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ARTICLE TYPE

## The System Ce-Zn-Si for <33.3% at. Ce:

### Phase Relations, Crystal Structures and Physical Properties

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Phase equilibria of the system Ce-Zn-Si have been determined for the isothermal section at 600° for <33.3 at.% Ce by XRPD and EPMA. The section is characterized by the formation of seven ternary compounds with homogeneity regions at constant Ce-content and partial substitution of Zn/Si:  $\tau_1$ - $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$  (unique type;  $0.45 \leq x \leq 0.99$ ),  $\tau_2$ - $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  (AlB<sub>2</sub>-type;  $0.36 \leq x \leq 0.73$ ),  $\tau_5$ - $\text{CeZn}(\text{Zn}_{1-x}\text{Si}_x)_2$  (CeNiSi<sub>2</sub>-type;  $0.68 \leq x \leq 0.76$ ),  $\tau_6$ - $\text{CeZn}_2(\text{Si}_{1-x}\text{Zn}_x)_2$  (ThCr<sub>2</sub>Si<sub>2</sub>-type;  $0.25 \leq x \leq 0.30$ ) and  $\tau_7$ - $\text{Ce}_{37}\text{Zn}_{48}\text{Si}_{15}$  (structure unknown). Whereas  $\tau_1$ ,  $\tau_2$  and  $\tau_5$  are stable at 600 and 800 °C, the phases  $\tau_6$ ,  $\tau_7$  are unstable at 800°C. Atom site distribution in the crystal structures of  $\tau_5$ ,  $\tau_6$  and the  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  have been elucidated from X-ray intensity refinements on single crystals. The small amounts of the stabilizing tetravalent element in  $\{\text{La,Ce}\}_7\text{Zn}_{21}[\text{Zn}_{1-x}\text{Si}(\text{Ge})_x]_2$  suggest a hypothetical binary phase “ $\{\text{La,Ce}\}_7\text{Zn}_{23}$ ”. The stabilizing effect of Ge in  $\text{Ce}_7\text{Zn}_{23-x}\text{Ge}_x$  has been elucidated from density functional theory (DFT) calculations discussing the electronic structure in terms of the density of states (DOS) and defining enthalpies of formation for  $\text{Ce}_7\text{Zn}_{23-x}\text{Ge}_x$  ( $x=0, 0.5, 2$ ) as well as for several neighbouring binary Ce-Zn phases. A Schultze-Scheil diagram for the solidification behaviour in the (Zn,Si)-rich part of the diagram was constructed from DTA measurements in closed silica crucibles along with partial isothermal sections determined in the temperature range from 400 to 900°C. The phases  $\tau_5$  and  $\tau_6$  both form in degenerate ternary peritectic reactions:  $\text{L} + (\text{CeSi}_2, \beta\text{-Ce}_2\text{Zn}_{17}) \rightleftharpoons \tau_5$  at  $865 \pm 5^\circ\text{C}$  and  $\text{L} + (\tau_5, \text{CeZn}_{11}) \rightleftharpoons \tau_6$  at  $695 \pm 5^\circ\text{C}$ , respectively. Magnetic susceptibility, specific heat and resistivity measurements of  $\tau_5$ - $\text{CeZn}(\text{Si}_{1-x}\text{Zn}_x)_2$  revealed Kondo lattice behavior with ferromagnetic ordering below  $T_C=4.4$  K, whereas susceptibility and specific heat studies of  $\tau_6$ - $\text{CeZn}_2(\text{Zn}_{0.28}\text{Si}_{0.72})_2$  revealed Curie-Weiss paramagnetic behaviour down to 3 K. The effective paramagnetic moments of Ce obtained from Curie-Weiss fits of  $\tau_5$  ( $2.48 \mu_B$ ) and  $\tau_6$  ( $2.34 \mu_B$ ) reveal a ground state close to trivalent Ce.

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## ARTICLE TYPE

## 1. Introduction

Ternary compounds Ce-T-Si (T is one of the late transition metals) have been known for their interesting physical properties, such as heavy fermion and unconventional superconductors,<sup>1,2</sup> Kondo-behaviour and quantum criticalities,<sup>3</sup> intermediate valency,<sup>4</sup> thermoelectric features,<sup>5</sup> etc. Most ternary Ce-T-Si systems have been explored,<sup>6</sup> except for group 12 elements (Zn, Cd, Hg). The high vapor pressure of these metals complicates sample preparation, and requests careful control of compositions. Therefore conventional preparation methods such as arc melting or induction melting in open crucibles cannot be used. However, a few investigations were already concerned with the Ce-Zn-Si system. Kido et al.<sup>7</sup> reported paramagnetism and metallic behavior of REZnSi compounds (RE = Ce, Nd, Sm, Gd, Tb, Ho) in the temperature range of 77-300 K. Recently, phase equilibria for the Ce-Zn-Si system have been derived at 800°C by Malik et al.<sup>8</sup> and revealed the existence of 4 ternary compounds, labeled as  $\tau_1$  to  $\tau_4$ . Whilst the crystal structures of  $\tau_1$  and  $\tau_2$  and their La-homologues have been elucidated from single crystal X-ray data, the crystal structures of the other compounds remained unresolved. A recent study of RE<sub>7</sub>Zn<sub>21</sub>Tt<sub>2</sub>-phases (Tt is a tetrel element) by Nian-Tzu Suen and Bobev<sup>9</sup>, prompted among other rare earth elements (La-Nd) the formation of novel cerium compounds Ce<sub>7</sub>Zn<sub>21</sub>{Ge,Sn,Pb}<sub>2</sub> crystallizing with the structure type first determined by Malik et al.<sup>8</sup> for {La,Ce}<sub>7</sub>Zn<sub>21</sub>(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub>. In their latest publication, they also investigated the single crystals of {Ce-Pr}<sub>7</sub>Zn<sub>21</sub>(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub> and their magnetic properties.<sup>10</sup> Their result, especially on the crystal structure of Ce<sub>7</sub>Zn<sub>21.95</sub>Si<sub>1.05</sub> confirms the work of Malik et al.<sup>8</sup>

The absence of ternary compounds in the Ce-poor part (< 33 at.% Ce) of the isothermal section Ce-Zn-Si seems unusual, particularly ternary compounds with ThCr<sub>2</sub>Si<sub>2</sub> structure or derivative types are encountered in most Ce-T-Si systems (T is a transition metal from Cr to Cu).<sup>11</sup> Therefore also the possibility of compound formation at lower temperature needs to be explored. Indeed the investigation of the Zn/Si-rich part of the Ce-Zn-Si phase diagram at 800°C<sup>8</sup> revealed hints for a ternary compound (labelled as  $\tau_5$ ) with composition close to Ce(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>3</sub>; x≈0.5. Our further attempts to investigate this phase at 700°C prompted another ternary compound (labelled as  $\tau_6$ ) with composition of Ce<sub>20</sub>Zn<sub>53</sub>Si<sub>27</sub>, which is also formed from the melt. An electron count on  $\tau_5$ -CeZn<sub>1.5</sub>Si<sub>1.5</sub>, considering the valencies of Ce = +3, Zn = +2 and Si = -4 yields balanced electronic charges suggesting a Zintl behaviour interesting for thermoelectric application.

Therefore this work focuses on the investigation of phase equilibria and crystal structures of  $\tau_5$  and  $\tau_6$ , as well as their mechanism of formation and stability. Furthermore the magnetic ground state of cerium in these compounds was of interest. Particularly the small amount of tetrel elements (Tt) to stabilize {La,Ce}<sub>7</sub>Zn<sub>21</sub>(Zn<sub>1-x</sub>Tt<sub>x</sub>)<sub>2</sub> was investigated by DFT calculations for Tt=Ge to get insight into the electronic DOS, bonding behavior and ground state energies of hypothetical binary Ce<sub>7</sub>Zn<sub>23</sub> in

comparison with ternary Ce<sub>7</sub>Zn<sub>23-x</sub>Ge<sub>x</sub> (x=0.5, 2).

## 2. Experimental Methods and Density Functional Theory Calculation

Most samples were prepared by mixing and cold pressing proper blends of ball milled powders of CeSi<sub>x</sub> master alloys with Zn filings inside an Ar filled glove box. Master alloys CeSi<sub>x</sub> were prepared by argon arc melting of Ce and Si pieces on a water-cooled copper hearth with a tungsten electrode, while Zn filings were prepared from purified Zn drops. Samples in the Zn-rich corner were then sealed under vacuum or argon and annealed at 600°C for 4 to 14 days. Samples with low Si(Ge) content (close to binary Ce-Zn) were prepared in a different way. Ce filings, Zn filings, and Si(Ge) powder were mixed in proper ratio, cold pressed, sealed and then subjected to the same heat treatment. All starting materials had a purity of better than 99.9 mass%.

After heat treatment, samples were quenched by submersing the quartz capsules in cold water and analyzed by X-ray powder diffraction with Ge-monochromated CuK $\alpha_1$ -radiation employing a Guinier-Huber image plate recording system. X-ray powder diffraction analyses were performed via Rietveld refinement using the FULLPROF program.<sup>12</sup> Precise lattice parameters were determined referring to Ge as internal standard ( $a_{\text{Ge}} = 0.565791$  nm). Special treatments were needed to prepare samples for Electron Probe Microanalysis (EPMA) due to their powder-like consistency. Coarse powders of samples were mixed and cold pressed with fine powders of conductive resin in a small steel die (5-6 mm in diameter) prior to hot compacting them together into a coarse powder/granule of conductive resin. Samples were ground and polished under glycerin in order to avoid oxidation and/or hydrolysis. Microstructures and compositions were examined by light optical microscopy (LOM) and scanning electron microscopy (SEM) and EPMA on a Zeiss Supra 55 VP equipped with an energy dispersive X-ray analysis (EDX) detector operated at 20 kV.

Single crystals of  $\tau_5$  and  $\tau_6$  were grown from Zn flux. Powders of a multiphase alloy with nominal composition Ce<sub>20</sub>Zn<sub>50</sub>Si<sub>30</sub> were mixed and cold pressed with Zn filings in a weight ratio of 1:45 and 1:57 for  $\tau_5$  and  $\tau_6$ , respectively. The sample billets were sealed under vacuum in quartz capsules, heated to 800°C, kept at this temperature for 1 hour, and were then slowly cooled with a rate of 6°C/h to 735°C and 670°C for  $\tau_5$  and  $\tau_6$ , respectively. After quenching in cold water, the Zn flux matrix was dissolved in cold diluted HCl. No reaction of the single crystal material with HCl was observed during leaching.

Single crystals of {La,Ce}<sub>7</sub>Zn<sub>21</sub>(Zn<sub>1-x</sub>Ge<sub>x</sub>)<sub>2</sub> were prepared from cold pressed mixtures of La/Ce filings, Zn filings and Ge powder with nominal composition of La<sub>25</sub>Zn<sub>73</sub>Ge<sub>2</sub> and Ce<sub>25</sub>Zn<sub>70</sub>Ge<sub>5</sub>, respectively. The Ce-containing pellet was sealed under vacuum into a quartz ampoule, heated to 600°C with a rate of 60°C/h, kept at this temperature for 12 hrs, further heated to 1050°C at 600°C/h, and then slowly cooled to 800°C with a rate of 10°C/h.

A slightly different heat treatment was performed to grow single crystals of  $\text{La}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  heating the pellet to 600°C at 60°C/h, keeping this temperature for 12 hrs, followed by further heating to 900°C at a rate of 600°C/h, resting at this temperature for 30 minutes, and then slowly cooling to 800°C at a rate of 6°C/h. Single crystals were then mechanically isolated and selected from the crushed regulus.

Inspections on an AXS D8-GADDS texture goniometer assured high crystal quality, unit cell dimensions and Laue symmetry of the single crystal specimens prior to X-ray intensity data collections at room temperature on a Bruker APEXII diffractometer equipped with a CCD area detector and an Incoatec Microfocus Source  $\mu\text{S}$  (30 W, multilayer mirror,  $\text{Mo-K}\alpha$ ,  $\lambda = 0.071069$  nm). Orientation matrices and unit cell parameters were derived using the Bruker APEXII software suite.<sup>13</sup> No additional absorption corrections were performed because of the rather regular crystal shapes and small dimensions of the investigated specimens. The structures were solved by direct methods (SHELXS-97) and were refined with the SHELXL-97<sup>14</sup> program within the Windows version WINGX.<sup>15</sup> Crystal structure data were standardized using program STRUCTURE-TIDY.<sup>16</sup>

In order to investigate the thermal stability of  $\tau_5$  and  $\tau_6$  and to determine the corresponding ternary reaction isotherms, DTA measurements were performed using a Netzsch STA 409 CD/3/403/5/G apparatus. Due to the high vapor pressure of Zn, measurements were performed in closed thin-walled quartz crucibles. Single-phase material of  $\tau_5$  and  $\tau_6$  was measured from room temperature to 900°C with a heating/cooling rate of 5°C/min. Isothermal annealing served to confirm the phase fields related to the four-phase reactions observed in DTA: for this purpose two alloys in the Zn rich part with nominal compositions,  $\text{Ce}_{5.9}\text{Zn}_{59.8}\text{Si}_{34.3}$  and  $\text{Ce}_{7.6}\text{Zn}_{78.4}\text{Si}_{14}$ , were prepared from powders of  $\text{CeSi}_x$  and Zn filings and annealed at 500°C for 4 days. After first reaction, the alloys were powderized to a grain size below 53  $\mu\text{m}$  inside the glove box and were then cold compacted in a steel die (diameter=10 mm). The pellets were dry-cut into several pieces and sealed in quartz tubes under about 300 mbar Ar and annealed at 400°C, 650°C, 710°C, 750°C, 770°C, 790°C, 810°C, 850°C, 860°C, 870°C, 880°C and 900°C for 1 day each. Single phase samples of  $\tau_5$  and  $\tau_6$  were prepared in a similar way. The second annealing temperature was 700 and 600 °C for  $\tau_5$  and  $\tau_6$ , respectively. The furnaces were calibrated with standard thermocouples and Sb (melting point = 631°C).

Dc magnetic susceptibility measurements were performed with a SQUID magnetometer for  $\tau_5$  and  $\tau_6$  from 2-300 K with various magnetic fields from 0.006 to 6 T on freely rotating single crystals with a total mass of 0.80 mg (individual crystals with a typical mass of 100  $\mu\text{g}$ ) and on sintered polycrystalline samples of about 20 mg. Ac susceptibility measurements were carried out on sintered polycrystalline samples of about 200 mg with a Lakeshore 7000 ac susceptometer applying an ac-field with amplitude of 325A/m and a frequency of 100 Hz. Specific heat measurements were performed on a commercial Quantum Design PPMS calorimeter on a sintered  $\tau_6$  sample and on  $\tau_5$  single crystals. Parts of a sintered sample of  $\tau_5$  were also used for resistivity and Seebeck coefficient measurements. Resistivity measurements were performed from 2-300 K in a home-made equipment using the ac bridge resistance technique, while the

high temperature part (300-673 K) was measured simultaneously with the Seebeck coefficient in a ZEM-3 ULVAC.

The density functional theory (DFT) calculations were performed by using the Vienna ab initio simulation package (VASP)<sup>17,18</sup> and applying the pseudopotential construction according to the projector-augmented-wave method.<sup>19</sup> For the exchange-correlation functional the generalized gradient approximation according to Perdew et al. (PBE)<sup>20</sup> was chosen. The VASP calculations were done with high precision using the predefined/default values as provided by the VASP package. The energy cutoff was chosen at 350 eV. Spin polarized calculations were done assuming ferro/ferrimagnetic ordering. For the  $\mathbf{k}$  space integration the Gaussian smearing method with a value for  $\sigma$  of 0.1 eV was taken.  $\mathbf{k}$  space grids were constructed by the method outlined in Ref. 21, namely  $11 \times 11 \times 11$  for  $\text{CeZn}$ ;  $7 \times 5 \times 5$  for  $\text{Ce}_4\text{Zn}_8$  ( $\text{CeZn}_2$ );  $7 \times 3 \times 5$  for  $\text{Ce}_4\text{Zn}_{12}$  ( $\text{CeZn}_3$ );  $3 \times 3 \times 7$  for  $\text{Ce}_{14}\text{Zn}_{46}$  ( $\text{Ce}_7\text{Zn}_{23}$ ) and related compounds;  $7 \times 3 \times 2$  for  $\text{Ce}_6\text{Zn}_{22}$  ( $\text{Ce}_3\text{Zn}_{11}$ ). No additional many-body treatment was made for the localized character of the f-like states of Ce, since the compounds under study are all in a metallic state with f-occupation of  $\sim 1$  per Ce atom. PBE is considered to reasonably capture the localization properties in terms of spin-polarization as it does for 3d transition metals. Assuming the experimental structure as starting point for all cases, the atomic positions as well as the unit cell parameters were fully relaxed. The Ge substitution was made according to Table 3 at the experimentally defined M1 sites.

### 3. Results and Discussions

#### 3.1. Binary boundary systems

The Zn-Si system (calculated) and the Ce-Zn system were accepted after Massalski<sup>22</sup> taking also into account a more recent investigation on the low temperature modification of  $\alpha\text{Ce}_2\text{Zn}_{17}$  ( $\alpha\text{Ce}_{1-x}\text{Zn}_{5+2x}$ ) with  $\text{TbCu}_7$ -type.<sup>23</sup> For the Ce-Si system we rely on the version of Malik et al.,<sup>8</sup> which essentially is based on the investigation by Bulanova et al.<sup>24</sup> but also includes further phases such as  $\text{Ce}_2\text{Si}_{3-x}$ <sup>25</sup> and the high pressure phases  $\text{CeSi}_5$  and  $\text{Ce}_2\text{Si}_7$ .<sup>26</sup> The La-Zn system was taken from the latest experimental investigation by Berche et al.<sup>27</sup> with recent data on the crystal structure of  $\text{LaZn}_4$ .<sup>28</sup> Detailed crystallographic data for unary and binary boundary phases are summarized in Table S1 (Supporting Information), those for ternary compounds are listed in Table 1, respectively.

#### 3.2. Crystal structure of ternary compounds in the Ce-Zn-Si system

##### 3.2.1. Crystal structure of $\tau_5$ - $\text{CeZn}(\text{Zn}_{1-x}\text{Si}_x)_2$ , $x = 0.71$

The X-ray diffraction pattern of a suitable flux grown single crystal of  $\tau_5$  was fully indexed in orthorhombic symmetry ( $a = 0.42079(1)$ ,  $b = 1.76522(3)$ ,  $c = 0.41619(1)$  nm). Analysis of systematic extinctions suggested three possible space group types  $Cmcm$ ,  $Cmc2_1$ ,  $C2cm$  (non-standard setting) and consequently structure solution employing direct methods was attempted in the space group type  $Cmcm$  of highest symmetry (see Table 2). In order to find mixed Zn/Si sites, refinements were first performed with Ce and Zn only. Two of the three Zn sites (M1, M2) were found to have an unusually high atomic displacement parameter (ADP), indicating partial substitution by Si atoms.



Table 1. Crystallographic data of ternary solid phases of the system Ce-Zn-Si.

Phase Temperature range (°C)	Space group, Prototype	Lattice parameters (nm)			Comments
		a	b	c	
$\tau_1$ -Ce <sub>7</sub> Zn <sub>21</sub> (Zn <sub>1-x</sub> Si <sub>x</sub> ) <sub>2</sub>	<i>Pbam</i> Ce <sub>7</sub> Zn <sub>21</sub> (Zn <sub>1-x</sub> Si <sub>x</sub> ) <sub>2</sub>	1.55722(3)	1.71942(3)	0.44772(1)	x=0.28 <sup>8</sup> SC 0.28<x<0.98 at 800°C <sup>8</sup> 0.45<x<0.99 at 600°C [this work]
$\tau_2$ -Ce(Zn <sub>1-x</sub> Si <sub>x</sub> ) <sub>2</sub>	<i>P6/mmm</i> AlB <sub>2</sub>	0.4223	-	0.4238	<sup>7</sup> x=0.50 <sup>8</sup> SC at x=0.44 0.36≤x≤0.76 at 800°C <sup>8</sup> x=0.75 <sup>8</sup> 0.36≤x≤0.73 at 600°C [this work] x=0.57 [This work]
		0.41827(2)	-	0.42747(2)	
		0.4421(2)	-	0.38960(3)	
		0.42206(5)	-	0.42334(6)	
$\tau_3$ -Ce(Zn <sub>x</sub> Si <sub>1-x</sub> )	unknown	-	-	-	0.17<x<0.23 at 800°C <sup>8</sup>
$\tau_4$ -Ce <sub>40</sub> Zn <sub>37</sub> Si <sub>23</sub>	unknown	-	-	-	at. % <sup>8</sup>
$\tau_5$ -CeZn(Zn <sub>1-x</sub> Si <sub>x</sub> ) <sub>2</sub> <865±5 [this work]	<i>Cmcm</i> CeNiSi <sub>2</sub>	0.42079(1)	1.76522(3)	0.41619(1)	x=0.71 [SC] [This work] 0.68≤x≤0.76 at 600°C [this work]
$\tau_6$ -CeZn <sub>2</sub> (Si <sub>1-x</sub> Zn <sub>x</sub> ) <sub>2</sub> <695±5 [this work]	<i>I4/mmm</i> ThCr <sub>2</sub> Si <sub>2</sub>	0.41757(1)	-	1.05073(2)	x=0.30 SC [This work] 0.25≤x≤0.30 at 600°C [This work]
$\tau_7$ -Ce <sub>37</sub> Zn <sub>48</sub> Si <sub>15</sub> <800	unknown	-	-	-	This work

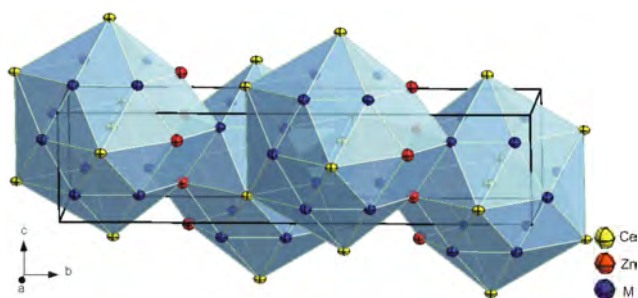


Figure 1. Crystal structure of  $\tau_5$ -CeZn(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub>, x = 0.71 showing atoms with anisotropic displacement parameters from X-ray single crystal refinement.

Further refinement with anisotropic ADPs for all atoms converged to  $R_F = 0.020$  and residual electron densities smaller than  $\pm 3.04 \text{ e}/\text{\AA}^3$ . The final formula obtained, CeZn(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub> with x = 0.71 corresponds to the composition Ce<sub>25.0</sub>Zn<sub>39.7</sub>Si<sub>35.3</sub> (in at.%), which perfectly fits to the value derived from EPMA (Ce<sub>24.9</sub>Zn<sub>39.6</sub>Si<sub>35.5</sub>). Details on crystal data along with ADPs are summarized in Table 2. A Rietveld X-ray powder diffraction refinement confirms the structure model for  $\tau_5$ . Furthermore, lattice parameters, crystal symmetry, and Wyckoff positions proved that this compound is isotypic with the structure type of CeNiSi<sub>2</sub> (see Figure 1).

Interatomic distances are given in Table S2 (Supporting Information). Comparing atom distances with the sum of atomic radii, direct bonding is neither revealed between M1-Zn3 nor for M2-M2. However, stronger bonding is inferred from the distances among M1-M1, M1-M2 and M2-Zn3 atoms, particularly taking into account the Zn/Si random occupancy. At 600°C the phase  $\tau_5$ -CeZn(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub> exhibits a compositional range,  $0.68 \leq x \leq 0.76$ , excluding any stoichiometric composition (for details see section 3.4).

Compounds with the CeNiSi<sub>2</sub> type are known in many Ce-T-Si systems (T = Fe to Cu, Rh, Ir, Pt, and Sn) and exist in both stoichiometric and non-stoichiometric forms.<sup>11</sup> For  $\tau_5$ -CeZn(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub>, however, only the non-stoichiometric composition could

be found, whereas the Ce-Cu-Si system,<sup>29</sup> which is the closest homologous system, contains two individual phases of same symmetry (isotypic with CeNiSi<sub>2</sub>), namely CeCu<sub>1.6</sub>Si<sub>1.4</sub> (=CeCu(Cu<sub>0.6</sub>Si<sub>0.4</sub>)Si) and stoichiometric CeCuSi<sub>2</sub>, both separated by a two-phase equilibrium: Ce(Cu<sub>1-x</sub>Si<sub>1+x</sub>)<sub>2</sub> (AlB<sub>2</sub>-type) + CeCu<sub>2</sub>Si<sub>2</sub>. It should be noted that the atom preference in the mixed sites in  $\tau_5$ -CeZn(Zn<sub>0.26</sub>Si<sub>0.74</sub>)(Zn<sub>0.31</sub>Si<sub>0.69</sub>) - where Zn/Si randomly fill two 4c-sites with y=0.03338(5) and y=0.16921(5) - differs from non-stoichiometric CeCu(Cu<sub>0.6</sub>Si<sub>0.4</sub>)Si where Cu and Si atoms only share the 4c-site with y=0.038. However, we have to note here that the reliability of the X-ray single crystal study on photographs for CeCu<sub>1.6</sub>Si<sub>1.4</sub> is low, as  $R_F$  was only 17.7%.<sup>30</sup> The discussion on TbFe<sub>0.5</sub>Si<sub>2</sub> being a site exchange variant of the CeNiSi<sub>2</sub>-type has been solved from neutron diffraction data on HoFe<sub>0.5</sub>Si<sub>2</sub>,<sup>31</sup> which clearly revealed isotypism with the CeNiSi<sub>2</sub>-type. From the good correspondence of the composition refined from X-ray data with the composition derived from EDX, we can safely conclude that the structure of  $\tau_5$ -CeZn(Zn<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub> does not contain any defect sites like HoFe<sub>0.5</sub>Si<sub>2</sub>.

### 3.2.2. Crystal structure of $\tau_6$ -CeZn<sub>2</sub>(Si<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>, x = 0.30

Complete indexation of the X-ray single crystal diffraction data for  $\tau_6$  prompted a tetragonal unit cell. The systematic analysis of extinctions suggested *I4*, *I4*, *I4/m*, *I422*, *I4mm*, *I42m*, *I4m2* and *I4/mmm*, as possible space group types. Structure solution and refinement employing direct methods in the highest symmetry space group type *I4/mmm* converged to  $R_F = 0.008$  with residual electron densities smaller than  $\pm 0.32 \text{ e}/\text{\AA}^3$ . Details on crystal data along with ADPs are summarized in Table 2. Unit cell parameters, crystal symmetry, and Wyckoff sites confirm isotypism with the ThCr<sub>2</sub>Si<sub>2</sub> structure type (see Figure 2).

The final structure formula, CeZn<sub>2</sub>(Si<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub> with x=0.30, reveals one Zn/Si mixed atom site (M = 0.30Zn + 0.70 Si in 4e; 0,0,z), which in many cases provides close contacts among the tetrel elements (dumbbell formation).<sup>32</sup> The formula (Ce<sub>20.1</sub>Zn<sub>51.8</sub>Si<sub>28.1</sub>)<sub>2</sub> (in at.%) perfectly fits to the value derived from EDX: Ce<sub>20.0</sub>Zn<sub>52.0</sub>Si<sub>28.0</sub>.

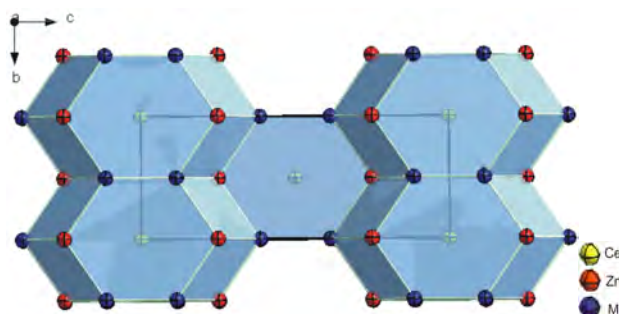


Figure 2. Crystal structure of  $\tau_6$ - $\text{CeZn}_2(\text{Si}_{1-x}\text{Zn}_x)_2$ ,  $x = 0.30$  showing atoms with anisotropic displacement parameters from X-ray single crystal refinement.

Interatomic distances are given in Table S2 (Supporting Information). As the M-site is mainly occupied by Si, distances M-M and M-Zn1 are much smaller than distances Zn1-Zn1. Taking into account the random occupancy Zn/Si in the 4e site, the M-M distance is smaller than the sum of radii<sup>33</sup> and is a good indication for dumbbell formation. Comparing the M-M and M-Zn1 distances with those in  $\text{YbZn}_2(\text{Si}_{1-x}\text{Zn}_x)_2$ ;  $x=0.25$ ,<sup>34</sup> which is hitherto the only far off-stoichiometric  $\text{REZn}_2\text{Si}_2$  crystallizing in the  $\text{ThCr}_2\text{Si}_2$  type, no significant difference can be found. Consistent with the mixed atom site,  $\tau_6$ - $\text{CeZn}_2(\text{Si}_{1-x}\text{Zn}_x)_2$  exists at 600°C in a small homogeneity range  $0.25 \leq x \leq 0.30$  (for details see section 3.4). Similar to  $\tau_5$  also the phase  $\tau_6$  does not include the stoichiometric composition  $\text{CeZn}_2\text{Si}_2$ , although first row transition metals mostly form ordered, stoichiometric compounds  $\text{CeT}_2\text{Si}_2$  ( $T = \text{Cr to Cu}$ ), some with only a small deviation from 1:2:2 stoichiometry.

### 3.2.3. Crystal structures of $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$ , $x = 0.75$ and $\text{La}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$ , $x = 0.10$

In a previous investigation Malik *et al.*<sup>8</sup> found that a surprisingly small amount of only 2 at.% Si was able to stabilize the ternary compound  $\tau_1$ - $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$  ( $x=0.28$ , unique structure type) at 800 °C. X-ray single crystal analysis proved  $\text{La}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$  ( $x=0.27$ ) to be isotypic.<sup>8</sup> Some controversy exists between the recently reported formation of  $\text{Ce}_7\text{Zn}_{21.3}\text{Ge}_{1.7}$ <sup>9</sup> (isotypic with  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ ) and the investigation of the isothermal section of the homologous system Ce-Zn-Ge at 470 K by Opainich,<sup>35</sup> who did not observe any compound near a composition  $\text{Ce}_7\text{Zn}_{21}\text{Ge}_2$ . In order to dissolve the controversy it seemed of interest to test the formation of Ge-homologues  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  as well as the extent of their homogeneity regions. Indeed microprobe analyses confirmed that in both systems  $\{\text{La,Ce}\}$ -Zn-Ge a phase exists with composition close to the RE-Zn boundary:  $\text{La}_{23.3}\text{Zn}_{71.6}\text{Ge}_{5.1}$  and  $\text{Ce}_{23.3}\text{Zn}_{71.7}\text{Ge}_{5.0}$  (in at.%; see Figure 3 b,c). Indexing of the X-ray diffraction data from a suitable single crystal of  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  was complete for an orthorhombic unit cell corresponding to the structure type of  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ . The structure solution, employing direct methods in space group  $Pbam$  with the highest symmetry, compatible with the set of systematic extinctions, resulted in the same atom arrangement as for  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ . Despite the small difference in the X-ray scattering power of Zn and Ge atoms, one mixed Zn/Ge site could unambiguously be identified from the rest of the fully occupied Zn sites. It is the same site as in the parent  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$  type revealing a slightly smaller ADP and thus requests the presence of an atom with a slightly higher scattering power.

Table 2. X-ray single crystal data for  $\tau_5$ - $\text{CeZn}(\text{Zn}_{1-x}\text{Si}_x)_2$ ,  $x = 0.71$ ; space group  $Cmcm$ , No. 63 and for  $\tau_6$ - $\text{CeZn}_2(\text{Si}_{1-x}\text{Zn}_x)_2$ ,  $x = 0.30$ ; space group  $I4/mmm$ , No. 139.

Parameter/compound	$\tau_5$ - $\text{CeZn}(\text{Zn}_{1-x}\text{Si}_x)_2$ , $x=0.71$	$\tau_6$ - $\text{CeZn}_2(\text{Si}_{1-x}\text{Zn}_x)_2$ , $x=0.30$
Phase composition (EPMA, at.%)	$\text{Ce}_{24.9}\text{Zn}_{39.6}\text{Si}_{35.5}$	$\text{Ce}_{20.1}\text{Zn}_{51.8}\text{Si}_{28.1}$
Refinement composition (at.%)	$\text{Ce}_{25.0}\text{Zn}_{39.7}\text{Si}_{35.3}$	$\text{Ce}_{20.0}\text{Zn}_{52.0}\text{Si}_{28.0}$
Structure type	$\text{CeNiSi}_2$	$\text{ThCr}_2\text{Si}_2$
2 $\theta$ range (deg)	$2 \leq 2\theta \leq 80.32$	$2 \leq 2\theta \leq 72.72$
a [nm]	0.42079(1)	0.41757(1)
b [nm]	1.76522(3)	0.41757(1)
c [nm]	0.41619(1)	1.05073(2)
Reflections in refinement	$537 \geq 4\sigma(F_o)$ of 556	$157 \geq 4\sigma(F_o)$ of 157
Mosaicity	0.55	0.48
Number of variables	20	11
$R_{F2} = \sum  F_o^2 - F_c^2  / \sum F_o^2$	0.0203	0.0077
wR2	0.0402	0.0197
$R_{int}$	0.0432	0.0311
GOF	1.349	1.370
Extinction (Zachariasen)	0.0059(3)	0.034(1)
Ce; occ.	4c (0,y,¼), y = 0.39888(1); 1.00(-)	2a (0,0,0); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> ;U <sub>13</sub> ;U <sub>12</sub>	0.0052(1); 0.0073(1); 0.0038(1); 0; 0; 0	0.00567(9); 0.00567(9); 0.0096(1); 0; 0; 0
M1; occ.	4c (0,y,¼), y = 0.03338(5); 0.26(1) Zn1 + 0.74 Si1	4d (0,½,¼); 1.00(-) Zn1.
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ; U <sub>23</sub> ;U <sub>13</sub> ;U <sub>12</sub>	0.0137(4); 0.0062(4); 0.0050(4); 0; 0; 0	0.0101(1); 0.0101(1); 0.0090(1); 0; 0; 0
M2; occ.	4c (0,y,¼), y = 0.16921(5); 0.31(1) Zn2 + 0.69 Si2	4e (0,0,z); z = 0.38507(5); 0.30(1) Zn2+0.70(1) Si1
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ; U <sub>23</sub> ;U <sub>13</sub> ;U <sub>12</sub>	0.0087(4); 0.0080(4); 0.0064(4); 0; 0; 0	0.0087(2); 0.0087(2); 0.0090(2); 0; 0; 0
Zn3; occ.	4c (0,y,¼), y = 0.74962(3); 1.00 Zn3	
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ; U <sub>23</sub> ;U <sub>13</sub> ;U <sub>12</sub>	0.0099(2); 0.0082(2); 0.0080(2); 0; 0; 0	
Residual electron density; max; min in (electron/nm <sup>3</sup> ) × 10 <sup>3</sup>	2.61; -3.04	0.32; -0.81

Table 3. X-ray single crystal data for  $Ce_7Zn_{21}(Zn_{1-x}Ge_x)_2$ ,  $x = 0.75$  and  $La_7Zn_{21}(Zn_{1-x}Ge_x)_2$ ,  $x = 0.10$ ; space group *Pbam*, No. 55. Standardized<sup>d</sup> with program Structure Tidy<sup>16</sup>.

Parameter/compound	$Ce_7Zn_{21}(Zn_{1-x}Ge_x)_2$ , $x = 0.75$	$La_7Zn_{21}(Zn_{1-x}Ge_x)_2$ , $x = 0.10$
Phase composition (EPMA, at.%)	$Ce_{23.2}Zn_{71.9}Ge_{5.0}$	$La_{23.5}Zn_{75.9}Ge_{0.6}$
Refinement composition (at.%)	$Ce_{23.3}Zn_{71.7}Ge_{5.0}$	$La_{23.3}Zn_{76.0}Ge_{0.7}$
Structure type	$Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$	$Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$
2 $\theta$ range (°)	2 $\leq$ 2 $\theta$ $\leq$ 72.58	2 $\leq$ 2 $\theta$ $\leq$ 72.64
a[nm]	1.55215(2)	1.57043(2)
b[nm]	1.71447(2)	1.73321(3)
c [nm]	0.44836(1)	0.45076(1)
Reflections in refinement	2706 $\geq$ 4 $\sigma$ ( $F_o$ ) of 3103	2732 $\geq$ 4 $\sigma$ ( $F_o$ ) of 3196
Mosaicity	0.45	0.50
Number of variables	94	94
$R_{F2} = \sum  F_o^2 - F_c^2  / \sum F_o^2$	0.0215	0.0330
wR2	0.0532	0.0609
$R_{int}$	0.0147	0.0147
GOF	0.774	1.325
Extinction (Zachariasen)	0.00094(4)	0.00028(3)
RE1 in 4h (x,y,½); occ.	x = 0.16459(2); y = 0.04538(1); 1.00(-)	x = 0.16342(2); y = 0.04474(2); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0093(1); 0.0094(1); 0.0076(1); -0.0004(1)	0.0099(1); 0.0084(2); 0.0067(1); -0.0003(1)
RE2 in 4g (x,y,0); occ.	x = 0.16580(2); y = 0.31940(1); 1.00(-)	x = 0.16739(2); y = 0.31848(2); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0086(1); 0.0087(1); 0.0076(1); -0.00002(7)	0.0096(1); 0.0091(2); 0.0072(1); -0.0005(1)
RE3 in 4g (x,y,0); occ.	x = 0.41826(2); y = 0.24008(3); 1.00(-)	X = 0.41760(2); y = 0.24148(3); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0093(1); 0.0195(1); 0.0118(1); -0.0019(1)	0.0104(2); 0.0269(2); 0.0125(2); 0.0037(1)
RE4 in 2c (0,½,0); occ.	1.00(-)	1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0103(1); 0.0143(2); 0.0115(2); -0.0030(1)	0.0137(2); 0.0166(3); 0.01304(2); 0.0056(2)
M1 in 4h (x,y,½); occ. <sup>b</sup>	x = 0.02039(3); y = -0.35860(3); 0.25 Zn1+0.75 Ge1 <sup>b</sup>	x = 0.02098(5); y = -0.35861(4); 0.90 Zn1+ 0.10 Ge1 <sup>b</sup>
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0091(2); 0.0104(2); 0.0131(2); 0.0001(2)	0.0108(3); 0.0107(4); 0.0165(3); 0.0001(3)
Zn2 in 4h (x,y,½); occ.	x = 0.07520(4); y = 0.21623(3); 1.00(-)	x = 0.07441(5); y = 0.21634(4); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0143(2); 0.0097(2); 0.0110(2); -0.0008(2)	0.01500(3); 0.0093(3); 0.0102(3); -0.0005(3)
Zn3 in 4h (x,y,½); occ.	x = 0.15224(4); y = 0.44824(3); 1.00(-)	x = 0.15203(5); y = 0.44898(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0128(2); 0.0102(2); 0.0102(2); -0.0019(2)	0.01432(3); 0.01062(4); 0.0096(3); -0.0023(3)
Zn4 in 4h (x,y,½); occ.	x = 0.25707(4); y = 0.21844(3); 1.00(-)	x = 0.25851(5); y = 0.21716(4); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0134(2); 0.0096(2); 0.0105(2); 0.0005(2)	0.0166(3); 0.0085(3); 0.0093(3); 0.0001(3)
Zn5 in 4h (x,y,½); occ.	x = 0.30414(4); y = 0.35837(3); 1.00(-)	x = 0.30569(5); y = 0.35746(4); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0128(2); 0.0120(2); 0.0115(2); -0.0032(2)	0.0132(3); 0.0114(4); 0.0107(3); -0.0037(3)
Zn6 in 4h (x,y,½); occ.	x = 0.36349(4); y = 0.09927(3); 1.00(-)	x = 0.36446(5); y = 0.09913(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0105(2); 0.0111(2); 0.0200(3); -0.0005(2)	0.0114(3); 0.0124(4); 0.0223(4); -0.0011(3)
Zn7 in 4h (x,y,½); occ.	x = 0.46584(4); y = 0.40147(4); 1.00(-)	x = 0.46662(5); y = 0.40073(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0103(2); 0.0179(3); 0.0172(3); 0.0029(2)	0.0106(3); 0.0176(4); 0.0178(4); 0.0030(3)
Zn8 in 4g (x,y,0); occ.	x = 0.07303(4); y = 0.14088(3); 1.00(-)	x = 0.07359(6); y = 0.14124(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0217(3); 0.0141(2); 0.0104(2); 0.0043(2)	0.0260(4); 0.0144(4); 0.0096(3); 0.0046(3)
Zn9 in 4g (x,y,0); occ.	x = 0.24865(4); y = 0.14674(3); 1.00(-)	x = 0.24920(6); y = 0.14602(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0226 (3); 0.0119(2); 0.0109(2); -0.0050(2)	0.0295(4); 0.0123(4); 0.0099(3); -0.0079(3)
Zn10 in 4g (x,y,0); occ.	x = 0.29957(4); y = 0.00600(4); 1.00(-)	x = 0.29942(5); y = 0.00570(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0144(3); 0.0197(3); 0.0106(2); 0.0067(2)	0.0166(4); 0.0240(4); 0.0100(3); 0.0099(3)
Zn11 in 4g (x,y,0); occ.	x = 0.35248(4); y = 0.41919(3); 1.00(-)	x = 0.35252(6); y = 0.41889(5); 1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0223(3); 0.0135(2); 0.0100(2); -0.0021(2)	0.0250(4); 0.0134(4); 0.0093(3); -0.0031(3)
Zn12 in 2a (0,0,0); occ.	1.00(-)	1.00(-)
U <sub>11</sub> ;U <sub>22</sub> ;U <sub>33</sub> ;U <sub>23</sub> =U <sub>13</sub> =0;U <sub>12</sub>	0.0147(4); 0.0175(4); 0.0178(4); -0.0010(3)	0.0139(5); 0.0205(6); 0.0172(5); -0.0020(4)
Residual electron density; max;	1.59; -1.70	1.71; -2.13
min in (electron/nm <sup>3</sup> ) $\times 10^3$		

<sup>a</sup>The earlier data sets for single crystal  $Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$ ,  $x = 0.28$ <sup>8</sup> and for isotypic  $La_7Zn_{21}(Zn_{1-x}Si_x)_2$ ,  $x = 0.27$ <sup>8</sup>, as well as the sets for  $\{La-Nd\}_7Zn_{21+x}(Tl)_{2-x}$ <sup>9,10</sup> were not standardized correctly.

<sup>b</sup>The occupancy value is fixed after EPMA

Even though it was possible to refine the occupancy of Zn/Ge (yielding 0.45(5) Zn1+0.55(5) Ge1), the ratio Zn/Ge was fixed in accord with the composition obtained from EPMA (0.25 Zn1+0.75Ge1). A final refinement with anisotropic ADPs converged to  $R_F = 0.0215$  with a residual electron density less than 1.7 e/Å<sup>3</sup>. Detailed crystal data and atomic displacement parameters are summarized in Table 3. The structure refinement essentially confirmed the data obtained by Suen et al.<sup>9</sup> but here for an even lower Ge-content.

Although EPM analyses in the La-Zn-Ge system prompted a

phase with composition of  $La_{23.3}Zn_{71.6}Ge_{5.1}$  (see Figure 3b), attempts to grow a single crystal with this Ge content were unsuccessful. However, for lower Ge-contents a suitable single crystal could be obtained (see Figure 3a). Following the same steps and arguments as for  $Ce_7Zn_{21}(Zn_{1-x}Ge_x)_2$ , structure solution and refinement of the single crystal data clearly showed isotypism with  $Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$ . However, due to the low amount of Ge atoms in the unit cell, it was not possible to identify the Zn/Ge mixed site from the rest of the Zn sites. Therefore Ge atoms were placed at the corresponding Si-site as in  $Ce_7Zn_{21}(Zn_{1-x}$



$x\text{Si}_x)_2$  with the occupancy taken from EPMA ( $\text{La}_{23.3}\text{Zn}_{76.0}\text{Ge}_{0.7}$  in at.%).

Detailed crystal data and atomic displacement parameters are listed in Table 3. As expected from the isotypism with  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ , the atomic arrangement in  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  also gives a similar zig-zag chain of distorted  $\text{AuCu}_3$  and  $\text{BaAl}_4$  blocks along the b-axis (see Figure 4). This arrangement is similar to  $\text{Ce}_3\text{Zn}_{11}$  with  $\text{La}_3\text{Al}_{11}$ -type, which is the neighbouring phase of  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$ . Due to the comparable size of Zn and Ge atoms, no significant difference could be found in the interatomic distances between fully occupied Zn and mixed Zn/Ge sites.

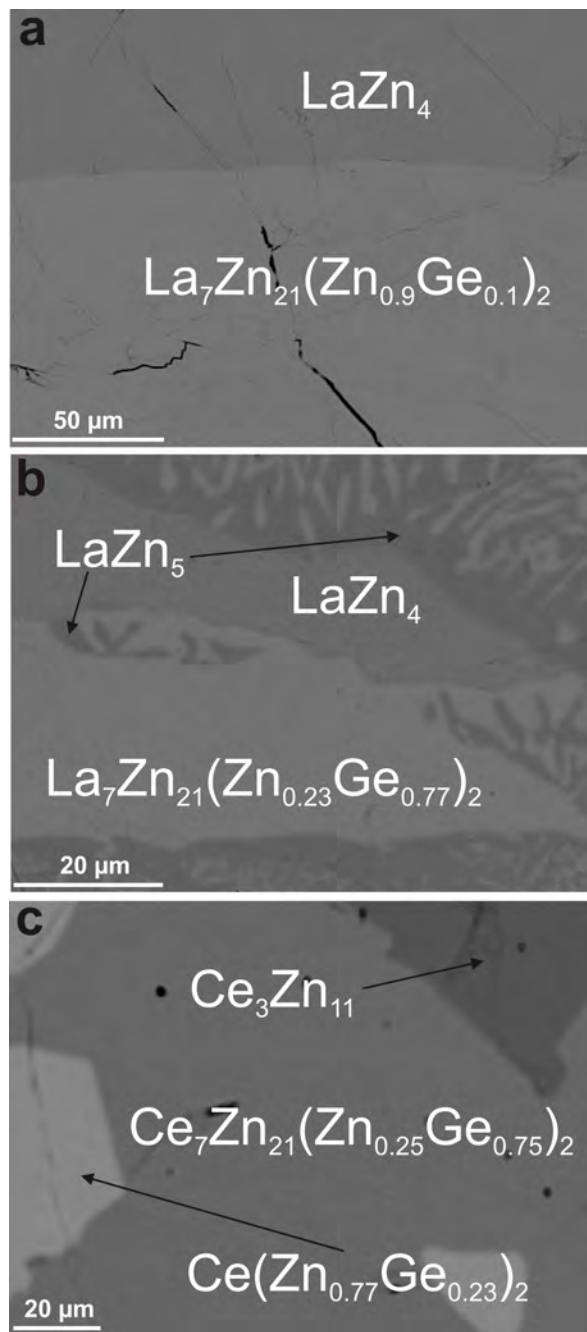


Figure 3. Micrographs of samples revealing the phase  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  in contact with binary phases from the systems  $\{\text{La,Ce}\}-\text{Zn}$ .

The amount of Ge necessary to stabilize the ternary compounds  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$  is even less than for isotopic  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$  and with less than 1 atom percent of Ge infers a rather small degree of thermodynamic instability for the hypothetical binary phases “ $\text{La}_7\text{Zn}_{23}$ ” and “ $\text{Ce}_7\text{Zn}_{23}$ ”.

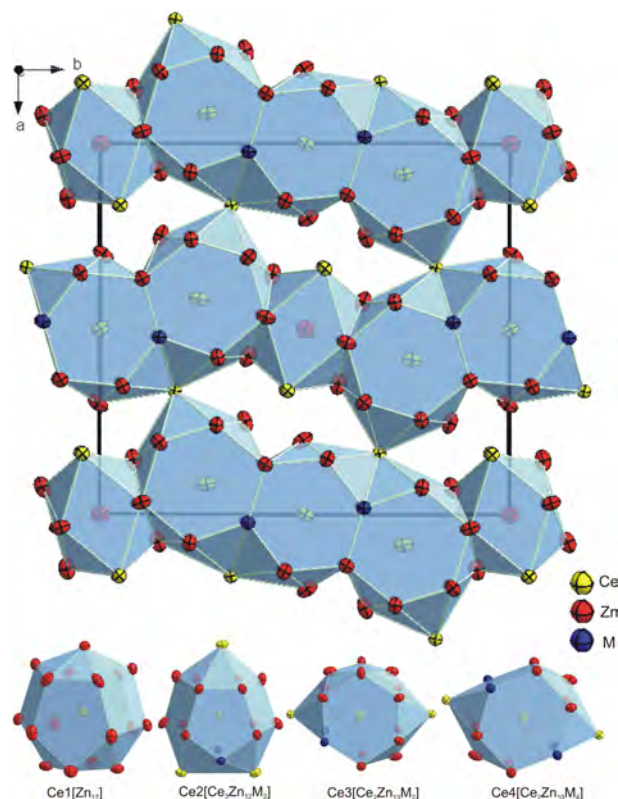


Figure 4. Crystal structure of  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$ ,  $x = 0.75$  projected along the c-axis and the coordination polyhedra for the Ce atoms. Atoms are drawn with anisotropic displacement parameters from X-ray single crystal refinement. Please note that (with respect to the previously incorrect standardization of  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ ) the origin of the unit cell is now shifted by  $(\frac{1}{2} 0 0)$ .

### 3.3. Phase stability of $\text{Ce}_7\text{Zn}_{23-x}\text{Ge}_x$

#### 3.3.1. DFT phase stabilities

The enthalpy of formation  $\Delta H_{\text{DFT}}$  at  $T=0$  K was derived from the DFT total energies  $E_{\text{DFT}}^{\text{tot}}$  as obtained from VASP according to:

$$\Delta H_{\text{DFT}}(\text{Ce}_x\text{Zn}_{1-x}) = E_{\text{DFT}}^{\text{tot}}(\text{Ce}_x\text{Zn}_{1-x}) - (xE_{\text{DFT}}^{\text{ref}}(\text{Ce}) + (1-x)E_{\text{DFT}}^{\text{ref}}(\text{Zn})) \quad (1)$$

As reference energies of the pure phases we defined:

$$E_{\text{DFT}}^{\text{ref}}(\text{Ce}) = E_{\text{DFT}}^{\text{tot}}(\text{Ce}) - E_{\text{adj}}(\text{Ce}), \text{ and } E_{\text{DFT}}^{\text{ref}}(\text{Zn}) = E_{\text{DFT}}^{\text{tot}}(\text{Zn}) - E_{\text{adj}}(\text{Zn}) \quad (2)$$

The DFT energies for the pure phases were calculated for solid nonmagnetic  $\alpha$ -fcc-Ce and solid hcp-Zn. It was necessary to adjust the reference energies by  $E_{\text{adj}}(\text{Ce})$  and  $E_{\text{adj}}(\text{Zn})$  for a direct comparison with the results of the thermodynamic modeling of Wang et al.,<sup>36</sup> and experimental work by Chiotti et al.<sup>37</sup> and Johnson et al.,<sup>38</sup> because of the choice of different reference ground states. Then the values for  $E_{\text{adj}}$  were extracted by linearly fitting the DFT results (column DFT in Table 4) to the thermodynamic modeling data (column “model”) for the four given compounds, and by that  $E_{\text{adj}}(\text{Ce}) = 27.87$  and  $E_{\text{adj}}(\text{Zn}) =$



4.38 kJ mol<sup>-1</sup> were obtained.

Table 4 summarizes results of the DFT calculations. The DFT derived adjusted enthalpy of formation compares very well with data of the thermodynamic modelling by Wang et al.<sup>36</sup>

Concerning magnetic properties, as taken from the listed magnetic moments, CeZn does not spin polarize, whereas for the other listed compounds Ce<sub>x</sub>Zn<sub>1-x</sub> the magnetic moment per Ce atom decreases with decreasing Ce content, starting with CeZn<sub>2</sub> which has the largest local moment per Ce atom of 0.71 μ<sub>B</sub>. For (hypothetical) Ce<sub>14</sub>Zn<sub>46</sub> (x=0.23) the local moment is still sizeable amounting to 4.06 μ<sub>B</sub> for the total magnetic moment of the unit cell. Replacing Zn by Ge in Ce<sub>14</sub>Zn<sub>46-x</sub>Ge<sub>x</sub> strongly reduces the magnetic moment to less than 0.07 μ<sub>B</sub> for x=1. The gain in spin-polarization energy is very small being about 0.01 kJ/mol per Ce atom, which hints at a spin fluctuation system. If x=4 than there is no spin polarization anymore.

Table 4. DFT derived equilibrium heat of formation (DFT) for T = 0 K (in kJ/mol) for Ce<sub>x</sub>(Ge,Zn)<sub>1-x</sub> as a function of Ce concentration x, in comparison to the adjusted DFT values (DFT-adj, see text) and T=0 extrapolation of the thermodynamic modeling (model) of Wang et al.<sup>36</sup>. For Ce the α-phase was taken as reference. Local magnetic moment per Ce-atom m<sub>loc</sub> (in μ<sub>B</sub>) and the equilibrium volume per atom V<sub>0</sub> (in Å<sup>3</sup>) are also given.

Compound	x <sub>Ce</sub>	DFT	DFT-adj	Model	m <sub>loc</sub>	V <sub>0</sub>
CeZn	0.50	-17.81	-33.94	-34.04	0	23.72
CeZn <sub>2</sub>	0.333	-28.16	-40.37	-40.06	0.71	21.22
CeZn <sub>3</sub>	0.25	-28.00	-38.25	-38.47	0.25	19.23
Ce <sub>14</sub> Zn <sub>46</sub>	0.233	-26.76	-36.62	-	0.29	19.29
Ce <sub>14</sub> Zn <sub>42</sub> Ge <sub>4</sub>	0.233	-34.16	-43.73	-	0.19	19.16
Ce <sub>14</sub> Zn <sub>45</sub> Ge	0.233	-28.47	-38.33	-	0.08	19.16
Tie-line	0.233	-27.75	-37.61	-	-	-
Ce <sub>3</sub> Zn <sub>11</sub>	0.214	-27.47	-36.89	-36.88	0.65	18.66

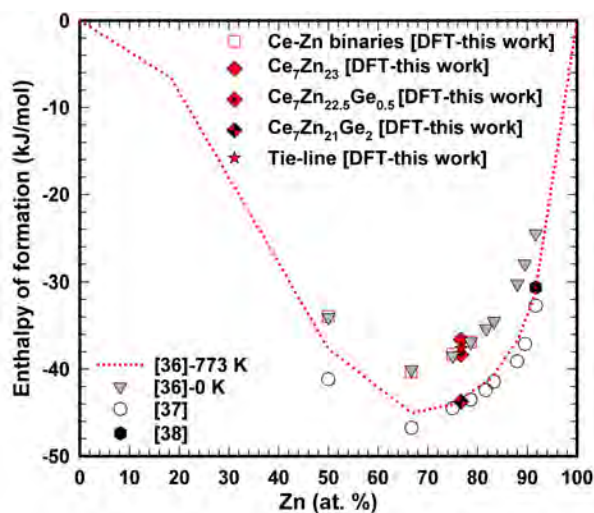


Figure 5. Comparison between experimental and DFT derived adjusted calculated enthalpies of formation for Ce-Zn binaries and Ce<sub>7</sub>Zn<sub>23-x</sub>Ge<sub>x</sub>.

The enthalpy of formation for Ce<sub>x</sub>(Ge,Zn)<sub>1-x</sub> compounds was derived similarly to the procedure described above. As a reference, solid Ge was taken in its ground state in the diamond structure. Most noticeable for our study is the stability for the Ge-doped compounds. Even for one Ge atom per formula unit, Ce<sub>14</sub>Zn<sub>45</sub>Ge<sub>1</sub>, ΔH<sub>DFT</sub> is below the tie-line connecting neighboring Zn-compounds. Here we assume, that in fact the ternary system

can be approximately described as a binary one (see Figure 5).

Why Ge stabilizes the compound is analyzed in the following discussing the electronic structure in terms of the density of states (DOS).

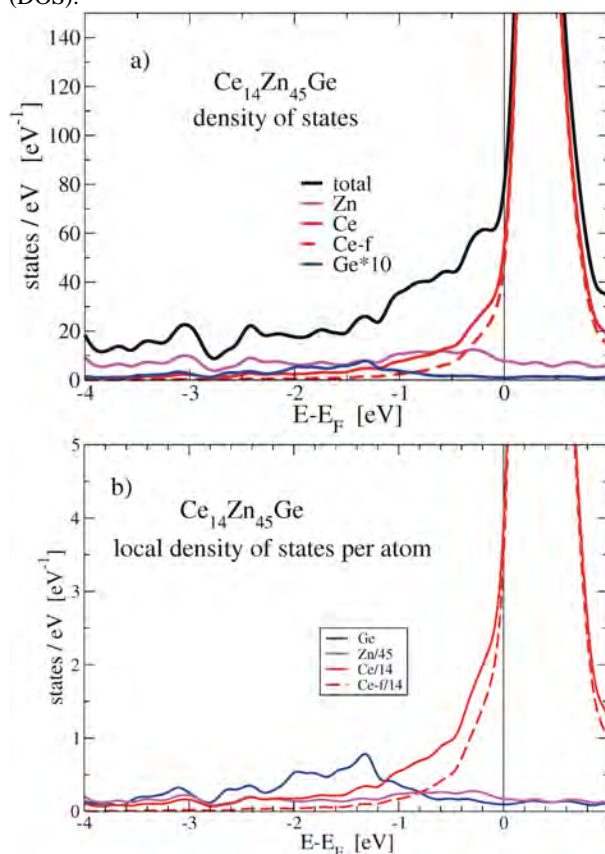


Figure 6. Panel (a): Total and local density of states (DOS) for non spin-polarized Ce<sub>7</sub>Ge<sub>0.5</sub>Zn<sub>22.5</sub>. panel (b): local DOS per atom. For better visibility, the local DOS for Ge is multiplied by a factor of 10.

### 3.3.2. DFT phase stabilities for Ce<sub>7</sub>Zn<sub>23-x</sub>Ge<sub>x</sub> (Z=2).

Panel (a) of Figure 6 presents the total and atom projected local DOS for Ce<sub>14</sub>Zn<sub>45</sub>Ge<sub>1</sub>. The Fermi energy falls into a sharp uprise of the DOS, which clearly is attributed to the f-states of Ce. At lower energies the DOS is a mixture of Zn and Ce states depending on the energy region. The Ge-DOS features in the range -2.7 < E < -1 eV indicate a more covalent bonding as compared to Zn, which is more pronounced in panel (b) of Figure 6 showing the local DOS per atom. There the Zn-like DOS is more uniformly spread out in the energy region shown.

The stabilization property of Ge-substitution can be understood by inspecting Figure 7 showing a reduction of the total DOS at Fermi energy when one Zn is replaced by Ge. This is mainly due to the reduction of the f-like DOS for Ce<sub>14</sub>Zn<sub>45</sub>Ge<sub>1</sub>. The corresponding γ values of the electronic specific heat are 3.43 (DOS at E<sub>F</sub> = 87.3 states per eV for Ce<sub>14</sub>Zn<sub>46</sub>) and 3.25 mJ mol<sup>-1</sup> K<sup>-2</sup> (DOS at E<sub>F</sub> = 82.7 states per eV for Ce<sub>14</sub>Zn<sub>45</sub>Ge<sub>1</sub>) indicating poor metals. Analyzing the Ce-f states it turns out that the magnetic moments break down upon Ge substitution, which is responsible for the DOS reduction. The reduction is due to the destruction of the magnetic moment of Ce atoms in 2c position, because these states are predominant at the Fermi energy for spin polarized Ce<sub>14</sub>Zn<sub>46</sub>. They carry the largest magnetic moment of all Ce atoms and are therefore the most localized f-states with the

largest uprise of all f-DOSes and therefore the largest value at Fermi energy. For  $\text{Ce}_{14}\text{Zn}_{46}$  the local f-moments are 0.27, 0.21, and 0  $\mu_B$  for the 4-fold coordinated atoms, and 0.74  $\mu_B$  for the Ce atoms in 2c position. The breakdown of the magnetic moment upon substitution indicates also a weaker localization and consequently the DOS at Fermi energy is lowered: this leads to the reduction of the total DOS and indicates the thermodynamic stabilization of  $\text{Ce}_{14}\text{Zn}_{45}\text{Ge}_1$ . Summarizing, the more pronounced covalent bonding between Ce and Ge seems to be the main factor for the stabilization. By substituting 4 Ge atoms the stabilization with respect to the tie-line is considerably enhanced.

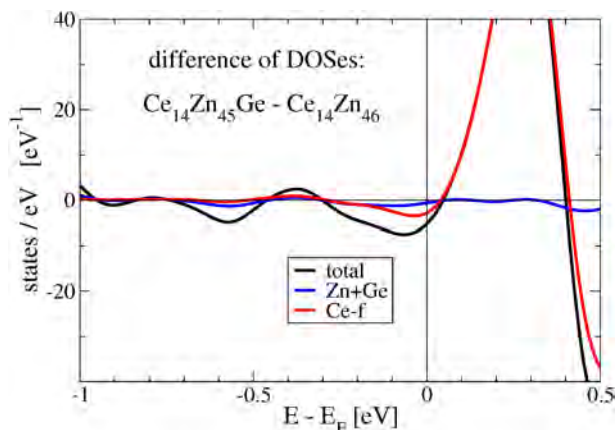


Figure 7. Differences of total and local density of states,  $\text{Ce}_7\text{Ge}_{0.5}\text{Zn}_{22.5}$  minus  $\text{Ce}_7\text{Zn}_{23}$ .

### 3.4. Partial isothermal section at 600°C for less than 33.3 at% Ce

The partial isothermal section at 600°C in the Ce-poor part of the ternary system Ce-Zn-Si was established from EPMA and X-ray powder diffraction of about 45 alloys (see Figure 8). Considering the high stability of the phase  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  with the  $\alpha\text{ThSi}_2$  type and the relatively slow reaction kinetic at 600°C (diffusion in cast alloys) the samples were prepared by powder metallurgical techniques i.e. via isothermal reaction synthesis starting from compacts of powder/filings in order to ensure establishment of true phase relations at this temperature.

In addition to the ternary compounds  $\tau_1\text{-Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ ,  $0.45 \leq x \leq 0.99$  and  $\tau_2\text{-Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$ ,  $0.36 \leq x \leq 0.73$ , both established previously in the 800°C isothermal section (for details see ref. 8), three new phases, which previously were not encountered at 800°C<sup>8</sup>, were found to exist at 600°C:  $\tau_5\text{-CeZn}(\text{Zn}_{1-x}\text{Si}_x)_2$ ,  $\tau_6\text{-CeZn}_2(\text{Zn}_{1-x}\text{Si}_x)_2$ , and  $\tau_7\text{-Ce}_{37}\text{Zn}_{48}\text{Si}_{15}$ . Moreover binary  $\text{CeZn}_{11}$  enters the phase equilibria at 600°C. Similar to 800°C, solubility of Si is negligible for all binary compounds  $\text{CeZn}_x$  with  $x > 2$ . Extended homogeneity regions were established for  $\tau_1$  and  $\tau_2$ , as well as for  $\tau_5$  and  $\tau_6$  (Table 1 for details see Table 5). The homogeneity range of  $\tau_1\text{-Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$  becomes slightly smaller at 600°C as compared to 800°C. The maximum concentration of Si in this phase practically remained the same, while the minimum amount of Si required to stabilize this phase slightly increased from  $x = 0.28$  (1.9 at. % Si) at 800°C to  $x = 0.45$  (3.0 at. % Si) at 600°C. The homogeneity range of  $\tau_1$  at 800°C, studied by combination of XRPD, XRSC, and EPMA contradicts the claim of Hoos et al.<sup>10</sup> regarding 3.5 at. % Si as minimum amount of Si in this phase. The three-phase regions involving binary Ce-Zn phases with more than 75 at. % Zn at 600°C resemble those observed at 800°C.

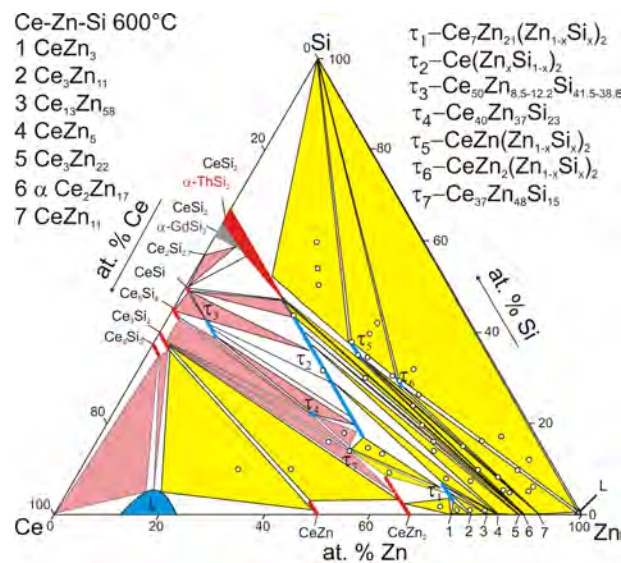


Figure 8. Partial isothermal section at 600°C (<33.3 at. % Ce). The circles represent nominal compositions of alloys. The pink three phase fields are taken from Ref. 8.

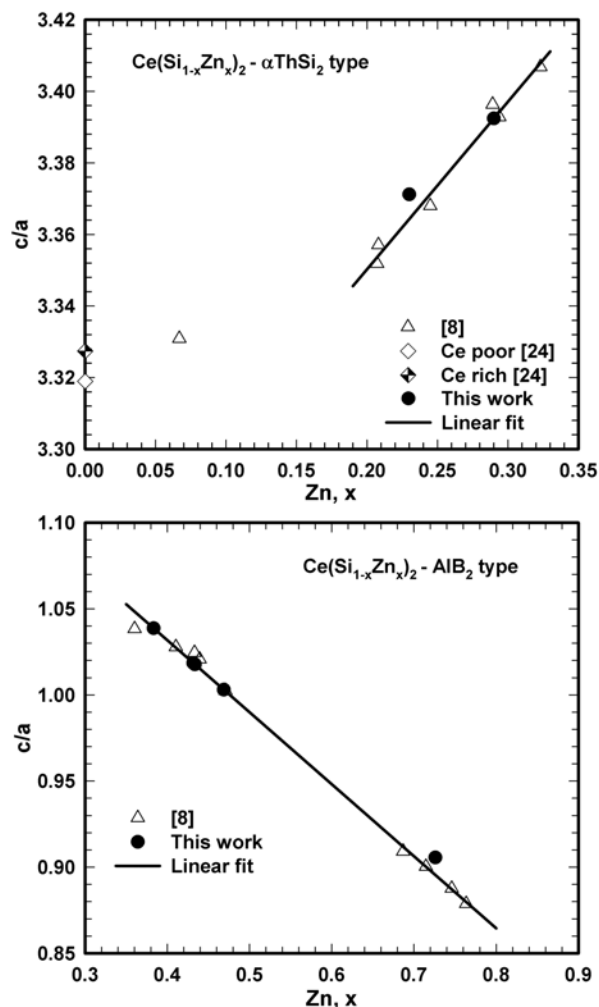


Figure 9. Compositional dependence of  $c/a$  ratio for  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  with  $\alpha\text{ThSi}_2$  (left) and  $\text{AlB}_2$  (right) type.

Despite all these three-phase equilibrium triangles are narrow, we were able to prepare corresponding samples and to define by

EPMA the composition of the equilibrium phases involved. Ternary phases  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  ( $\alpha$ - $\text{ThSi}_2$  type),  $\tau_2$ , and  $\tau_5$  that coexist in three-phase equilibria with binary  $\text{CeZn}_x$  ( $x \geq 5$ ) crystallized in fine microstructures, which made quantitative analyses by EPMA unreliable. The fine grains could not be agglomerated even with longer annealing time (more than two weeks). Therefore the ternary phases  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  with  $\alpha$ - $\text{ThSi}_2$  type,  $\tau_2$ , and  $\tau_5$ , and their composition were determined via Rietveld refinement in combination with the compositional dependence of lattice parameters presented in Figure 9.

Microstructures of selected three-phase equilibria are given in

Table 5. Three phase equilibria and lattice parameters of alloys annealed at 600°C.

phase region	Phases	Structure type	EPMA (at%)			Lattice parameters (nm)		
			Ce	Zn	Si	a	b	c
$\tau_5 + \tau_6 + \text{Si}$	$\tau_5$	$\text{CeNiSi}_2$	25	36.8	38.2	0.4209(1)	1.7662(5)	0.4177(1)
	$\tau_6$	$\text{ThCr}_2\text{Si}_2$	20.5	49.8	29.7	0.41881(6)	-	1.0560(4)
	Si	$\text{C}_{\text{diamond}}$	-	-	-	0.54297(5)	-	-
$\text{CeSi}_2 + \tau_5 + \text{Si}$	$\text{CeSi}_2$	$\text{ThSi}_2$	33.0	15.2	51.8	0.42025(3)	-	1.4172(4)
	$\tau_5$	$\text{CeNiSi}_2$	24.8	38.1	37.1	0.42046(7)	1.7699(3)	0.41713(3)
	Si	$\text{C}_{\text{diamond}}$	0.3	0.5	99.2	-	-	-
$\tau_6 + \text{L}(\text{Zn}) + \text{Si}$	$\tau_6$	$\text{ThCr}_2\text{Si}_2$	19.9	52.0	28.1	0.41848(3)	-	1.05615(6)
	$\text{L}(\text{Zn})$	Mg	-	-	-	-	-	-
	Si	$\text{C}_{\text{diamond}}$	0.0	0.4	99.6	0.54298(4)	-	-
$\tau_6 + \text{L}(\text{Zn}) + \text{CeZn}_{11}$	$\tau_6$	$\text{ThCr}_2\text{Si}_2$	19.8	51.9	28.3	0.41830(6)	-	1.0558(3)
	$\text{L}(\text{Zn})$	Mg	0.4	99.3	0.3	-	-	-
	$\text{CeZn}_{11}$	$\text{BaCd}_{11}$	8.6	91.1	0.3	1.0662(1)	-	0.6866(1)
$\tau_5 + \text{CeZn}_{11} + \text{Ce}_2\text{Zn}_{17}$	$\tau_5$	$\text{CeNiSi}_2$	-	-	-	0.4210(1)	1.767(1)	0.4165(1)
	$\text{CeZn}_{11}$	$\text{BaCd}_{11}$	-	-	-	1.0661(1)	-	0.6865(1)
	$\alpha\text{-Ce}_2\text{Zn}_{17}$	$\text{TbCu}_7$	10.8	88.8	0.4	0.5253(1)	-	0.4433(1)
$\tau_5 + \tau_6 + \text{CeZn}_{11}$	$\tau_5$	$\text{CeNiSi}_2$	-	-	-	0.42173(1)	1.75258(2)	0.41738(1)
	$\tau_6$	$\text{ThCr}_2\text{Si}_2$	-	-	-	0.41872(7)	-	1.0558(1)
	$\text{CeZn}_{11}$	$\text{BaCd}_{11}$	-	-	-	1.0662(1)	-	0.6868(2)
$\tau_2 + \text{CeSi}_2 + \text{Ce}_2\text{Zn}_{17}$	$\tau_2$	$\text{AlB}_2$	33.3	25.6	41.1 <sup>a</sup>	0.41365(5)	-	0.42967(5)
	$\text{CeSi}_2$	$\text{ThSi}_2$	33.3	19.4	47.3 <sup>a</sup>	0.42029(6)	-	1.4258(4)
	$\alpha\text{-Ce}_2\text{Zn}_{17}$	$\text{TbCu}_7$	-	-	-	0.52571(3)	-	0.44397(7)
$\tau_2 + \text{Ce}_3\text{Zn}_{22} + \text{Ce}_2\text{Zn}_{17}$	$\tau_2$	$\text{AlB}_2$	33.3	28.8	37.9 <sup>a</sup>	0.41816(1)	-	0.42592(2)
	$\text{Ce}_3\text{Zn}_{22}$	$\text{Ce}_3\text{Zn}_{22}$	12.1	87.7	0.2	0.89375(2)	-	2.13790(2)
	$\alpha\text{-Ce}_2\text{Zn}_{17}$	$\text{TbCu}_7$	10.7	89.0	0.3	0.52482(6)	-	0.44295(2)
$\tau_2 + \text{CeZn}_5 + \text{Ce}_3\text{Zn}_{22}$	$\tau_2$	$\text{AlB}_2$	33.3	28.9	37.8 <sup>a</sup>	0.41857(7)	-	0.4260(2)
	$\text{CeZn}_5$	$\text{CaCu}_5$	16.7	82.8	0.5	-	-	-
	$\text{Ce}_3\text{Zn}_{22}$	$\text{Ce}_3\text{Zn}_{22}$	12.2	87.4	0.4	0.8937(4)	-	2.138(1)
$\tau_2 + \text{CeZn}_5 + \tau_1$	$\tau_2$	$\text{AlB}_2$	33.3	31.3	35.4 <sup>a</sup>	0.42206(5)	-	0.42334(6)
	$\text{CeZn}_5$	$\text{CaCu}_5$	-	-	-	0.54236(4)	-	0.42553(5)
	$\tau_1$	$\text{Ce}_7\text{Zn}_{23-x}$	22.8	70.6	6.6	-	-	-
$\tau_1 + \text{CeZn}_5 + \text{Ce}_{13}\text{Zn}_{58}$	$\tau_1$	$\text{Ce}_7\text{Zn}_{23-x}$	23.1	70.8	6.1	1.4882(2)	1.7238(4)	0.4491(1)
	$\text{CeZn}_5$	$\text{CaCu}_5$	16.6	83.3	0.1	0.54256(9)	-	0.42542(8)
	$\text{Ce}_{13}\text{Zn}_{58}$	$\text{Gd}_{13}\text{Zn}_{58}$	18.0	81.9	0.1	1.4622(2)	-	1.4178(3)
$\tau_1 + \text{Ce}_{13}\text{Zn}_{58} + \text{Ce}_3\text{Zn}_{11}$	$\tau_1$	$\text{Ce}_7\text{Zn}_{23-x}$	23.1	72.4	4.4	-	-	-
	$\text{Ce}_{13}\text{Zn}_{58}$	$\text{Gd}_{13}\text{Zn}_{58}$	17.9	81.9	0.2	-	-	-
	$\text{Ce}_3\text{Zn}_{11}$	$\text{La}_3\text{Al}_{11}$	21.5	78.3	0.2	-	-	-
$\tau_1 + \text{Ce}_3\text{Zn}_{11} + \text{CeZn}_3$	$\tau_1$	$\text{Ce}_7\text{Zn}_{23-x}$	23.1	73.6	3.3	-	-	-
	$\text{Ce}_3\text{Zn}_{11}$	$\text{La}_3\text{Al}_{11}$	21.4	78.4	0.2	0.4514(1)	0.8879(2)	1.3463(3)
	$\text{CeZn}_3$	$\text{CeZn}_3$	24.7	75.1	0.2	-	-	-
$\tau_1 + \text{CeZn}_2 + \text{CeZn}_3$	$\tau_1$	$\text{Ce}_7\text{Zn}_{23-x}$	23.3	72.8	4.0	1.5498(4)	1.7107(4)	0.4502(1)
	$\text{CeZn}_3$	$\text{CeZn}_3$	25.2	74.5	0.3	0.46254(6)	1.0448(5)	0.6641(1)
	$\text{CeZn}_2$	$\text{CeCu}_2$	32.9	63.8	3.3	0.46417(6)	0.7596(7)	0.7508(1)
$\tau_1 + \tau_7 + \tau_2$	$\tau_1$	$\text{Ce}_7\text{Zn}_{23-x}$	23.3	71.1	5.6	-	-	-
	$\tau_2$	$\text{AlB}_2$	33.3	48.4	18.3	0.4388(1)	-	0.39738(7)
	$\tau_7$	unknown	36.9	48.5	14.6	-	-	-

<sup>a</sup> The values are calculated from compositional dependence of corresponding lattice parameters (Figure 9).

Table 5 summarizes data on composition and lattice parameters of all phases coexisting in equilibrium at 600°C. The only uncertainty concerns the maximal solubility of Si in binary  $\text{CeZn}_2$ . Our various attempts to prepare samples in the

Figure 10. Alloys in equilibrium with Si, which were prepared from  $\text{CeSi}_x$  master alloys containing  $\text{CeSi}_2$ , did not reach complete equilibrium even after re-powderization followed by hot pressing and/or long term annealing.  $\text{Ce}(\text{Zn}_x\text{Si}_{1-x})_2$ ,  $x \leq 0.25$ , with  $\alpha$ - $\text{ThSi}_2$  type was always observed in those alloys. Moreover, long term annealing generally shifted the overall alloy composition due to unavoidable evaporation of Zn, especially for alloys in the Zn-rich corner. However, equilibrated samples were easily obtained in case binary Ce-Si precursors with Ce content above 40 at.% were used.

corresponding three-phase region  $\tau_7 + \text{CeZn}_2 + \tau_1$  resulted in non-equilibrium alloys with about 5 at. % Si in the  $\text{CeZn}_2$ -phase. It is noteworthy that the phase triangulation in this part of the phase diagram at 600°C is different from that established at 800°C<sup>8</sup> and



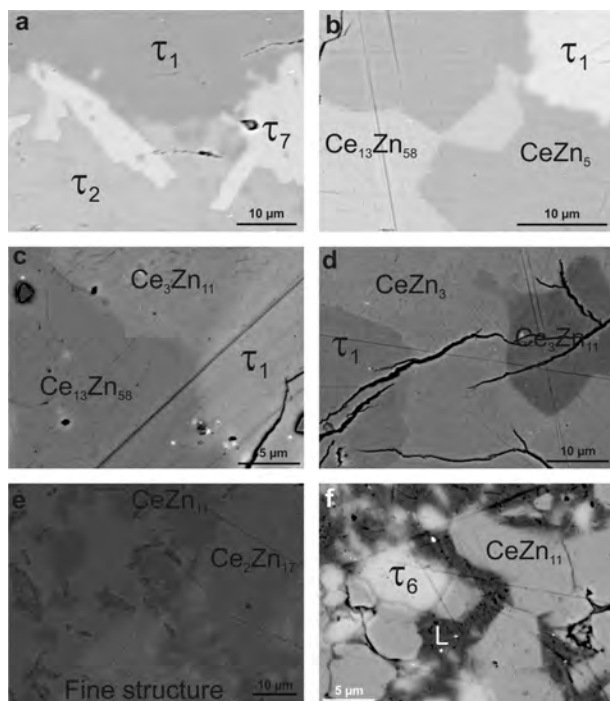


Figure 10. Selected micrograph of Ce-Zn-Si alloys annealed at 600°C: (a)  $\text{Ce}_{32}\text{Zn}_{54}\text{Si}_{14}$ , (b)  $\text{Ce}_{18}\text{Zn}_{81}\text{Si}_1$ , (c)  $\text{Ce}_{21}\text{Zn}_{78}\text{Si}_1$ , (d)  $\text{Ce}_{23}\text{Zn}_{76}\text{Si}_1$ , (e) diffusion couple  $\text{Ce}_{70}\text{Si}_{30}\text{-Zn}$  (12 hours), and (f) diffusion couple  $\text{Ce}_{50}\text{Si}_{50}\text{-Zn}$  (12 hours) (nominal composition in at. %).

this is essentially due to the formation of  $\tau_7$ . Thus, two three-phase regions:  $\text{Ce}(\text{Zn}_{1-x}\text{Si}_x)_2(\text{CeCu}_2\text{-type})+\tau_2+\tau_1$  and  $\text{Ce}(\text{Zn}_{1-x}\text{Si}_x)_2(\text{CeCu}_2\text{-type})+\tau_2+\tau_4$ , which were observed at 800°C are now changed into two three-phase regions:  $\tau_7+\tau_2+\tau_1$  and  $\tau_7+\text{Ce}(\text{Zn}_{1-x}\text{Si}_x)_2$  (CeCu<sub>2</sub>-type)+ $\tau_1$ , possibly due to the peritectoid formation of  $\tau_7$  ( $\tau_2+\tau_4+\text{Ce}(\text{Zn}_{1-x}\text{Si}_x)_2 \rightleftharpoons \tau_7$ ), and a U-type reaction ( $\tau_2+\text{Ce}(\text{Zn}_{1-x}\text{Si}_x)_2 \rightleftharpoons \tau_1+\tau_7$ ) in the temperature interval 600°C < T < 800°C.

### 3.5. Formation of $\tau_5$ and $\tau_6$ and partial Schulz-Scheil diagram

Due to the high melting point of cerium silicides  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  and the high vapour pressure of Zn at elevated temperatures, it is difficult to obtain homogeneous cast alloys for the determination of the crystallization behaviour of alloys. On the other hand, the established isothermal section at 600°C shows that three-phase regions involved in equilibria with binary Ce-Zn compounds are very narrow and our attempts to equilibrate the samples at higher temperature resulted in a significant change of the overall compositions. Filling the ampoules with argon slightly suppressed the Zn losses, but even in this case samples were heterogeneous, which at first did not allow us to reliably determine the change in phase equilibria via annealing at different temperatures. This shift of the compositions during thermal treatment also hinders the interpretation of DTA. For instance, DTA measurements on single-phase  $\tau_5$  and  $\tau_6$  resulted in a sequence of several thermal effects that are difficult to reconcile with the phase triangulation. Investigation of the specimens after DTA by SEM/EDX showed that samples became heterogeneous and contained regions with different phases (see Figure 11). Reliable temperatures for isothermal reactions were only obtained for wide three-phase regions:  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2+\tau_5+(\text{Si})$ ,  $\tau_5+\tau_6+(\text{Si})$ ,

$\tau_6+\text{CeZn}_{11}+(\text{Si})$ ,  $\text{CeZn}_{11}+(\text{Zn})+(\text{Si})$ . The temperatures of invariant reactions that correspond to these fields were derived as follows: 727°C, 634°C, 561°C and 412°C, respectively. These four isothermal reaction temperatures were confirmed by DTA from the Zn-rich sample that contains  $\tau_6$ , (Si), and  $\text{CeZn}_{11}$  (close to the tie line (Si)+ $\text{CeZn}_{11}$ ) (see Figure 12). After three DTA runs the sample contains additionally  $\tau_5$ , (Zn), and  $\text{CeSi}_2$ , which suggests incongruent formation of both  $\tau_5$  and  $\tau_6$ .

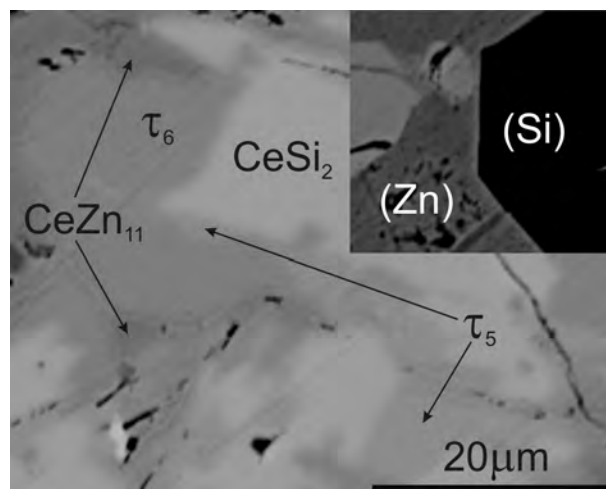


Figure 11. Micrograph of  $\tau_5$  after DTA, showing sequence of crystallization:  $\text{CeSi}_2\text{-}\tau_5\text{-}\tau_6$

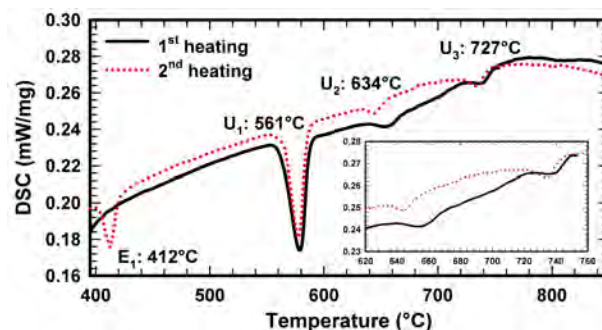


Figure 12. DTA curve of alloy  $\text{Ce}_{5.9}\text{Zn}_{59.8}\text{Si}_{34.3}$ .

All invariant reactions determined are summarized in the Scheil reaction scheme in Figure 13 along with the partial isothermal sections (Figure 14) at temperatures between the thermal effects established by DTA. Selected microstructures of alloys are presented in Figure 15 and Figure 16. Comparing the phase equilibria at 500°C (Figure 14a) with those observed at 600°C (Figure 14b) we conclude on the existence of a transition type reaction  $U_1$  (561°C after DTA):  $L+\tau_6 \rightleftharpoons \text{CeZn}_{11}+(\text{Si})$ .

The characterization of sample  $\text{Ce}_{5.9}\text{Zn}_{59.8}\text{Si}_{34.3}$  shows that  $\tau_6$  coexists in equilibrium with (Si) and L(Zn) at 600°C (Figure 15a), however after annealing at 650°C  $\tau_6$  was not observed in this sample, instead  $\tau_5$  enters the equilibrium with L(Zn) and silicon (Figure 14c and Figure 15b). Such a change of phase equilibria requests another transition type reaction  $U_2$ :  $L+\tau_5 \rightleftharpoons \tau_6+(\text{Si})$  to occur between 600 and 650°C (634° after DTA).

Although  $\tau_6$  was observed in the sample  $\text{Ce}_{7.6}\text{Zn}_{78.4}\text{Si}_{14}$  annealed at this temperature,  $\tau_6$  does not participate in the equilibria at 710°C (Figure 14d). It has to be noted that the microstructure of this sample contains four phases ( $\tau_6$ ,  $\tau_5$ ,  $\text{CeZn}_{11}$ , and L(Zn)), see



Figure 16b) and one of these phases has to be considered as non-equilibrium phase. Comparing this microstructure with the three-phase structure ( $\tau_5$ ,  $\text{CeZn}_{11}$  and  $\text{L}(\text{Zn})$ ) obtained for this sample annealed at  $750^\circ\text{C}$  (Figure 16c) we may safely conclude that  $\tau_6$  is the non-equilibrium phase that forms during quenching from  $710^\circ\text{C}$ . On the other hand, the same sample annealed at  $690^\circ\text{C}$  showed only 3 phases ( $\tau_6$ ,  $\text{CeZn}_{11}$  and  $\text{L}(\text{Zn})$ ). Based on these observations, the invariant reaction for the formation of  $\tau_6$  is supposed to occur in the temperature range between  $690$  and  $700^\circ\text{C}$  (see Figure 13).

Three peritectic-type reactions may be responsible for the formation of this phase: (i)  $\text{L}+\tau_5 \rightleftharpoons \tau_6$ , (ii)  $\text{L}+\tau_5+\text{CeZn}_{11} \rightleftharpoons \tau_6$  and (iii)  $\text{L}+\tau_5+(\text{Si}) \rightleftharpoons \tau_6$ . The latter reaction requests the existence of a three-phase field  $\tau_5+\tau_6+(\text{Si})$  at a temperature just below this invariant reaction. However, this three-phase field is not observed at  $650^\circ\text{C}$  (see Figure 14c), and thus rules out reaction (iii). Rietveld analysis of a sample with composition of  $\text{Ce}_{24.5}\text{Zn}_{37.5}\text{Si}_{38.0}$  annealed at  $650^\circ\text{C}$  showed three phases:  $\text{L}(\text{Zn})+\tau_5+\tau_6$ . However due to porosity of the sample it was not possible to reliably analyze the microstructure. Due to a strong degeneracy of the three-phase field  $\text{L}(\text{Zn})+\tau_5+\tau_6$  (compositions of these phases lie almost on one line; (see Figure 14c), the two remaining possible invariant reactions (i) and (ii) are almost identical from a thermodynamic point of view.

The existence of a maximum on the solidus in the two-phase field  $\tau_5+\tau_6$  would infer a three-phase invariant peritectic  $\text{L}+\tau_5 \rightleftharpoons \tau_6$ , but due to the difficulties in the interpretation of DTA we cannot provide such evidence. Thus the type of this reaction remains uncertain and is therefore denoted as a degenerated peritectic:  $\text{L}+\tau_5, \text{CeZn}_{11} \rightleftharpoons \tau_6$  in the temperature range  $690 \leq T \leq 700^\circ\text{C}$  ( $\text{P}_{\text{D1}}$ ; Figure 13). The invariant reaction recorded by DTA at  $727^\circ\text{C}$  (Figure 12) is defined as transition type reaction  $\text{U}_3$ ,  $\text{L}+\text{CeSi}_2 \rightleftharpoons \tau_5+(\text{Si})$ . Confirmation is available from a comparison of the isothermal sections and microstructures of the alloys annealed at  $710$  (the micrograph is not shown due to its similarity to  $650^\circ\text{C}$ ) and  $750^\circ\text{C}$  (Figure 14d,e and Figure 15b,c). Similar to the narrow three-phase field  $\text{L}(\text{Zn})+\tau_5+\tau_6$ , Rietveld analysis of sample  $\text{Ce}_{22.7}\text{Zn}_{42.9}\text{Si}_{34.4}$  annealed at  $750^\circ\text{C}$  revealed three phase constituents:  $\text{L}(\text{Zn})$ ,  $\tau_5$ , and  $\text{CeSi}_2$  consistent with the three-phase

field  $\text{L}(\text{Zn})+\tau_5+\text{CeSi}_2$ .

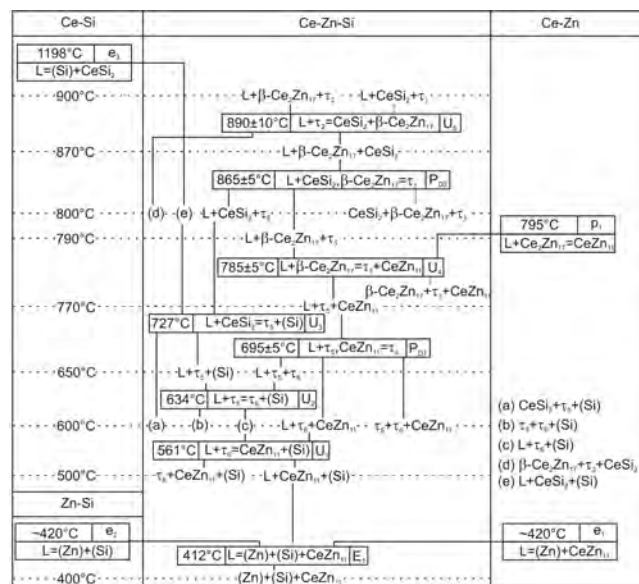
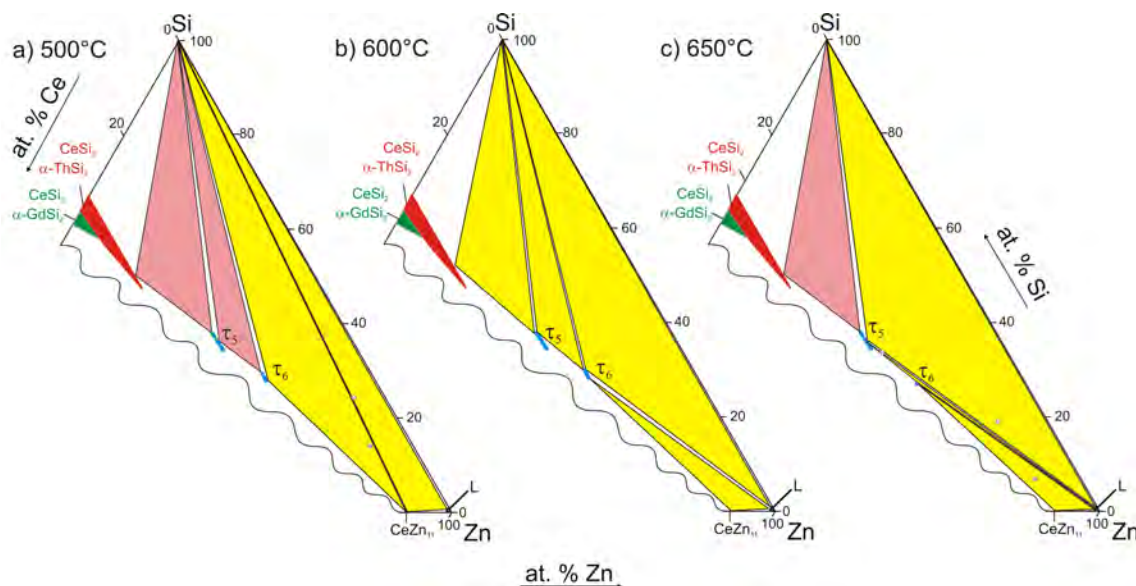


Figure 13. Scheil diagram for the Zn-rich corner

The previously reported isothermal section at  $800^\circ\text{C}$ <sup>8</sup> suggested that  $\tau_5$  is unstable at this temperature and decomposes into  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  with  $\alpha\text{-ThSi}_2$  type,  $\text{L}(\text{Zn})$ , and possibly  $\text{CeZn}_{11}$  or  $\beta\text{-Ce}_2\text{Zn}_{17}$ . Indeed DTA runs of sample  $\text{Ce}_{7.6}\text{Zn}_{78.4}\text{Si}_{14}$  up to  $850^\circ\text{C}$  gave two signals between  $780$ – $790^\circ\text{C}$ . Surprisingly EPM analysis of this sample after three DTA runs did not show any trace of  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$ . In order to confirm these observations the remaining pieces of  $\text{Ce}_{7.6}\text{Zn}_{78.4}\text{Si}_{14}$  alloys were heat treated at  $770$ ,  $790$ ,  $810$ ,  $850$ ,  $860$ ,  $870$ ,  $880$  and  $900^\circ\text{C}$ .

Rietveld refinement and EPM analysis clearly showed that  $\tau_5$  is still stable up to  $850^\circ\text{C}$  and is in equilibrium with  $\text{L}(\text{Zn})$  and  $\beta\text{-Ce}_2\text{Zn}_{17}$ , while at  $900^\circ\text{C}$  it disappears completely yielding a three-phase field  $\text{L}(\text{Zn})+\beta\text{-Ce}_2\text{Zn}_{17}+\tau_2$ . Such a peritectic reaction involving  $\tau_2$  is not compatible with the existence of the three-phase field  $\tau_2+\text{CeSi}_2+\beta\text{-Ce}_2\text{Zn}_{17}$ . Careful heat treatment between



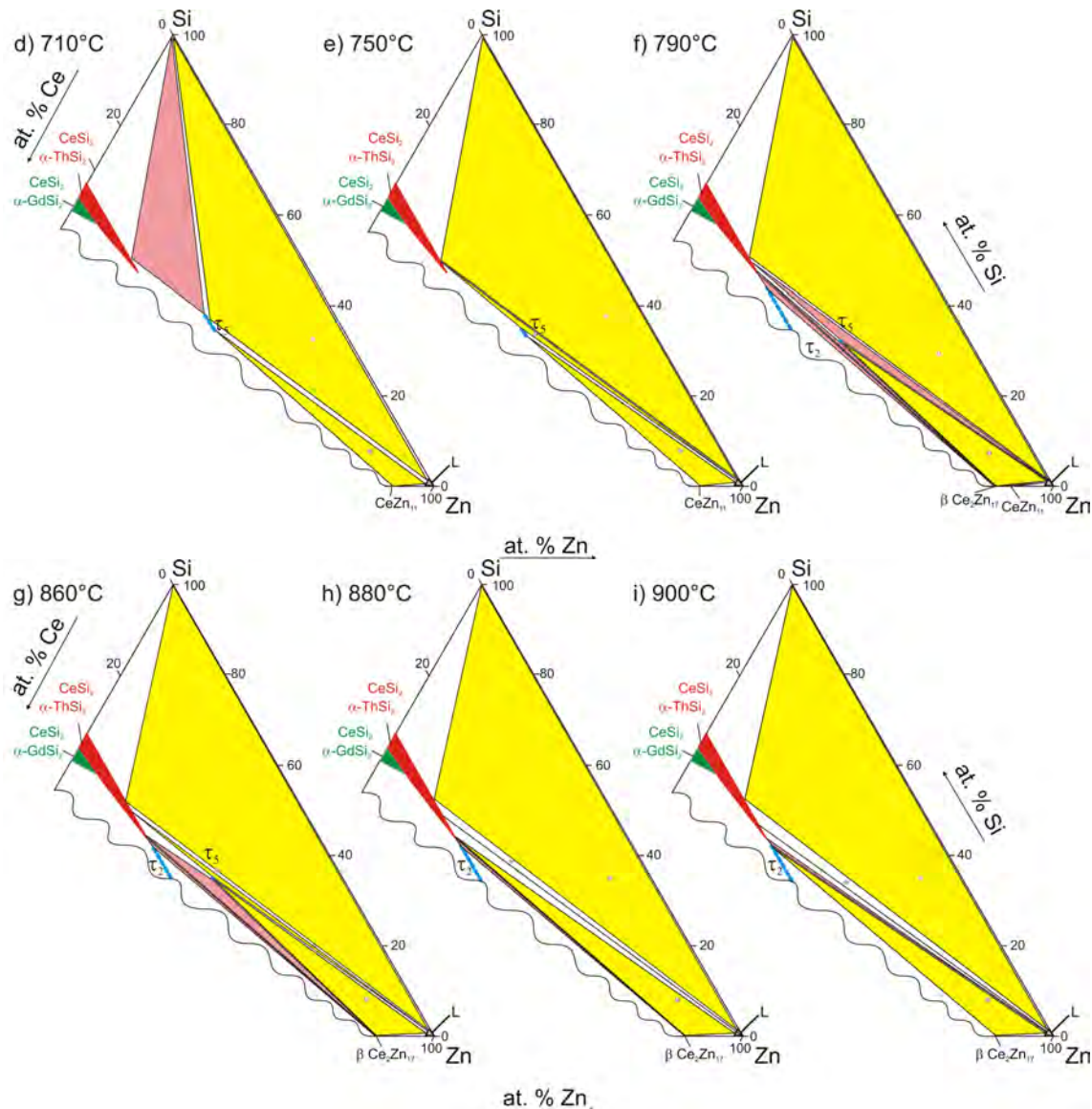


Figure 14. Partial isothermal sections in the Zn-corner at various temperatures..

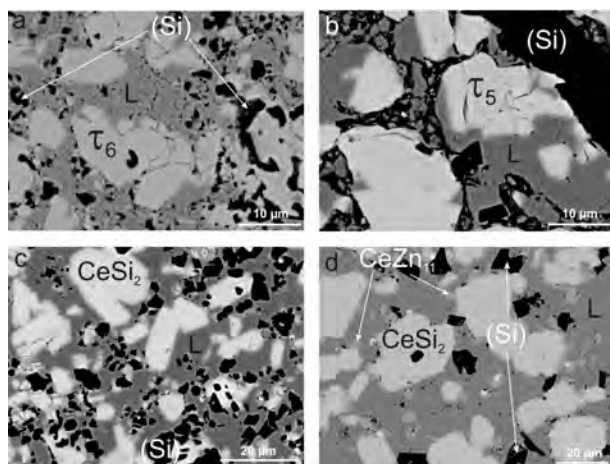


Figure 15. Microstructure of alloy  $\text{Ce}_{5.5}\text{Zn}_{59.8}\text{Si}_{34.3}$  annealed at different temperatures: (a) 600°C, (b) 650°C, (c) 750°C, (d) 900°C for one day each under Argon.

850-900°C followed by XRPD and EPM analysis showed that an alloy annealed at 860°C gives the same phase constituents as in 850°C, while at 870°C  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  with  $\alpha\text{-ThSi}_2$  type is additionally present in this sample. This fact narrows down the decomposition temperature of  $\tau_5$  to  $865 \pm 5^\circ\text{C}$ , and confirms the participation of  $\text{Ce}(\text{Si}_{1-x}\text{Zn}_x)_2$  with  $\alpha\text{-ThSi}_2$  type in the peritectic formation of  $\tau_5$ . Taking into consideration similar arguments, as discussed above for the formation of  $\tau_6$ , a degenerated invariant reaction of peritectic type  $\text{P}_{\text{D2}}: \text{L} + \text{CeSi}_2, \beta\text{-Ce}_2\text{Zn}_{17} \rightleftharpoons \tau_5$  is assigned. The equilibria observed at 900°C could be explained by a transition type reaction  $\text{U}_5: \text{L} + \tau_2 \rightleftharpoons \text{CeSi}_2 + \beta\text{-Ce}_2\text{Zn}_{17}$  that occurs at  $890 \pm 10^\circ\text{C}$ .

One of the afore-mentioned thermal effects observed between 780-790°C could be attributed to a transition type reaction  $\text{U}_4: \text{L} + \beta\text{-Ce}_2\text{Zn}_{17} \rightleftharpoons \tau_5 + \text{CeZn}_{11}$ . The phase field  $\text{L}(\text{Zn}) + \tau_5 + \text{CeZn}_{11}$  was still observed up to 770°C, while at 790°C it changed to  $\text{L}(\text{Zn}) + \tau_5 + \beta\text{-Ce}_2\text{Zn}_{17}$ . Note that in some samples  $\text{CeZn}_{11}$  and/or  $\tau_6$  were observed as the fourth or fifth phase. Based on the amount and morphology, those phases were considered to be formed



during the quenching process.

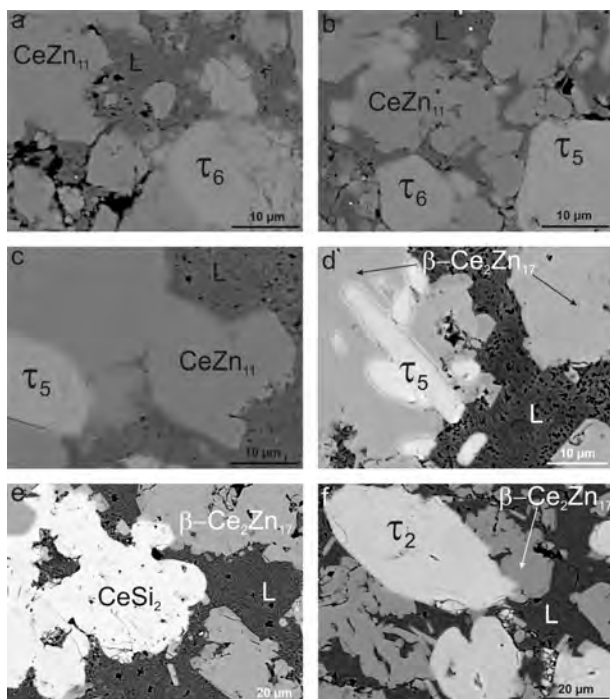


Figure 16. Microstructure of alloy  $\text{Ce}_{7.6}\text{Zn}_{78.4}\text{Si}_{14}$  annealed at different temperatures: (a) 650°C, (b) 710°C, (c) 750°C, (d) 790°C, (e) 880°C, and (f) 900°C for one day each under Argon.

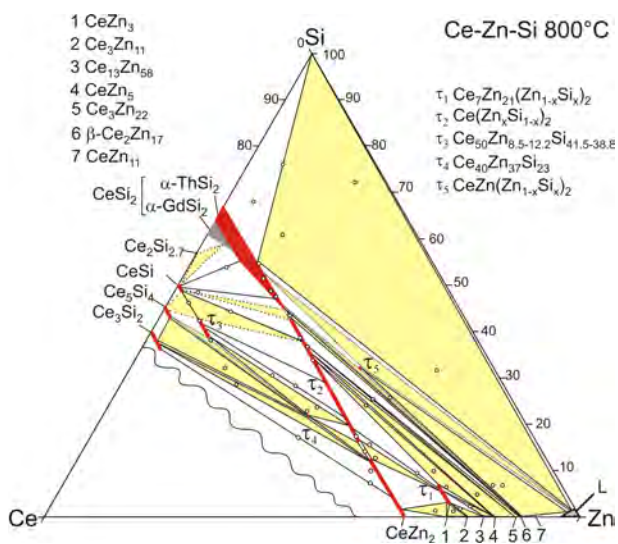


Figure 17. Isothermal section at 800°C (modified after ref. 8; see text)

The stability of  $\tau_5$  at 800°C has been incorporated in the new isothermal section shown in Figure 17. It supersedes the older version by Malik *et al.*<sup>8</sup> In addition to the three-phase field  $L(\text{Zn})+\tau_5+\beta\text{-Ce}_2\text{Zn}_{17}$ , two narrow three-phase fields are required to complete the section:  $\text{CeSi}_2+\tau_5+\beta\text{-Ce}_2\text{Zn}_{17}$  and  $L(\text{Zn})+\tau_5+\text{CeSi}_2$ . Note that the three-phase field  $L(\text{Zn})+\text{CeSi}_2+(\text{Si})$  is still stable up to 900°C. Such narrow phase fields are complicated to investigate, and without careful control of the overall sample composition it may earlier have led to a wrong conclusion regarding the stability of  $\tau_5$ .

The results on the phase equilibria are consistent (i) with the single crystal growth experiments, which reveal a large

20 crystallization field of the  $\alpha\text{ThSi}_2$ -type phase  $\text{Ce}(\text{Zn}_x\text{Si}_{1-x})_2$  extending far into the Zn-rich corner (up to 95 at. % Zn), and consequently (ii) with a rather steep liquidus surface in the Zn-rich region, which infers a high degeneracy in the isothermal reactions involving the Zn-rich liquid.

### 25 3.6. Physical Properties of $\tau_5\text{-CeZn}(\text{Zn}_{1-x}\text{Si}_x)_2$ and $\tau_6\text{-CeZn}_2(\text{Zn}_{0.28}\text{Si}_{0.72})_2$

Ac magnetic susceptibility measurements on a polycrystalline sample of  $\tau_5$   $\text{CeZn}(\text{Zn}_{0.32}\text{Si}_{0.68})_2$  revealed a  $\delta$ -shape magnetic anomaly near  $T_C \sim 5$  K (see Figure 18) which is indicative of a 30 ferromagnetic transition. Accordingly, we performed dc magnetisation and dc susceptibility measurements on a few freely rotating, flux-grown single crystals of  $\tau_5$  (with a total mass of 0.8 mg). Field dependent isothermal (see Figure 19) as well as temperature dependent magnetisation (Figure 20) measurements 35 confirm ferromagnetic ordering below about 4.4 K with a saturation moment near  $1 \mu_B$  at 1.9 K and 6 T. The slightly lower  $T_C$  of the flux-grown single crystals as compared to the polycrystalline bulk samples relates to slightly different compositions of  $\tau_5$  bulk samples as compared to flux grown  $\tau_5$  40 crystals  $\text{CeZn}(\text{Zn}_{0.29}\text{Si}_{0.71})_2$ .

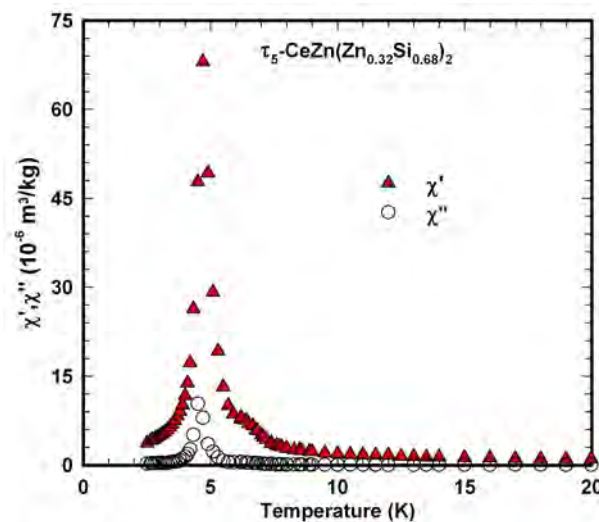


Figure 18. Temperature dependent in-phase and out-of-phase ac susceptibility components,  $\chi'$  and  $\chi''$ , measured on polycrystalline  $\tau_5\text{-CeZn}(\text{Zn}_{0.32}\text{Si}_{0.68})_2$  with a field amplitude of 325 A/m and frequency of 100 Hz.

The ferromagnetic phase transition at  $T_C \sim 4.4$  K is corroborated by distinct anomalies of the specific heat and electrical resistivity in Figure 21 and Figure 22, respectively.

The analysis of the inverse dc magnetic susceptibility in terms of a modified Curie-Weiss fit,  $\chi(T) = \chi_0 + C/(T - \Theta_p)$ , in Figure 20 reveals an effective paramagnetic moment of Ce near  $2.5 \mu_B$  which is close to the effective moment of free  $\text{Ce}^{3+}$  ( $2.54 \mu_B$ ). The negative value of the paramagnetic Curie temperature of  $-10$  K obtained from analysing the data of freely rotating crystals refers 55 to Kondo correlations rather than to a specific type of magnetic coupling (whether antiferro- or ferromagnetic). The relevance of Kondo correlations for  $\tau_5$  is further revealed by the temperature dependence of the electrical resistivity in Figure 22, showing typical Kondo lattice features, and by the specific heat data in

Figure 21. The magnitude of the specific heat anomaly at  $T_C$  of  $\tau_5$ -CeZn( $\text{Zn}_{0.29}\text{Si}_{0.71}$ )<sub>2</sub> single crystals is significantly reduced as compared to the value expected from a basic local moment mean-field approach. We thus analyse the temperature dependence and magnitude of the magnetic specific heat contribution in terms of a simple model for a ferromagnetic Kondo lattice system based on the resonant level model by Schotte and Schotte.<sup>39,40</sup> The details of this model calculations are explained e.g. in ref. 41.

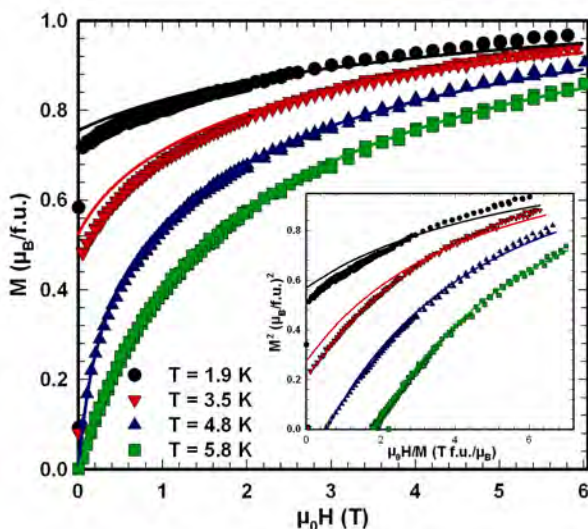


Figure 19. Isothermal magnetisation measurements of single crystalline  $\tau_5$ -CeZn( $\text{Zn}_{0.29}\text{Si}_{0.71}$ )<sub>2</sub>; the inset shows the corresponding Arrott plot,  $M^2$  vs.  $H/M$ . The solid lines display a model calculation in terms of the resonant level model by Schotte and Schotte.

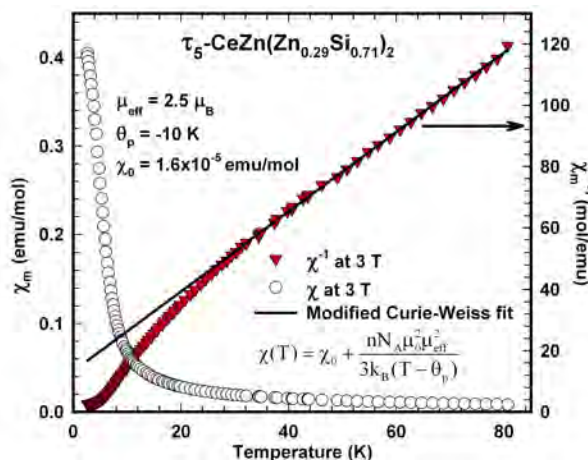


Figure 20. Temperature dependent dc magnetic susceptibility,  $\chi(T)$  at left axis, and inverse magnetic susceptibility,  $1/\chi(T)$  at right axis, of freely rotating  $\tau_5$ -CeZn( $\text{Zn}_{0.29}\text{Si}_{0.71}$ )<sub>2</sub> single crystals measured at 3 T; the solid line displays a modified Curie-Weiss fit of the inverse susceptibility.

The corresponding fit to the experimental data, indicated as solid line in Figure 21, yields a ferromagnetic exchange coupling  $J = 14.6$  K and a Kondo temperature  $T_K = 5$  K, thus, suggesting a ferromagnetic Kondo lattice ground state of  $\tau_5$ -CeZn( $\text{Zn}_{0.32}\text{Si}_{0.68}$ )<sub>2</sub>. The largest deviation between the applied model and the experimental data is observed right above the ferromagnetic phase transition and relates to short range order and phonon contributions which are not included in the model. Using the same values for  $J$  and  $T_K$  and an effective Landé factor

$g = 2$  to adjust the model for the unknown  $4f$  wave function of the crystal field ground state doublet, we calculated the temperature and field dependent magnetisation displayed as solid lines in Figure 19. The approximate agreement with the experimental data further supports the validity of a ferromagnetic Kondo model.

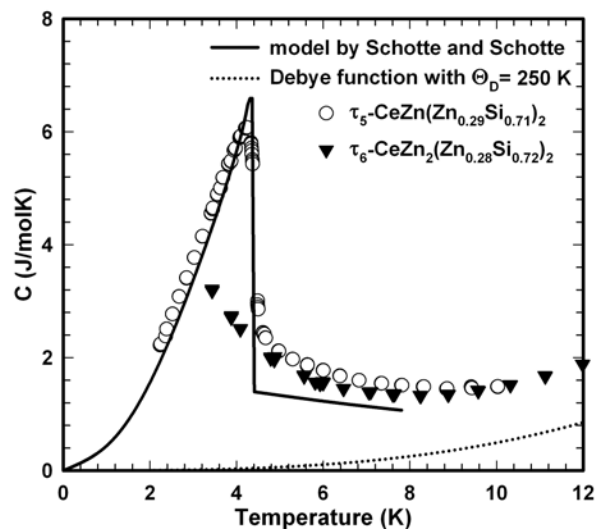


Figure 21. Specific heat data of  $\tau_5$ -CeZn( $\text{Zn}_{0.29}\text{Si}_{0.71}$ )<sub>2</sub> single crystals and polycrystalline  $\tau_6$ -CeZn<sub>2</sub>( $\text{Zn}_{0.28}\text{Si}_{0.72}$ )<sub>2</sub>; the solid and dotted lines refer to the analysis of  $\tau_5$  data in terms of the resonant level model by Schotte and Schotte and a tentative phonon contribution represented by a Debye function, respectively.

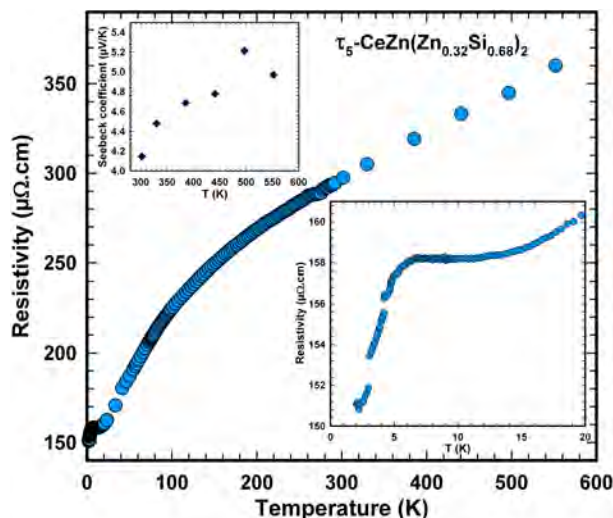


Figure 22. Resistivity data of polycrystalline  $\tau_5$ -CeZn( $\text{Zn}_{0.32}\text{Si}_{0.68}$ )<sub>2</sub>. Bottom right inset shows the kink at ordering temperature, top left inset shows the Seebeck coefficient above room temperature.

The magnetic ground state properties of polycrystalline bulk samples of  $\tau_6$  CeZn<sub>2</sub>( $\text{Zn}_{0.28}\text{Si}_{0.72}$ )<sub>2</sub> were studied by means of specific heat as well as dc and ac magnetic susceptibility measurements at temperatures down to 3 K. Within the experimental temperature range the  $\tau_6$  phase displays a Curie-Weiss type paramagnetic behaviour as demonstrated by the dc magnetic susceptibility depicted in Figure 23. A modified Curie-Weiss fit of the inverse susceptibility in the temperature interval 80-300 K is indicated as solid line in Figure 23 and yields a



temperature independent Pauli component  $\chi_0 = 1.0 \times 10^{-4}$  emu/mol, a paramagnetic Curie-Weiss temperature  $\Theta_p = -0.5$  K being indicative for weak antiferromagnetic or very weak Kondo correlations. Via the Curie constant of this fit an effective paramagnetic moment  $\mu_{\text{eff}} = 2.34 \mu_B$  is calculated, which is markedly reduced as compared to the  $\text{Ce}^{3+}$  free ion value (2.54  $\mu_B$ ). The heat capacity data of  $\tau_6$   $\text{CeZn}_2(\text{Zn}_{0.28}\text{Si}_{0.72})_2$  in Figure 21 display an upturn at lowest temperatures, which may either refer to short range correlations above a magnetic phase transition taking place below 3K or refer to Kondo correlations with a rather small characteristic energy of the order of one Kelvin.

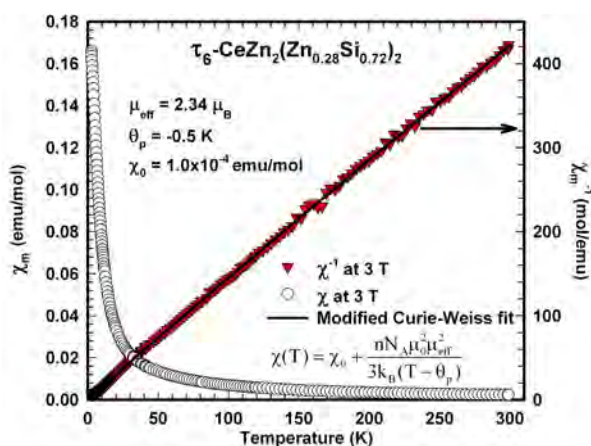


Figure 23. Temperature dependent dc magnetic susceptibility,  $\chi(T)$  at left axis, and inverse magnetic susceptibility,  $1/\chi(T)$  at right axis, of polycrystalline  $\tau_6$ - $\text{CeZn}_2(\text{Zn}_{0.28}\text{Si}_{0.72})_2$  measured at 3T; the solid line displays a modified Curie-Weiss fit of the inverse susceptibility.

Consistent with the small Seebeck coefficient (see top left inset in Figure 22) electrical resistivity of  $\tau_5$  indicates metallic type behaviour ruling out any thermoelectrically interesting behaviour.

#### 4. Conclusions

As the Ce-Zn-Si system is an important part of multinary Mg-based Mg-Zn-Mn-RE-(Si) high strength lightweight alloys for automotive applications, we have explored the constitution of the Ce-Zn-Si subsystem and particularly have determined in this work the phase equilibria for the isothermal section at 600°C in the region with <33.3 at.% Ce. Five ternary compounds ( $\tau_1$ ,  $\tau_2$ ,  $\tau_5$  to  $\tau_7$ ) exist at 600°C. Several four-phase reactions in the Zn rich corner were detected by DTA, including the peritectic decomposition temperatures of  $\tau_5$  and  $\tau_6$  at  $865 \pm 5^\circ\text{C}$  and  $695 \pm 5^\circ\text{C}$ , respectively. To provide details on the solidification of Ce-poor alloys, a Schultz-Scheil diagram was constructed from DTA measurements and partial isothermal sections determined at various temperatures. The crystal structures of  $\tau_5$  (CeNiSi<sub>2</sub>-type, *Cmcm*,  $a = 0.42079(1)$ ,  $b = 1.765218(3)$ ,  $c = 0.41619(1)$  nm), and  $\tau_6$  (ThCr<sub>2</sub>Si<sub>2</sub>-type, *I4/mmm*,  $a = 0.41757(1)$ ,  $c = 1.05073(2)$  nm) were solved from X-ray single crystal diffraction data. An interesting case was met in the stabilization by extremely small amounts of Ge (less than ~2 atom percent of Ge) of the ternary phases  $\{\text{La,Ce}\}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Ge}_x)_2$ , both isotypic with the structure of  $\text{Ce}_7\text{Zn}_{21}(\text{Zn}_{1-x}\text{Si}_x)_2$ . DFT calculations elucidated the extent and nature of the stabilizing effect of Ge in  $\text{Ce}_7\text{Zn}_{23-x}\text{Ge}_x$  discussing the electronic structure in terms of the density of states (DOS) and determining enthalpies of formation for  $\text{Ce}_7\text{Zn}_{23-x}\text{Ge}_x$  ( $x=0$ ,

0.5, 2) as well as for several neighbouring binary Ce-Zn phases. Physical property measurements document that neither  $\tau_5$  nor  $\tau_6$  are near a metal to insulator transition and thus exhibit rather metallic than semiconducting (thermoelectric) behaviour. Magnetic measurements as well as specific heat and electrical resistivity data reveal interesting ferromagnetic Kondo lattice behaviour for  $\tau_5$ - $\text{CeZn}(\text{Zn}_x\text{Si}_{1-x})_2$  with a Curie temperature  $T_C = 4.4$  K, whereas  $\tau_6$  displays Curie-Weiss type paramagnetic behavior down to 3 K. The effective paramagnetic moments of Ce obtained from Curie-Weiss fit of  $\tau_5$  (2.48  $\mu_B$ ) and  $\tau_6$  (2.34  $\mu_B$ ) suggest that the ground state of Ce-ions in these compounds is trivalent or close to 3+.

#### 5. Acknowledgements

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- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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