$ [1969Rie]
		$c = 421.4$	
		$a = 407.5$	at $x = 0.333$ [1969Rie]
		$c = 428.0$	
		$a = 407.7$	for Ce(Cu,Si) <sub>2</sub> [1965Gla]
		$c = 431.4$	
Ce <sub>2</sub> Cu <sub>3</sub> Si <sub>5</sub>	<i>oI40</i>	$a = 997.4$	900°C [2004Ish]
	<i>Ibam</i>	$b = 1158$	
	U <sub>2</sub> Co <sub>3</sub> Si <sub>5</sub>	$c = 584.4$	



**Fig. 1: Ce-Cu-Si.**  
Isothermal section at  
600°C (0 - 33.3  
at.% Ce) and 400°C  
(> 33.3 at.% Ce)



**Fig. 2: Ce-Cu-Si.**  
Phase relations  
around τ<sub>1</sub> at about  
600°C





B, T

