Cerium – Copper – Tin

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Introduction

The ternary R-T-X alloys formed by rare earths elements (R) with a transition element (T) and an element X of the p-block of the Periodic Table have often been described as promising materials, in particular, due to their specific electrical and magnetic properties. Therefore the attention of investigators of the ternary system formed by the rare-earth element cerium with the transition metal copper and p-element tin was concentrated mainly on these aspects besides crystal structures of the ternary compounds [1968Rie, 1976Dwi, 1982Sko, 1983Kom, 1984Kom, 1985Cor, 1988Kom, 1989Goe, 1990Fra, 1994Nak, 1994Sle, 1996Guz, 1996Lid, 1997For, 1997Ria1, 1997Ria2, 1997Sko, 1998For, 1998Ria, 2000Isn, 2000Sin, 2001Sin, 2002Zah, 2005Cha]. The publications about phase equilibria belong to 1996 year and later [1996Mar, 1997Din, 1997Ria1, 1997Ria2, 1998Ria, 2001Sin]. Isothermal section at 400°C [1996Mar, 1997Din, 1997Ria2, 1998Ria], partial liquidus surface projection [1997Ria1, 1998Ria] as well as reaction scheme [1998Ria] are presented in these works. Critical assessment of the available data about crystal structures and phase relations was carried out by [1998Ria]. Table 1 gives an overview on the experimental methods and the temperature / concentration regimes studied in the above works. The knowledge about the phase equilibria in the Ce-Cu-Sn system, however, is still incomplete. In particular, data concerning solidus and solvus surfaces as well as temperature-composition sections are lacking. Information on the liquidus surface and the isothermal sections at 400°C are confined to the Ce rich region. Thermodynamic properties of several phases in the Ce-Cu-Sn system were studied at very low temperatures to indicate magnetic transformations [2000Sin, 2001Sin, 2002Zah]. Such kind of information can not be applied to Calphad-type assessment.

Binary Systems

Data concerning the Ce-Cu system were evalated by [2002Per]. The Ce-Sn system (Fig. 1) is accepted mainly from [1998Ria] who compiled phase diagram information based on experimental works of [1988Fra1] and [1988Fra2]. The ψ,Ce_2Sn_3 compound was determined by [2003For] and is incorportaed into the present phase diagram, Fig. 1. The invariant lines coresponding to the polymorphic transformations in cerium are incorportaed as well, shown as dashed lines at 61°C and 13°C. For the temperature of the eutectoid reaction (δCe) ⇌ θ + (γCe) a balanced mean value was adopted between [1988Fra1] and [1998Ria] which is now consistent with the ternary invariant reaction U_4 (see “Invariant Equilibria” section). The Cu-Sn system is accepted as given by [Mas2].

Solid Phases

Crystallographic data for unary, binary and ternary phases are listed in Table 2. The solid solubilities of copper and tin in cerium as well as those of cerium and copper in tin are negligible. All the binary phases in the Ce-Cu system have very small homogeneity ranges. The same is valid for the Ce-Sn system with exception of σ phase. According to available experimental data, the majority of binary phases in the above mentioned systems do not dissolve third component. Exceptions are the $\beta CeCu_6$ and σ phases at 400°C (see chapter “Isothermal Sections”). Noticable solubilities of cerium in the binary Cu-Sn phases were not found so far. Information about existence of ten ternary phases is available in literature. High-temperature stability limits were reported only for the τ_7 and τ_{10} phases (Table 2), both phases are formed by peritectic reactions [2001Sin]. Among all the ternary phases extended homogeneity regions were reported only for the τ_4 and τ_5 phase. [1984Kom] found that the τ_{10}, $CeCu_{9.4}Sn_{3.6}$ phase has a cubic structure ($NaZn_{13}$ type) at 500°C, while [1997Ria2] found a phase of the $CeCu_9Sn_4$ composition (labelled as τ_7) with the same structure. However, later investigation of [2001Sin] showed that the phase $CeCu_{9.4}Sn_{3.6}$ has cubic structure $NaZn_{13}$, while the phase $CeCu_9Sn_4$ possesses a tetragonal $LaFe_9Si_4$ structure being an ordered derivative of the cubic $NaZn_{13}$ structure. [2001Sin] also declared that the formation of cubic or tetragonal structures is related to the alloy composition rather than to the annealing temperature. No structural changes were observed by [2001Sin] in the samples of the $CeCu_9Sn_4$ composition after re-annealing at 500°C. It was noted by [2001Sin] that results of [1998Ria] are in contradiction with results of their investigation and [1984Kom] data. The reason of disagreement could be the uncertainty of composition determined by [1998Ria] or that equilibrium was not reached by [1998Ria] when executing the experiment. Both groups of authors [1997Ria2, 1998Ria] and [2001Sin] used induction melting for sample preparation, but the specimens obtained by [2001Sin] were annealed at higher temperatures during longer times (500 and 680°C, 720-1200 h) comparing with [1997Ria2, 1998Ria] (400 and 630°C, 250-720 h). This makes us assume that equilibrium conditions were better reached in the experiments of [2001Sin].

Quasibinary Systems

The e_1(max) point on the liquidus curve E_1U_2 corresponds to the maximum temperature of ~800°C and the composition belonging to τ_2(CeCuSn)-$CeCu_2$ section, *i.e.* approximately 33.3 at.% Ce, 63.5 at.% Cu and 3.2 at.% Sn. [1998Ria] and coworkers assumed that the $CeCu_2$-CeCuSn section probably is a quasibinary system, where the point e_1(max) is a eutectic point and micrographs of alloys close to its composition reveal a eutectic structure.

Invariant Equilibria

The partial Scheil reaction scheme is shown in Fig. 2. It is based on the [1997Ria1, 1998Ria] data obtained by differential scanning calorimetry by heating annealed samples. It should be mentioned that there is an inconsistency in the reaction scheme presented by [1998Ria]. This inconsistency is between the temperature of the binary eutectoid reaction e_5 and the temperature of the invariant reaction U_4. The type of the U_4 reaction was determined by [1997Ria1] as transitional, but its temperature is lower than that of e_5. We accepted the type and the temperature of the U_4 reaction and decreased the temperature of the e_5 reaction in the binary system within the experimental uncertainty limit given there (see section “Binary Systems”). Invariant reactions were studied in the composition range adjacent to the Ce-Cu binary system, up to 70 at.% Cu where eight four-phase and one three-phase invariant reactions were detected. The temperatures of the invariant points and the corresponding compositions of the liquid phase are listed in Table 3.

Liquidus, Solidus and Solvus Surfaces

The partial liquidus surface is shown in Fig. 3. It is based on [1997Ria1] and [1998Ria] data. Slight corrections of the isotherms positions according to the accepted binary systems are made. The resulting liquidus surface shows large extensions of primary fields related to the crystallization of the θ and βCe_5Sn_3 phases. Small primary regions are associated with the (δCe), (γCe), κ and λ phases. According to the assumption of [1998Ria], this may be related to the highly exothermic character of these alloys in comparison with the Ce-Cu and Cu-Sn systems. These characteristics appear to be dominant and substantially unaffected by the formation of ternary phases.
Data about solidus and solvus surfaces are lacking.

Isothermal Sections

Figure 4 presents an isothermal section at 400°C for the whole range of compositions composed from to the data of [1996Mar, 1997Ria2] and [1998Ria] with some corrections according to the accepted binary systems. For the binary Ce-Sn system these are in fact the data compiled by [1988Fra1] and [1988Fra2] while the composition of Sn rich liquid was plotted from data of [1997Ria2]. The L / L + χ border was plotted at about 96 at.% Sn, but according to the data of [1988Fra2] this position is closer to the Sn apex). It should be mentioned that the phase ψ, Ce_2Sn_3, is not shown in Fig. 4 because equilibria with participation of this phase in the ternary system have not been verified, [1997Ria2, 1998Ria]. The ϕ (Ce-Cu) phase found by [1984All] was also observed by [1998Ria] in equilibrium conditions though they assume that this phase is actually metastable, but stabilized by impurities [1998Ria]. According to the Ce-Cu binary phase diagram accepted in the present work the ϕ phase is not stable, that is why equilibrium with this phase is not shown in Fig. 4. Composition of the τ_{10} phase is marked. This phase at the temperature of 400°C should be stable along with the τ_7 phase according to the data of [2001Sin]. However, it is not possible to conclude the character of phase equilibria involving the τ_{10} phase from the available experimental information. The nature of the phase equilibria between (Cu), τ_3, τ_6 and τ_8 phases is uncertain. In this respect equilibria information reported by [1998Ria] are in disagreement and the corresponding place in Fig. 4 is marked by the symbol "?".

Notes on Materials Properties and Applications

Electrical and magnetic properties of the Ce-Cu-Sn alloys were investigated widely. The applied experimental techniques and studied types of properties are listed in Table 4.

The magnetic properties of the τ_2, CeCuSn phase were studied by [1983Kom, 1994Nak, 2005Cha]. Electric resistivity of τ_2 phase was measured between 4.2 and 300 K by [1994Nak]. Antiferromagnetic ordering was observed in this phase at 8.6 K according to the data of [1994Nak]. In contrast to these results showing broad features at 8-10 K, the onset of antiferromagnetic order was observed at about 12 K by [2005Cha] with an inflection in the temperature dependence of the magnetic intensities at about 8 K. Temperature dependence (between 1.3 and 15 K) of the specific heat of τ_2, CeCuSn phase in various applied magnetic fields (0 to 5 T) (Fig. 5) was established by [1994Nak]. [1983Kom] noted that magnetic susceptibility of the τ_2, CeCuSn phase changes according to the Curie-Weiss law, with paramagnetic Curie temperature of –13 K. The negative value of it indicates the possibility of antiferromagnetic ordering. In the B-*T* diagram of this phase (Fig. 6) [1994Nak] three different antiferromagnetic phase structures were detected. They are labelled as AF1 (exists between 7.35 and 8.6 K for magnetic fields below 1.5 T), AF2 (forms from AF1 below 7.35 K) and AF3 (forms at lower temperatures at magnetic field more than 2.5 T).

The specific heat, magnetic susceptibility and magnetisation of τ_3, $Ce_3Cu_4Sn_4$ phase, were measured by [2000Sin] and [2002Zah]. Using these data and data on neutron diffraction [2002Zah] reports on the microscopic picture of magnetic ordering. The data on specific heat C_p at low temperatures for the τ_3, $Ce_3Cu_4Sn_4$ phase measured by [2000Sin, 2002Zah] are in a good agreement with each other. According to [2000Sin] it exhibits three peaks at 10.2, 7.8 and 2.5 K. According to [2002Zha] there are peaks at T_N = 10.3 (Neel temperature), T_2 = 7.3 K and the beginning of upturn due to the transition at T_3 = 2.6 K. The temperature dependence of heat capacity of the τ_3, $Ce_3Cu_4Sn_4$ phase below 30 K is presented in Fig. 7 according to [2002Zah]. Upturn at 2.6 K is shown as a peak similar to [2000Sin]. The magnetic entropy *S* - temperature dependence for this phase obtained by [2002Zah] is presented in Fig. 8. A significant magnetic contribution to the entropy persists up to at least 30 K, revealing an existence of magnetic fluctuations far above T_N. The temperature dependence of electric resistivity of τ_3, $Ce_3Cu_4Sn_4$ phase was constructed by [2000Sin]. There is a rapid decrease of resistivity below ~40 K which is precursor to the magnetic transition occuring at ~10.4 K. The inverse susceptibility *versus* temperature dependences for this phase were established by [2000Sin] and [2002Zah]. The obtained values of paramagnetic Curie temperature were –12.5 and –11.6 K, respectively. The curves shape is similar.

The temperature dependence of magnetic susceptibility of the τ_5, $CeCu_{1-x}Sn_{2-y}$ phase determined on the $CeCu_{0.52}Sn_{1.83}$ alloy corresponds to the Curie-Weiss law [1988Kom]. Magnetic properties of the τ_6, $CeCu_2Sn_2$ phase were studied by [1982Sko] at 78-293 K using Faraday technique and by [1996Guz] at 1.5 -100 K using inelastic neutron scattering spectra. Temperature dependences of the inverse susceptibility were presented in both studies. Several other properties were reported for τ_6. Electrical resistivity at low temperature for τ_6 was measured by [1985Rau], ^{119}Sn Mössbauer spectra of between 4.2 and 300 K was studied by [1989Goe] and thermal expansion data at low temperature was obtained by [1994Sle].

Temperature dependences of the heat capacity of the τ_7, $CeCu_9Sn_4$ and τ_{10}, $CeCu_{9.4}Sn_{3.6}$ phases obtained by [2001Sin] are presented in Figs. 9 and 10, respectively. For the τ_7 phase the heat capacity curve shows peak at 5.5 K, and, in opinion of the authors, such anomalies typically arise due to the transition from the paramagnetic to the magnetically ordered state. The heat capacity data thus confirm the occurence of magnetic transitions. For the τ_{10} phase the heat capacity data show upturn below 3 K and indicate the occurence of magnetic transition below 1.5 K. The inverse susceptibilities of τ_7 and τ_{10} phases versus temperature dependences were constructed by [2001Sin]. The obtained values of paramagnetic Curie temperature are –14.5 and 1 K, respectively. Electrical resistivity and magnetization were also investigated. [1984Kom] obtained the Curie temperature value for $CeCu_{9.4}Sn_{3.6}$ similar to the data of [2001Sin]: 0 K. According to the results of [1997Sko], the τ_9, $CeCu_5Sn$ phase electrical resistivity curve is similar to that of heavy fermion compounds, but the maximum on it is much lower than that of the $CeCu_6$ heavy fermion system. The magnetic susceptibility χ of $CeCu_5Sn$ follows the Curie-Weiss law, however the χ (T) function becomes almost independent of the temperature below 10 K, may be due to a long range antiferromagnetic ordering below 10 K. [2000Isn] established that $CeCu_{5.25}Sn_{0.75}$ and $CeCu_5Sn$ alloys order antiferromagnetically at T_N = 4 and 10 K, respectively. Magnetoresistance, reciprocal magnetic susceptibility and thermopower were studies by them for the $CeCu_{6-x}Sn_x$ alloys (x = 0, 0.25, 0.75 and 1). It was noted in review of [2004Wu] that additions of cerium and lanthanum to the Sn-0.7Cu (mass%) increase its tensile strength, improve its wettability and decrease ductility and creep strain (substantially for the last property). The authors consider that the Pb free solder alloys doped with rare earth elements (the Sn-0.7Cu + Ce + La) alloy is among of them are now ready for reliability studies such as thermal shock and electromigration to prove their feasibility as working solders.

Miscellaneous

[1996Sle] have obtained the valence band and 3d core-level X-ray photoemission spectra (XPS) of the $CeCu_2Sn_2$ compound. An analysis of these spectra was carried out using the Gunnarsson-Schoenhammer model. A large hybridization of the f orbitals with a conduction band was found as characteristic for this compound. The XPS valence band was compared with self-consistent band structure calculations of the linear muffin-tin orbital (LMTO) type, and were discussed. The Ce L_{III} X-ray absorption spectra of the $CeCu_{6-x}Sn_x$ (x = 0, 0.25, 0.75 and 1) solid solutions have been studied by [2000Isn]. A trivalent state of cerium in the alloys containing Sn was shown.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1968Rie]	X-ray diffraction	Ce_5CuSn_3
[1976Dwi]	X-ray Debye-Scherrer powder diffraction	CeCuSn
[1982Sko]	X-ray diffraction	$CeCu_2Sn_2$
[1983Kom]	X-ray Debye-Scherrer diffraction	CeCuSn
[1984Kom]	X-ray Debye-Scherrer diffraction	$CeCu_{9.4}Sn_{3.6}$
[1985Cor]	X-ray single crystal diffractometry	$CeCu_2Sn_{1.9}$
[1988Kom]	X-ray powder diffraction	25 to 32 at.% Ce at 18 to 30 at.% Cu
[1989Goe]	X-ray diffraction; ^{119}Sn Moessbauer measurements	$CeCu_2Sn_2$
[1990Fra]	X-ray Guinier powder diffraction	$CeCu_{0.5}Sn_2$
[1994Nak]	X-ray polycrystal diffraction	CeCuSn
[1994Sle]	X-ray powder diffraction	< 27°C, $CeCu_2Sn_2$
[1996Guz]	Inelastic neutron scattering diffraction	$CeCu_2Sn_2$
[1996Lid]	X-ray Guinier powder diffraction; Moessbauer studies	$CeCu_2Sn_2$
[1996Mar]	X-ray diffraction; optical microscopy; EMPA	400°C, the region between $CeCu_2$-Ce_3Sn_7-Ce
[1997Din]	Preparatory and anaytical techniques	400°C, whole range of compositions
[1997For]	X-ray diffraction	$CeCu_5Sn$, $Ce_2Cu_9Sn_{2.65}$
[1997Ria1]	Differential scanning calorimetry; SEM; energy dispersive spectrometry	< 800°C,. the Ce rich part
[1997Ria2]	X-ray diffraction; optical microscopy; SEM; EMPA	400°C, whole range of compositions
[1997Sko]	X-ray powder diffraction	$CeCu_5Sn$
[1998For]	X-ray single crystal diffractometry	$CeCu_5Sn$, $Ce_2Cu_9Sn_{2.65}$, $Ce_3Cu_4Sn_4$
[1998Ria]	X-ray diffraction; differential scanning calorimetry; optical microscopy; SEM; EMPA	≤1300°C, whole range of compositions
[2000Isn]	X-ray powder diffraction	500°C, 14.3 at.% Ce at 71.4 to 85.7 at.% Cu
[2000Sin]	X-ray Guinier powder diffraction	$Ce_3Cu_4Sn_4$
[2001Sin]	X-ray Guinier powder diffraction; DTA	$CeCu_9Sn_4$, $CeCu_{9.4}Sn_{3.6}$
[2002Zah]	X-ray powder diffraction; neutron diffraction	$Ce_3Cu_4Sn_4$
[2005Cha]	Single crystal neutron diffraction	CeCuSn

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δCe) 798 - 726 $Ce_{1-x-y}Cu_xSn_y$	cI2 $Im\overline{3}m$ W	*a* = 412	at 757°C [1994Sub2] $x = 0$, $0 \le x \le$ ~0.02, 729°C [1994Sub2] $y = 0$, $0 \le x \le$ ~0.077, 708°C [1994Sub2]
(γCe) 726 - 61 $Ce_{1-x-y}Cu_xSn_y$	*cF*4 $Fm\overline{3}m$ Cu	*a* = 516.10	[1994Sub2] $y = 0$, $0 \le x \le$ ~0.0037, 708°C [1994Sub2]
(βCe) 61- (–177)	*hP*4 $P6_3/mmc$ αLa	*a* = 368.10 *c* = 1185.7	at 24°C [1994Sub2]
(αCe) < -177	*cF*4 $Fm\overline{3}m$ Cu	*a* = 485	at –196°C [1994Sub2]
(Cu) < 1084.62 $Ce_xCu_{1-x-y}Sn_y$	*cF*4 $Fm\overline{3}m$ Cu	*a* = 361.46	at 25°C [Mas2] at $x = 0$, $0 \le y \le 0.077$, 798°C [1944Ray, 1994Sau] at $x = 0$, $0 \le y \le 0.087$, 700°C [1970Tok, 1997Boc] at $x = 0$, $0 \le y \le 0.057$, 250°C [1970Tok, 1997Boc] at $x = 0$, $0 \le y \le 0.007$, 200°C [1944Ray, 1994Sau] at $y = 0$, $0 \le x \le 0.001$, 876°C [1994Sub1]
		a = 361.46 to 370.46 *a* = 361.8 *a* = 367.6	at $x = 0$, $0 \le y \le 0.091$ [1994Sau] at $x = 0.001$, $y = 0.001$, 400°C [1997Ria2] at $x = 0.002$, $y = 0.07$, 400°C [1997Ria2]
(βSn) 231.9681 - 13 $Ce_xCu_ySn_{1-x-y}$	*tI*4 $I4_1/amd$ βSn	*a* = 583.18 *c* = 318.18	at 25°C [Mas2] at $x = 0$, $0 \le y \le 0.0001$, [1939Hom, 1994Sau]
(αSn) < 13	*cF*8 $Fd\overline{3}m$ C (diamond)	*a* = 648.92	at 25°C [Mas2]
κ, CeCu < 516	*oP*8 *Pnma* FeB	*a* = 730 *b* = 430 *c* = 636	[1961Lar2]
		a = 719 *b* = 430 *c* = 623	[1965Wal, 1998Ria]
		a = 737 *b* = 462.3 *c* = 564.8	[1965Dwi, 1994Sub2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
λ, $CeCu_2$ < 817	*oI*12 *Imma* $CeCu_2$	 *a* = 443 *b* = 705 *c* = 745	dissolves ~1.4 at.% Sn at 1400°C [1997Ria2] at 0 at.% Sn [1961Lar1]
		a = 442.5 *b* = 705.7 *c* = 747.5	at 0 at.% Sn [1963Sto]
		a = 442.9 *b* = 706.1 *c* = 747.4	at 0 at.% Sn [1994Sub2]
		a = 444.1 *b* = 707.7 *c* = 745.9	at 33.5 at.% Ce, 0.1 at.% Sn, 400°C [1997Ria2]
		a = 444.1 *b* = 707.7 *c* = 745.9	at 33.8 at.% Ce, 1.4 at.% Sn, 400°C [1997Ria2]
μ, $CeCu_4$ < 796	*oP*20 *Pnnm* $CeCu_4$	*a* = 454 *b* = 810 *c* = 919	[1964Rhi, 1998Ria]
ν, $CeCu_5$ < 798	*hP*6 *P*6/*mmm* $CaCu_5$	*a* = 514.8 *c* = 410.8	[Mas2]
		a = 514 *c* = 411	[1964Rhi, 1996Pol]
		a = 513.4 *c* = 410.5	[1985Gir]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta CeCu_6$ 938 - (-43)	*oP*28 *Pnma* $\beta CeCu_6$	 *a* = 811.2 *b* = 510.2 *c* = 1016.2 *a* = 810.9 *b* = 510.0 *c* = 1016.2 *a* = 810.88 *b* = 510.04 *c* = 1016.21 *a* = 810.09 *b* = 509.78 *c* = 1015.48 *a* = 811.0 *b* = 510.2 *c* = 1016.1 *a* = 810.0 *b* = 510.3 *c* = 1018 *a* = 805 *b* = 504 *c* = 1018	dissolves ~7 at.% Sn at 400°C [1997Ria2] [1960Cro] [1986Vrt, 1998Ria] at 22°C [1990Vrt] at –23°C [1990Vrt] [1994Sub2] at 15.3 at.% Ce, 4.3 at.% Sn, 400°C [1997Ria2] at 14.0 at.% Ce, 7 at.% Sn, 400°C [1997Ria2]
$\alpha CeCu_6$ < –43	*mP*28 $P2_1/c$ $\alpha LaCu_6$	*a* = 509.5 *b* = 1014.66 *c* = 809.31 β = 90.485° *a* = 508.41 *b* = 1012.79 *c* = 807.31 β = 91.442°	at –73°C [1990Vrt] at –263°C [1990Vrt]
ϕ (Ce-Cu)	*hP*68 $Gd_{14}Ag_{51}$	*a* = 1185.8 *c* = 910.7	at 0 at.% Cu, 78.46 at.% Cu, labelled as "$Ce_{14}Cu_{51}$". Metastable, impurity stabilized(?) [1984All, 1998Ria]
θ, Ce_3Sn < 940	*cP4* $Pm\bar{3}m$ $AuCu_3$	*a* = 492.9 *a* = 493 to 494 *a* = 492.7 *a* = 492.3	[S] [1982Bor] [1988Fra1, 1998Ria] at 400°C [1997Ria2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
βCe_5Sn_3 1505 - 940	*hP*16 *P*6_3*/mcm* Mn_5Si_3	*a* = 933 *c* = 681	[1982Bor]
αCe_5Sn_3 < 940	*tI*32 *I*4*/mcm* W_5Si_3	*a* = 1259.1 *c* = 617.4 *a* = 1260 *c* = 617 *a* = 1259.9 *c* = 617.9 *a* = 1258 *c* = 615.3	[1979Fra] [1982Bor] [1988Fra1, 1998Ria] at 400°C [1996Mar]
ρ, Ce_5Sn_4 < 1515	*oP*36 *Pnma* Sm_5Ge_4	*a* = 833.7 *b* = 1605 *c* = 848.0 *a* = 834.8 *b* = 1603 *c* = 849.2 *a* = 836 *b* = 1607 *c* = 848.4	[1971For, 1998Ria] [1988Fra1, 1998Ria] at 400°C [1996Mar]
σ, $Ce_{11}Sn_{10}$ < 1375	*tI*84 *I*4*/mmm* $Ho_{11}Ge_{10}$	 *a* = 1220 *c* = 1790 *a* = 1197 *c* = 1782 *a* = 1206 to 1212 *c* = 1761 to 1795	dissolves 5 at.% Cu at 400°C [1997Ria2] [1988Fra1, 1998Ria] [1982Bor] [1998Ria]
ψ, Ce_2Sn_3	*aP*20 $P\bar{1}$ Nd_2Sn_3	*a* = 644.4 *b* = 851.0 *c* = 1119.5 α = 107.36° β = 96.78° γ = 99.42°	[2003For]
ξ, Ce_3Sn_5 < 1180	*oC*32 *Cmcm* Pu_3Pd_5	*a* = 1025 *b* = 822 *c* = 1058 *a* = 1024.3 *b* = 821.4 *c* = 1065.2	[1982Bor] at 400°C [1996Mar]
π, Ce_3Sn_7 < 1135	*oC*20 *Cmmm* Ce_3Sn_7	*a* = 452.4 *b* = 2574.2 *c* = 461.0	[1988Fra2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
φ, Ce_2Sn_5 < 1145	*oC*28 *Cmmm* Ce_2Sn_5	*a* = 455.9 *b* = 3501.4 *c* = 461.9 *a* = 459.0 *b* = 3514 *c* = 466.2	[1988Fra2] at 400°C [1997Ria2]
χ, $CeSn_3$ < 1170	*cP*4 $Pm\overline{3}m$ $AuCu_3$	*a* = 472.2 *a* = 472.1 *a* = 472.4	[S] [1988Fra2] at 400°C [1997Ria2]
β, $Ce_xCu_{1-x-y}Sn_y$ 798 - 586	*cI*2 $Im\overline{3}m$ W	*a* = 297.81 to 298.71 *a* = 298.1 to 299.1	$x = 0, 0.131 \le y \le 0.165$ [1994Sau] $x = 0, 0.134 \le y \le 0.157$ [1994Sau] $x = 0, 0.152 \le y \le 0.172$ [1939Isa, 1994Sau]
γ, Cu_3Sn 755 - 520	*cF*16 $Fm\overline{3}m$ BiF_3	 *a* = 606.05 to 611.76 *a* = 611.6 ± 0.06	15.5 - 27.5 at.% Sn [1994Sau] 16.6-25.0 at.% Sn, 710°C [1994Sau] at 25 at.% Sn, 700°C [1957Kno]
δ, $Cu_{41}Sn_{11}$ 590 - ~350	*cF*416 $F\overline{4}3m$ $Cu_{41}Sn_{11}$	 *a* = 1798.0	20 - 21 at.% Sn [1994Sau] labelled as "$Cu_{31}Sn_8$" [1979Cha] at 20.5 at.% Sn, 560°C [1977Boo]
ζ, $Cu_{10}Sn_3$ 640 - 582	*hP*26 $P6_3$ $Cu_{10}Sn_3$	 *a* = 733.0 *c* = 786.4	20.3 - 22.5 at.% Sn at 23.1 at.% Sn [1975Bra]
ε, Cu_3Sn < 676	*oC*80 *Cmcm* Cu_3Sn	 *a* = 552.9 *b* = 477.5 *c* = 432.3	24.5 - 25.9 at.% Sn at 25 at.% Sn [1983Wat, 1994Sau]
η, Cu_6Sn_5(h) 415 - 186	*hP*4 $P6_3/mmc$ NiAs	 *a* = 419.0 *c* = 508.6 *a* = 419.2 ± 0.2 *c* = 503.7 ± 0.2	43.5 - 45.5 at.% Sn at 45.45 at.% Sn, 0 at.% Ce [1994Sau] at 45.45 at.% Sn, 0 at.% Ce, 210°C [1973Gan]
η', Cu_6Sn_5(r) < 186	*h**	 *a* = 2087.0 *c* = 2508.1	~45.45 at.% Sn Superlattice based on NiAs-type structure [1994Sau] [1973Gan]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α' (Cu-Sn)	*hP*2		metastable
	$P6_3/mmc$		~8 - 11.5 at.% Sn [1963Der, 1967Deb,
	Mg		1994Sau]
		a = 2087.0	at ~8 at.% Sn, [1963Der]
		c = 2508.1	
		a = 2087.0	at 11.5 at.% Sn, [1984Sau, 1994Sau]
		c = 2508.1	in the alloy with 16.5 at.% Sn heated to 570°C for 10 min, and then aged at 100°C and 130°C. Labelled as "δ′" [1973Van]
ω (Cu-Sn)	*hP*12		metastable
			15 - 16 at.% Sn [1973Van, 1980Zak]
		a = 421	at 15.5 at.% Sn, 700°C [1980Zak]
		c = 1110	
X (Cu-Sn)	*hP*9		metastable
			on tempering of a quenched β single phase alloy [1932Isa, 1934Bug, 1957Bag]
		a = 728	at ~15 at.% Sn, [1932Isa, 1957Bag]
		c = 258	
		a = 740	at 15 at.% Sn, 100°C.
		c = 260	Labelled as "L" [1983Kuw]
β_2 (Cu-Sn)	ordered rhombic		metastable
		a = 1273	in a 15.5 at.% Sn, alloy quenched from
		b = 424	700°C and aged during 15 years [1980Zak]
		c = 600	
γ′ (Cu-Sn)	ordered cubic		metastable
		a = 899	in a 19.5 at.% Sn alloy, vapor quenched, below 200°C [1984Sau, 1994Sau]
* τ_1, Ce_5CuSn_3	*hP*18	*a* = 947.4	[1968Rie]
	$P6_3/mcm$	*c* = 669.9	
	Ti_5Ga_4		
		a = 948.3	at 400°C [1996Mar]
		c = 673.5	
		a = 948.6	[1998Ria]
		c = 671.2	

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_2, CeCuSn	*hP*6	*a* = 458	[1976Dwi]
	P6_3/*mmc*	*c* = 791	
	$CaIn_2$[a)]	*a* = 457.0	[1983Kom]
		c = 790.3	
		a = 459.1	at 400°C [1996Mar]
		c = 793.5	
		a = 458.8	[1998Ria]
		c = 791.9	
	*hP*6	*a* = 459	ordered structure, single crystal data
	P6_3*mc*	*c* = 790	[2005Cha]
	GaGeLi		
* τ_3, $Ce_3Cu_4Sn_4$	*oI*22	*a* = 1510.8	at 400°C [1996Mar]
	Immm	*b* = 702.6	
	$Gd_3Cu_4Ge_4$	*c* = 456.0	
		a = 1509.8	[2000Sin]
		b = 702.2	
		c = 459.7	
		a = 1490.3	at –264°C (11.5 K) [2002Zah]
		b = 692.5	
		c = 454.2	
* τ_4, (Ce-Cu-Sn)	*hP*3		31.5 to 36 at.% Ce at 21 to 7 at.% Cu, 400°C
	*P*6/*mmm*		[1997Ria2]
	AlB_2	*a* = 452	at 33 at.% Ce, 21 at.% Cu, 400°C
		c = 429	[1997Ria2]
		a = 439.5	at 36 at.% Ce, 7 at.% Cu, 400°C [1997Ria2]
		c = 450	
* τ_5, $CeCu_{1-x}Sn_{2-y}$	*oC*16		27.5 to 30 at.% Ce at 16 to 9 at.% Cu, 400°C
	Cmcm		[1997Ria2]
	$CeNiSi_2$	*a* = 449.2	at 397°C [1988Kom]
		b = 1785	
		c = 443.9	
		a = 449.4	$CeCu_{0.5}Sn_2$ [1990Fra]
		b = 1799	
		c = 444.5	
		a = 450	at 28 at.% Ce, 16 at.% Cu, 400°C
		b ≈ 1785	[1997Ria2]
		c = 445	
		a = 450	at 30 at.% Ce, 9 at.% Cu, 400°C [1997Ria2]
		b ≈ 1780	
		c = 444	

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_6, $CeCu_2Sn_2$	*tP*10 *P*4/*nmm* $CaBe_2Ge_2$	*a* = 445.6 *c* = 1047.5	[1982Sko]
		a = 442.9 *c* = 1042.6	$CeCu_2Sn_{1.9}$ single crystal [1985Cor]
		a = 445.8 *c* = 1048.4	[1989Goe]
		a = 445 *c* = 1035	after annealing between 600 and 700°C [1996Guz]
		a = 445.79 *c* = 1047.35	at 900°C [1996Lid]
		a = 445.3 *c* = 1047	at 400°C [1997Ria2]
* τ_7, $CeCu_9Sn_4$ < 745	*tI*56 *I*4/*mcm* $LaFe_9Si_4$	*a* = 862.6 *c* = 1238.2	[2001Sin]
* τ_8, $Ce_2Cu_9Sn_{2.65}$	*oP*56-1.4 *Pnnm* $Ce_2Cu_9In_3$	 *a* = 1066.9 *b* = 1673.4 *c* = 506.6	labelled as "$Ce_3Cu_{13}Sn_4$" [1997Ria2] [1997For, 1998For]
* τ_9, $CeCu_5Sn$	*oP*28 *Pnma* $CeCu_6$	*a* = 834.18 *b* = 506.88 *c* = 1065.1	[1997Sko]
		a = 831.7 *b* = 506.6 *c* = 1059.1	at 500°C [2001Sin]
		a = 832.3 *b* = 506.4 *c* = 1059.7	[1997For, 1998For] The $CeAuCu_5$-prototype - a ternary derivative of the $CeCu_6$ structure
* τ_{10}, $CeCu_{9.4}Sn_{3.6}$ < 800	*cF*112 $Fm\bar{3}c$ $NaZn_{13}$	*a* = 1215.3 *a* = 1217.7	at 500°C [1984Kom] [2001Sin]

a) Possibly, according to the assumption of [1998Ria], the τ_2 phase structure is of the ordered *hP*6 $P6_3mc$ NdPtSb type according to single-crystal data obtained from other RECuSn compounds [1996Poe]. Later the ordered $P6_3mc$ GaGeLi type was attributed by [2005Cha] to the structure of this phase (as a results of antiferromagnetic ordering experimental investigation)

Table 3: Invariant Equilibria

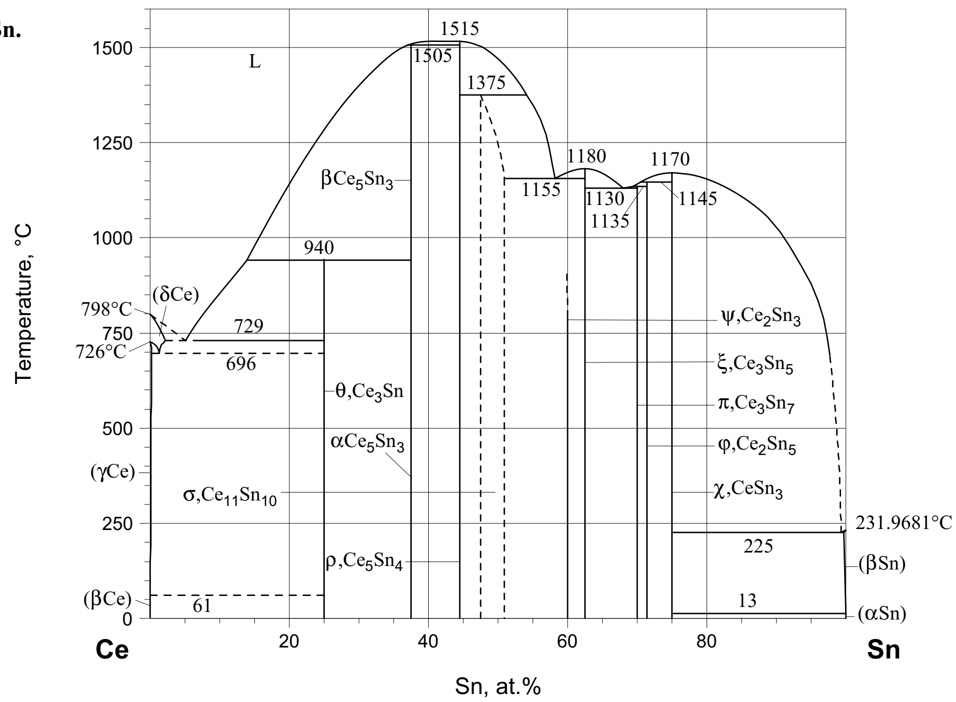
Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Ce	Cu	Sn
L ⇌ τ_2 + λ	~800	e_1	L	~33	~63.8	~3.2
L + ν ⇌ τ_2 + μ	780	U_1	L	23	75	2
L + τ_2 ⇌ τ_1 + λ	775	U_2	L	41	56	3
L + τ_1 ⇌ (Ce_5Sn_3) + λ	760	U_3	L	42.5	54.5	3
L ⇌ μ + λ + τ_2	740	E_1	L	25	73	~ 2
L + (δCe) ⇌ θ + (γCe)	699	U_4	L	91	5	4
L + Ce_5Sn_3 ⇌ θ + λ	530	U_5	L	56	42	2
L + λ ⇌ κ + θ	510	U_6	L	59.5	39.5	1
L ⇌ κ + θ + (γCe)	420	E_2	L	71	27.5	1.5

Table 4: Investigations of the Ce-Cu-Sn Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1982Sko]	Faraday method	Magnetic susceptibility of the $CeCu_2Sn_2$ compound
[1983Kom]	Faraday method	Magnetic susceptibility of the CeCuSn compound
[1984Kom]	Faraday method	Magnetic susceptibility of the $CeCu_{9.4}Sn_{3.6}$ compound
[1988Kom]	Faraday method	Magnetic susceptibility of the $CeCu_{0.52}Sn_{1.83}$ compound
[1989Goe]	^{119}Sn Moessbauer measurements	Isomer shift, recoil free fraction of the $CeCu_2Sn_2$ compound
[1994Nak]	Four-point probe method; SQUID pendulum magnetometer measurements; standard semi-adiabatic specific heat measurements	Electrical resistivity, magnetization of the CeCuSn
[1996Guz]	Magnetic susceptibility measurements	Reciprocal magnetic susceptibility of the $CeCu_2Sn_2$ single crystal
[1997Sko]	Electrical and magnetic properties measurements	Electrical resistivity, thermopower, magnetic susceptivbility of the $CeCu_{6-x}Sn_{1+x}$ (x = 0, 0.25, 0.50, 0.75 and 1) alloys
[2000Isn]	Extraction method; ac current four probes method; direct comparison of a copper-sample-copper chain to a standard thermocouple	Electrical resistivity, magnetoresistance, reciprocal magnetic susceptibility, thermopower of the $CeCu_{6-x}Sn_x$ (x = 0, 0.25, 0.75 and 1)

Reference	Method/Experimental Technique	Type of Property
[2000Sin]	Ac current four probes method; SQUID magnetometer measurements; semi-adiabatic, heat pulse method of heat capacity measurements	Inverse susceptibility, magnetization, electrical resistivity of the $Ce_3Cu_4Sn_4$ compound
[2001Sin]	Ac current four probes method; SQUID magnetometer measurements; semi-adiabatic, heat pulse method of heat capacity measurements;	Inverse susceptibility, magnetization, electrical resistivity of the $CeCu_9Sn_4$ and $CeCu_{9.4}Sn_{3.6}$ compounds
[2002Zah]	Quantum design physical property measurement system (PPMS) technique; specific heat measurements using a quantum design physical property measurement system (PPMS)	Magnetic susceptibility, magnetization of the $Ce_3Cu_4Sn_4$ compound
[2004Szy]	SQUID magnetometer technique	Magnetic susceptibility of the $Ce_3Cu_4Sn_4$ compound
[2004Wu]	Mechanical properties measurements	Tensile strength, ductility, creep strain, wettability
[2005Cha]	Single crystal neutron diffraction studies	Antiferromagnetic behavior of the CeCuSn compound

Fig. 1: Ce-Cu-Sn. The Ce-Sn phase diagram



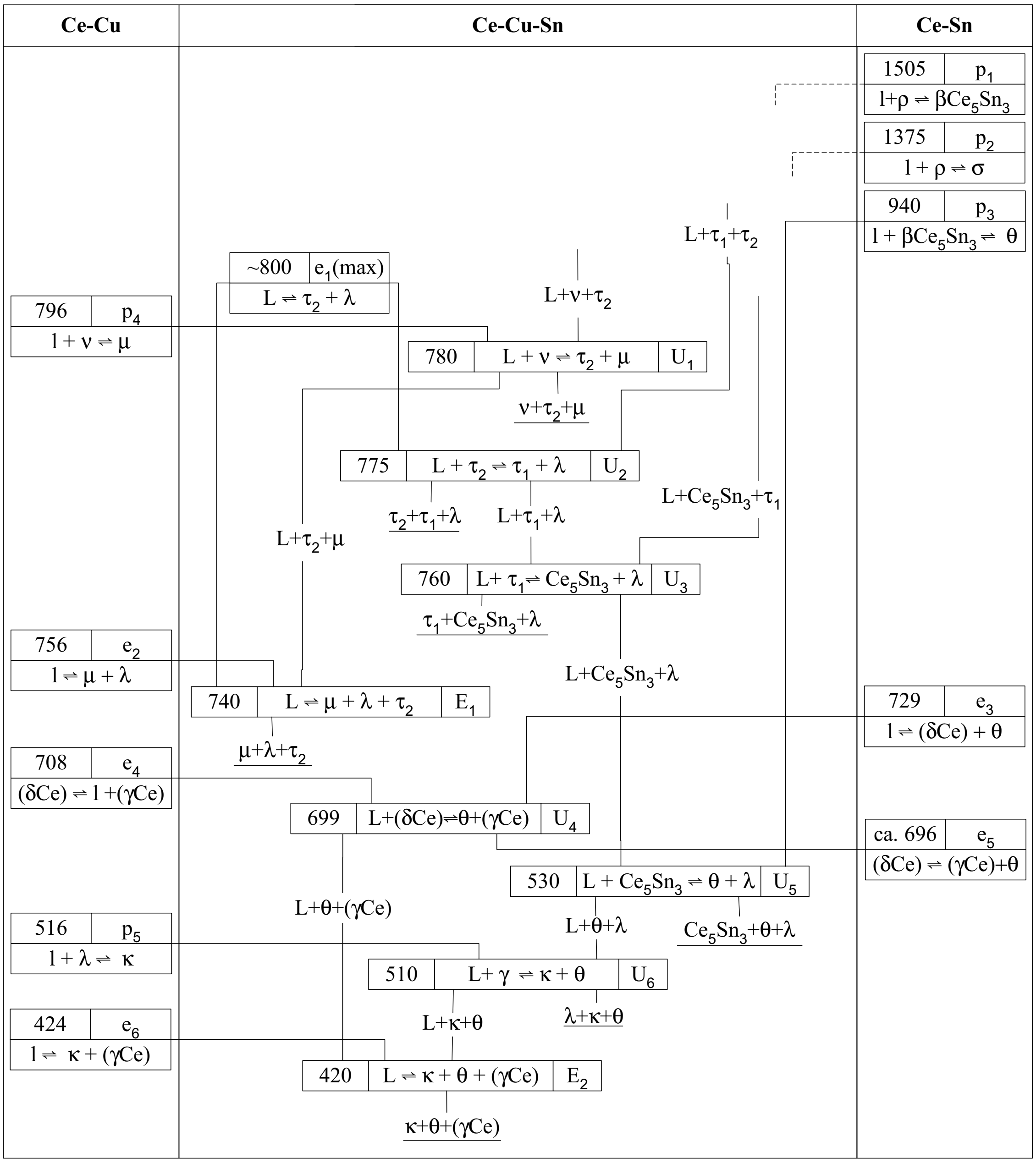


Fig. 2: Ce-Cu-Sn: Partial reaction scheme

Fig. 3: Ce-Cu-Sn. Liquidus surface projection in the Ce rich region

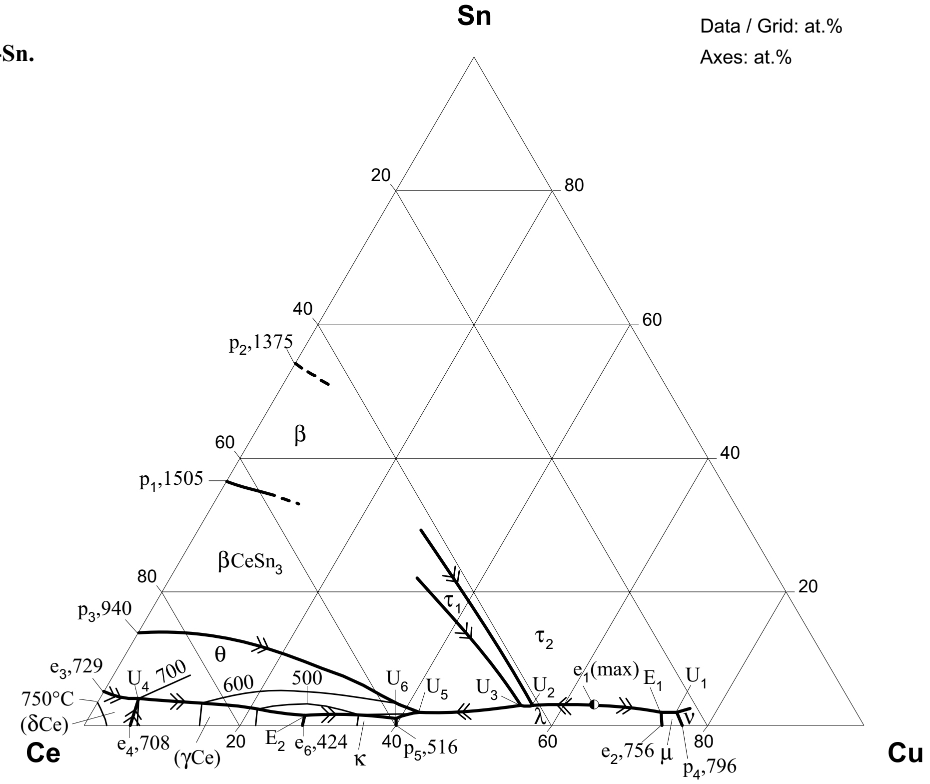


Fig. 4: Ce-Cu-Sn. Isothermal section at 400°C

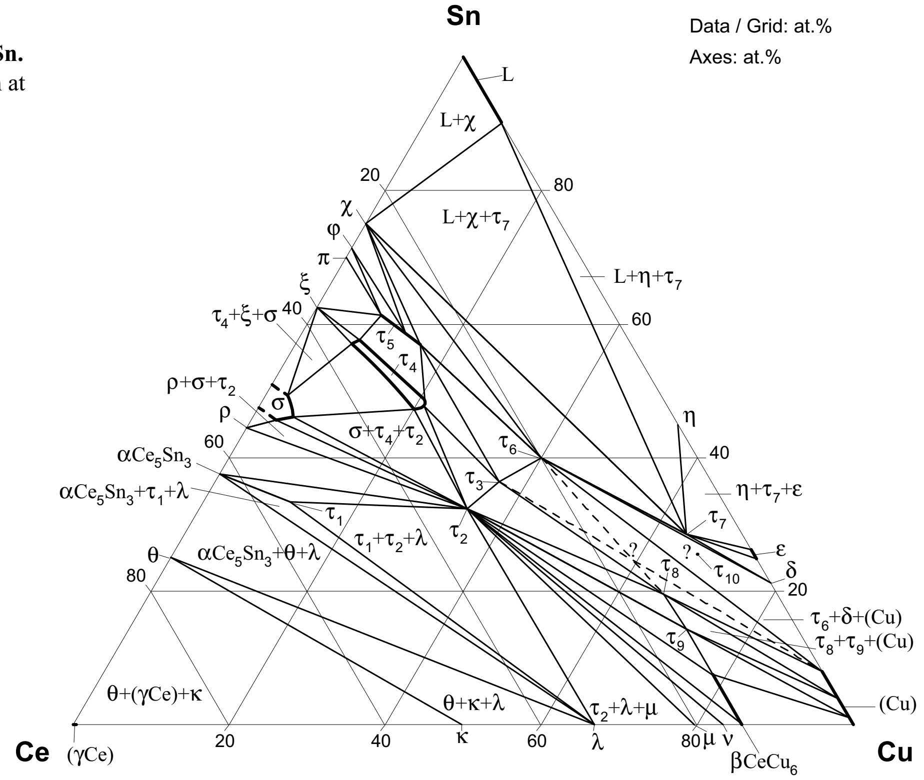


Fig. 5: Ce-Cu-Sn. Temperature dependence of the specific heat of CeCuSn in various magnetic fields

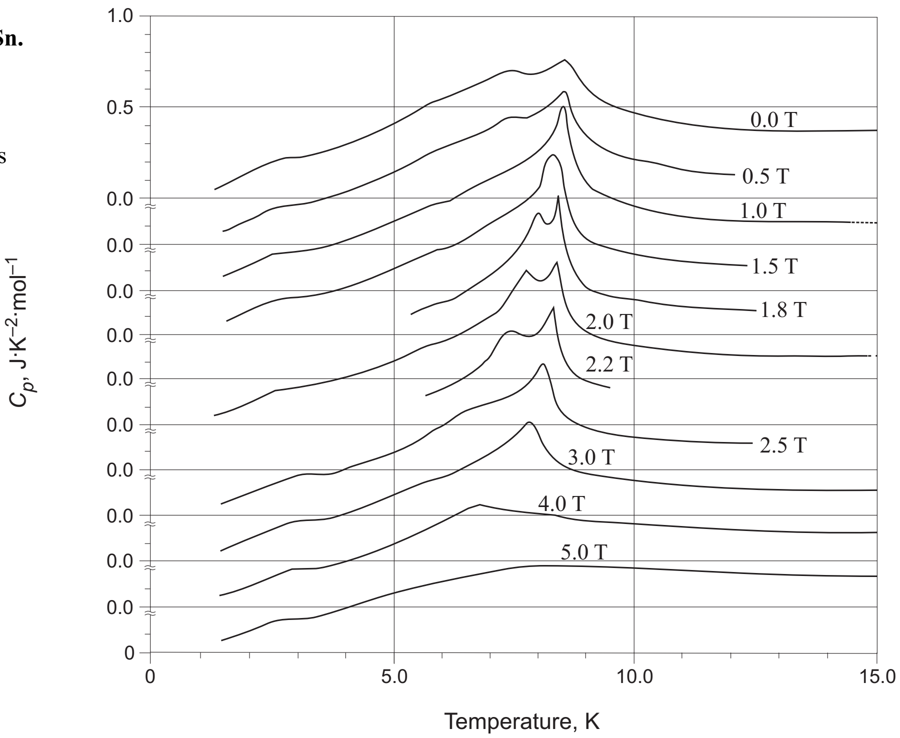


Fig. 6: Ce-Cu-Sn. Magnetic phase diagram of CeCuSn

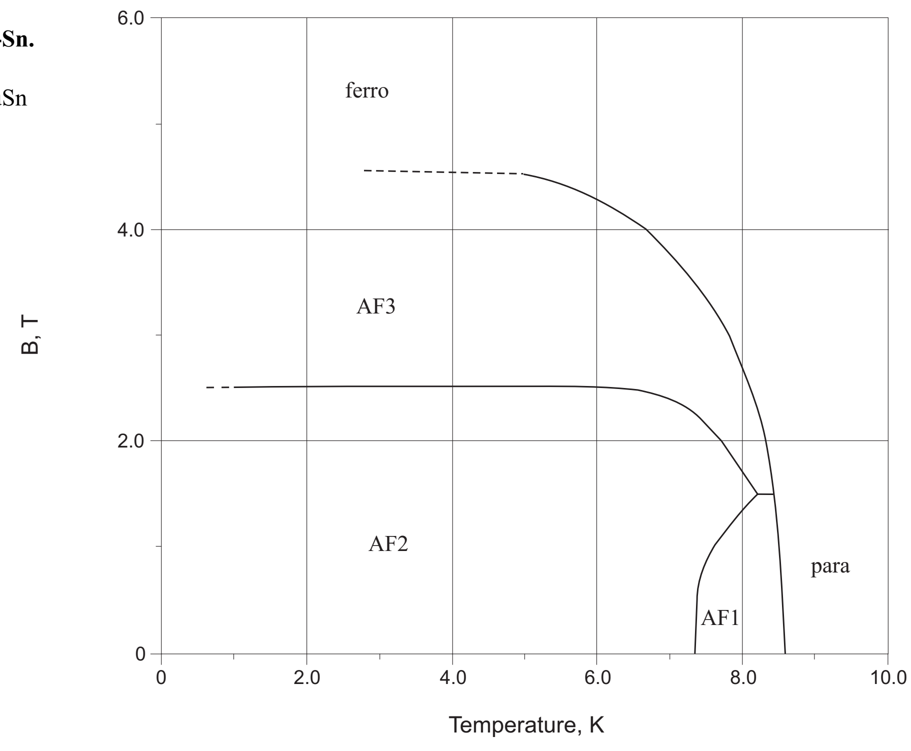


Fig. 7: Ce-Cu-Sn. The heat capacity of $Ce_3Cu_4Sn_4$ below 30 K

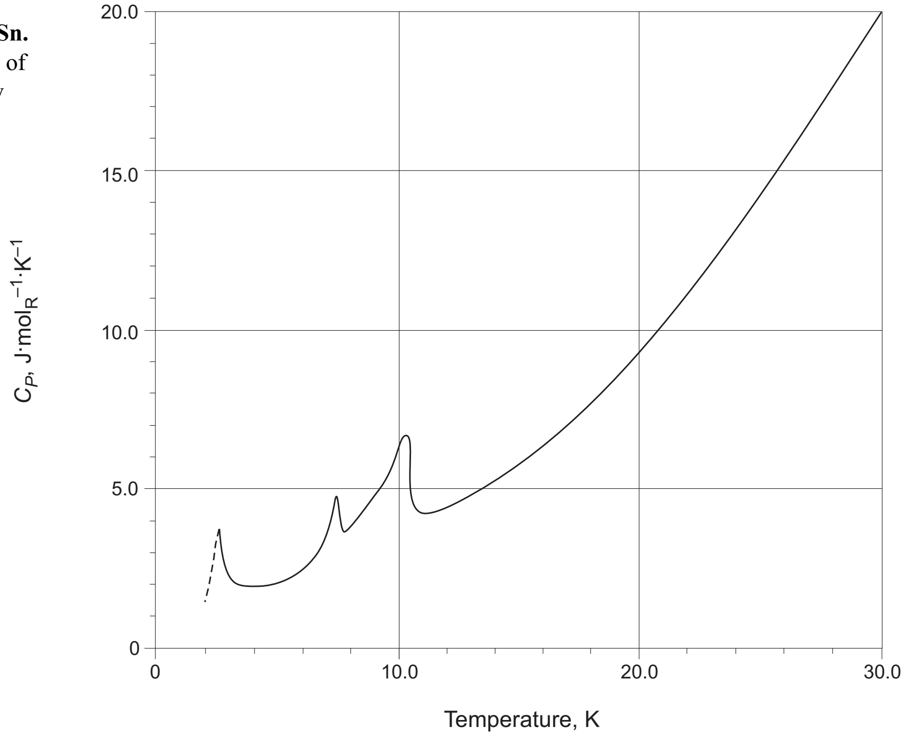
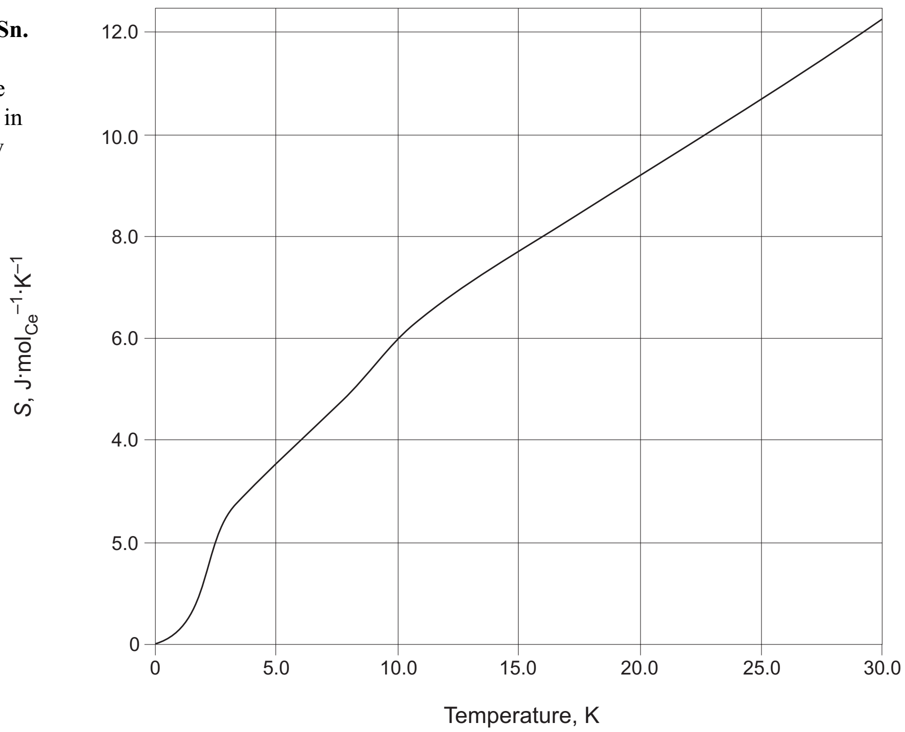


Fig. 8: Ce-Cu-Sn. Temperature dependence of the magnetic entropy in $Ce_3Cu_4Sn_4$ below 30 K



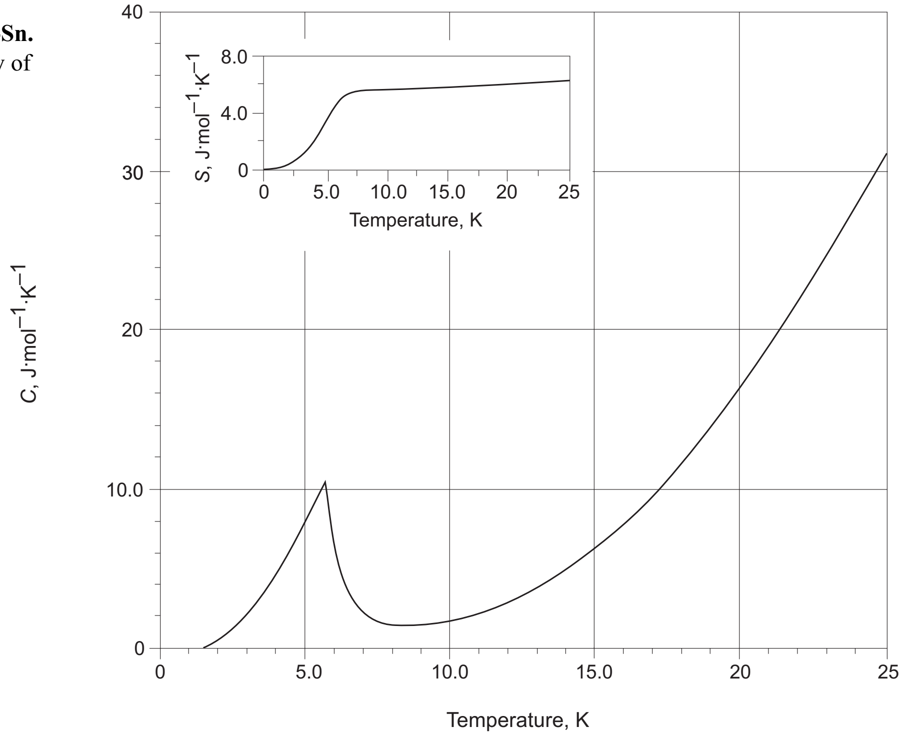


Fig. 9: Ce-Cu-Sn. The heat capacity of $CeCu_9Sn_4$

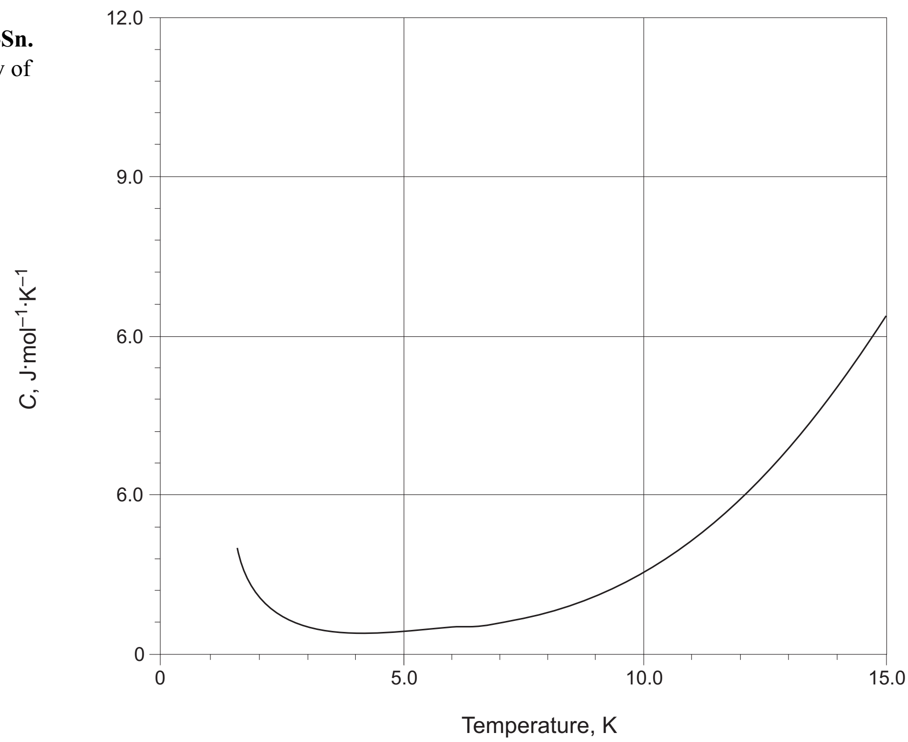


Fig. 10: Ce-Cu-Sn. The heat capacity of $CeCu_{9.4}Sn_{3.6}$