



Cite this: *Dalton Trans.*, 2016, **45**, 5262

BaAl₄ derivative phases in the sections {La,Ce}-Ni₂Si₂-{La,Ce}Zn₂Si₂: phase relations, crystal structures and physical properties†‡

Fainan Failamani,^a Zahida Malik,^{§a} Leonid Salamakha,^b Friedrich Kneidinger,^b Andriy Grytsiv,^{a,c} Herwig Michor,^b Ernst Bauer,^{b,c} Gerald Giester^d and Peter Rogl^{†a,c}

Phase relations and crystal structures have been evaluated within the sections LaNi₂Si₂-LaZn₂Si₂ and CeNi₂Si₂-CeZn₂Si₂ at 800 °C using electron microprobe analysis and X-ray powder and single crystal structure analyses. Although the systems La-Zn-Si and Ce-Zn-Si at 800 °C do not reveal compounds such as "LaZn₂Si₂" or "CeZn₂Si₂", solid solutions {La,Ce}(Ni_{1-x}Zn_x)₂Si₂ exist with the Ni/Zn substitution starting from {La,Ce}Ni₂Si₂ (ThCr₂Si₂-type; *I4/mmm*) up to $x = 0.18$ for Ce(Ni_{1-x}Zn_x)₂Si₂ and $x = 0.125$ for La(Ni_{1-x}Zn_x)₂Si₂. For higher Zn-contents $0.25 \leq x \leq 0.55$ the solutions adopt the CaBe₂Ge₂-type (*P4/nmm*). The investigations are backed by single crystal X-ray diffraction data for Ce(Ni_{0.61}Zn_{0.39})₂Si₂ (*P4/nmm*; $a = 0.41022(1)$ nm, $c = 0.98146(4)$ nm; $R_f = 0.012$) and by Rietveld refinement for La(Ni_{0.56}Zn_{0.44})₂Si₂ (*P4/nmm*; $a = 0.41680(6)$ nm, $c = 0.99364(4)$ nm; $R_f = 0.043$). Interestingly, the Ce-Zn-Si system contains a ternary phase CeZn₂(Si_{1-x}Zn_x)₂ of the ThCr₂Si₂ structure type ($0.25 \leq x \leq 0.30$ at 600 °C), which forms peritectically at $T = 695$ °C but does not include the composition "CeZn₂Si₂". The primitive high temperature tetragonal phase with the CaBe₂Ge₂-type has also been observed for the first time in the Ce-Ni-Si system at CeNi_{2+x}Si_{2-x}, $x = 0.33$ (single crystal data, *P4/nmm*; $a = 0.40150(2)$ nm, $c = 0.95210(2)$ nm; $R_f = 0.0163$). Physical properties (from 400 mK to 300 K) including specific heat, electrical resistivity and magnetic susceptibility have been elucidated for Ce(Ni_{0.61}Zn_{0.39})₂Si₂ and La(Ni_{0.56}Zn_{0.44})₂Si₂. Ce(Ni_{0.61}Zn_{0.39})₂Si₂ exhibits a Kondo-type ground state. Low temperature specific heat data of La(Ni_{0.56}Zn_{0.44})₂Si₂ suggest a spin fluctuation scenario with an enhanced value of the Sommerfeld constant.

Received 1st December 2015,

Accepted 6th February 2016

DOI: 10.1039/c5dt04705f

www.rsc.org/dalton

1. Introduction

Since its discovery in 1935 by Andress and Alberti,¹ the BaAl₄ structure type and its derivatives have been found in more than 200 intermetallic compounds, particularly the three tetragonal ternary variants: the ThCr₂Si₂-type by Ban and Sikirica² (or

CeAl₂Ga₂-type discovered independently by Zarechnyuk *et al.*³ in the same year), CaBe₂Ge₂ by Eisenmann *et al.*⁴ and the non-centrosymmetric variant BaNiSn₃ by Dörrscheidt and Schäfer.⁵ The BaAl₄ structure type furthermore is one of the building blocks of various structure types, such as U₃Ni₄Si₄, CeNiSi₂ (in combination with AlB₂-type slabs) and many others.⁶

Although phase equilibria in the Ce-Ni-Si system were investigated in the 70s by Bodak *et al.*^{7,8} more ternary phases were discovered afterwards: Ce₂Ni₃Si₅ (U₂Co₃Si₅-type, orthorhombic superstructure variant of BaAl₄),⁹ Ce₁₄Ni₆Si₁₁,¹⁰ Ce₃NiSi₃,¹¹ *etc.* Being the last member of the first row of transition metals, Zn containing ternary rare earth silicon systems had been one of the least investigated types of systems. Only some reports on the formation of ternary compounds could be found in the literature.¹² Recently our report¹³ on the Ce-Zn-Si system at 800 °C revealed the formation of several ternary phases. Surprisingly neither BaAl₄ nor its derivative structure could be found in the system at 800 °C, instead a far off-stoichiometric ThCr₂Si₂-type CeZn_{2+x}Si_{2-x} ($x \sim 0.5$, labelled as τ_6) was found to be stable at temperatures below 695 ± 5 °C.¹⁴

Compounds crystallizing in the BaAl₄ type or its derivatives are often associated with various exotic superconducting

^aInstitute of Materials Chemistry and Research, University of Vienna, Währingerstraße 42, A-1090 Vienna, Austria. E-mail: fai.failamani@gmail.com, zahida.malik@sns.nust.edu.pk, andriy.grytsiv@univie.ac.at, peter.franz.rogl@univie.ac.at; Fax: +43 142779524; Tel: +43 1427752456

^bInstitute of Solid State Physics, TU Wien, Wiedner Hauptstraße 8-10, A-1040 Vienna, Austria. E-mail: salamakhaleonid@rambler.ru, kneidinger@ifp.tuwien.ac.at, michor@ifp.tuwien.ac.at, bauer@ifp.tuwien.ac.at; Fax: +43 15880113199; Tel: +43 15880113160

^cChristian Doppler Laboratory for Thermoelectricity, Vienna, Austria

^dInstitute of Mineralogy and Crystallography, University of Vienna, Althanstraße 14, A-1090 Vienna, Austria. E-mail: gerald.giester@univie.ac.at; Fax: +43 14277853235; Tel: +43 1427753235

†Dedicated to Prof. Dr Wolfgang Jeitschko on the occasion of his 80th birthday.

‡Electronic supplementary information (ESI) available. See DOI: 10.1039/c5dt04705f

§Present address: Department of Chemistry, SNS, NUST, H-12, Islamabad, Pakistan.



phenomena, starting with the discovery of heavy fermion superconductivity in CeCu_2Si_2 by Steglich *et al.* in 1979,¹⁵ which breaks the previous belief of non-coexistence between magnetism and superconductivity. Spin density wave transition was found in BaFe_2As_2 ,¹⁶ followed by the discovery of superconductivity in K-doped¹⁷ and Co-doped BaFe_2As_2 .¹⁸ More recently, BCS-like superconductivity was found in non-centrosymmetric BaPtSi_3 (BaNiSn_3 -type)¹⁹ and isotypes.²⁰

In cerium and actinoid compounds the hybridization of the Ce-f electrons with the conduction band gives rise to various kinds of interesting physical phenomena. Systematic studies of the transport, magnetic and calorimetric properties and Ce L_{III} X-ray absorption spectra and XPS measurements characterized CeNi_2Si_2 as an intermediate valence (valence fluctuation) system with a characteristic Kondo-lattice temperature $T^* \sim 600$ K.^{21–26} The positive Seebeck coefficient, decreasing with the Si content in $\text{CeNi}_{2-x}\text{Si}_{2+x}$ was taken as a decrease of the electronic DOS particularly of the Ni-3d-states at the Fermi level concomitant with a narrowing of the Ce-4f level and a decreasing Ce-valence.²⁷ The replacement of Ni by Pd, Cu, Au drives the Ce from an intermediate valence (IV) to a non-IV ground state.^{21–27} Probably because of the non-existence of compounds “ LaZn_2Si_2 ” and “ CeZn_2Si_2 ”, the corresponding isopleths $\{\text{La,Ce}\}\text{Ni}_2\text{Si}_2$ – $\{\text{La,Ce}\}\text{Zn}_2\text{Si}_2$ have not attracted interest.

Therefore the present work intends to provide detailed information on the phase equilibria, crystal structures and physical properties of the novel BaAl_4 -derivative phases in the systems $\{\text{La,Ce}\}$ -Ni-Si as well as in the isopleths $\{\text{La,Ce}\}\text{Ni}_2\text{Si}_2$ – $\{\text{La,Ce}\}\text{Zn}_2\text{Si}_2$.

2. Experimental

Samples were prepared from cerium ingots (Alfa Aesar, purity >99.9 mass%), lanthanum ingots (Auer Remy, 99.9 mass%), zinc granules (Alfa Aesar, >99.9 mass%), Ni foil (Alfa Aesar, >99.8 mass%) and silicon pieces (Alfa Aesar, 6N). Zinc drops were purified in an evacuated quartz tube by heating them at ~ 750 °C, below the boiling point of Zn (907 °C). Cerium and lanthanum ingots were mechanically surface cleaned before use.

Polycrystalline bulk samples for the analysis of the quaternary isopleths $\{\text{La,Ce}\}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$ and for physical property studies were prepared from intimate blends of powders of arc melted master alloys $\{\text{La,Ce}\}\text{Ni}_{2-x}\text{Si}_2$ (various x ; powdered under cyclohexane) and fine Zn-filings in appropriate compositional ratios. These blends were cold compacted in a steel die without lubricants, vacuum-sealed in quartz tubes, heated from 420 °C to 800 °C at the rate of 1 °C min^{-1} and then annealed at this temperature for 7 days. After water quenching the samples were re-powderized (under cyclohexane) in order to ensure homogeneity. The samples were loaded into 10 mm diameter graphite dies for hot pressing under Ar in a uniaxial hot press system (HP W 200/250-2200-200-KS) at 800 °C for 1 hour employing a pressure of 56 MPa. Densities of the samples have been calculated from their dimensions and masses after removing a 0.5 mm thick surface layer (grinding with SiC paper).

X-ray powder diffraction data were collected from each alloy employing a Guinier–Huber image plate system with monochromatic $\text{CuK}\alpha_1$ radiation ($8^\circ < 2\theta < 100^\circ$). Precise lattice parameters were calculated by least squares fits to the indexed 2θ values calibrated with Ge as the internal standard ($a_{\text{Ge}} = 0.565791$ nm). Quantitative Rietveld refinements of the X-ray powder diffraction data were performed with the FULLPROF program.²⁸

Single crystals from the systems $\{\text{La,Ce}\}$ -Ni-Si were picked from crushed reguli. Quaternary single crystals were grown from Zn flux starting from a cold compacted pellet ($\text{Ce}_2\text{Ni}_4\text{Si}_8 + \text{Zn-filings} = \text{Ce}_2\text{Ni}_4\text{Si}_8\text{Zn}_{86}$ (in at.%)), which was heated to 900 °C at the rate of 1 °C min^{-1} and then cooled to 800 °C at the same rate. After annealing for 4 days at this temperature the sample was subsequently quenched in water and then boiled with 15% aqueous solution of HCl in a water bath in order to dissolve the extra Zn. Crystals were carefully washed with distilled water and dried.

Inspections on an AXS-GADDS texture goniometer assured the high crystal quality, unit cell dimensions and Laue symmetry of the specimens prior to the X-ray intensity data collections on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.071069$ nm). Orientation matrices and unit cell parameters were derived using the program DENZO.²⁹ Besides the general treatment of absorption effects using the multi-scan technique (redundancy of integrated reflections >8) 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 and were refined with the SHELXL-97 program³⁰ within the Windows version WinGX.³¹

After the reaction during annealing the samples had almost a powder-like consistency, too soft to be polished by standard procedures. This problem was overcome by casting the sample powder along with conducting glue into a cylindrical mould of ~ 5 mm diameter. After hardening several of the powder cylinders were hot compacted in conductive resin and were ground and polished under glycerine instead of water in order to avoid oxidation of the samples. Microstructures and compositions were examined by light optical microscopy (LOM) and scanning electron microscopy (SEM) *via* Electron Probe Micro-Analyses (EPMA) on a Zeiss Supra 55 VP equipped with an EDX system operated at 20 kV.

Physical property measurements (magnetic susceptibility, electrical resistivity, and specific heat) were performed on the hot pressed samples with methods described in our previous publications, *e.g.* ref. 32.

3. Results and discussion

3.1. The BaAl_4 -type derivative phases in the systems La-Ni-Si and Ce-Ni-Si

The system Ce-Ni-Si relevant to this work was investigated by Bodak and coworkers.^{7,8} The isothermal section of La-Ni-Si at 400 °C was established much later by Zhou *et al.*³³ Both



systems contain a compound $\{\text{La,Ce}\}\text{Ni}_2\text{Si}_2$ which was reported to crystallize in the ThCr_2Si_2 type³⁴ with a practically negligible homogeneity range. A thorough check on these findings prompted us to prepare samples with the nominal composition $\{\text{La,Ce}\}_{20}\text{Ni}_{40}\text{Si}_{40}$ (in at.%). As-cast alloys as well as samples annealed at 800 °C for 4 days revealed nearly a single phase condition with the ThCr_2Si_2 type, thus suggesting a congruent or a degenerate peritectic formation of these phases, and furthermore confirmed the crystal structure data from Bodak *et al.*³⁴ Levin *et al.*²⁷ studied the homogeneity range of CeNi_2Si_2 (ThCr_2Si_2 -type) at a relatively low temperature of 727 °C and discovered a rather large homogeneity range of 8 at.% ranging from 36 to 44 at.% Si. Our reinvestigation (EPMA)

of the phase relations around CeNi_2Si_2 at 800 °C reveals a smaller homogeneity range for the ThCr_2Si_2 type of ~4 at.% from 38.3 to 42.3 at.% Si. Our lattice parameters (see Fig. 1), however, agree well with the result of Levin *et al.*²⁷ In general the Ni/Si substitution does not affect the *a*-axis much, however one can see that the *c*-axis decreases almost linearly with increasing Ni content. In an attempt to investigate the crystal structure of CeNi_4Si ³⁵ we discovered a Ni-rich phase $\text{CeNi}_{2+x}\text{Si}_{2-x}$ ($x \sim 0.3$). EPM analysis of an as-cast alloy with a slightly higher Ni-content ($\text{Ce}_{20}\text{Ni}_{43}\text{Si}_{37}$) showed primary crystallization of $\text{Ce}_{20}\text{Ni}_{41}\text{Si}_{39}$ followed by a peritectic-like formation of a thin layer of $\text{Ce}_{20}\text{Ni}_{46}\text{Si}_{34}$ (see Fig. 2). The remaining liquid crystallized as CeNi_4Si and a novel phase

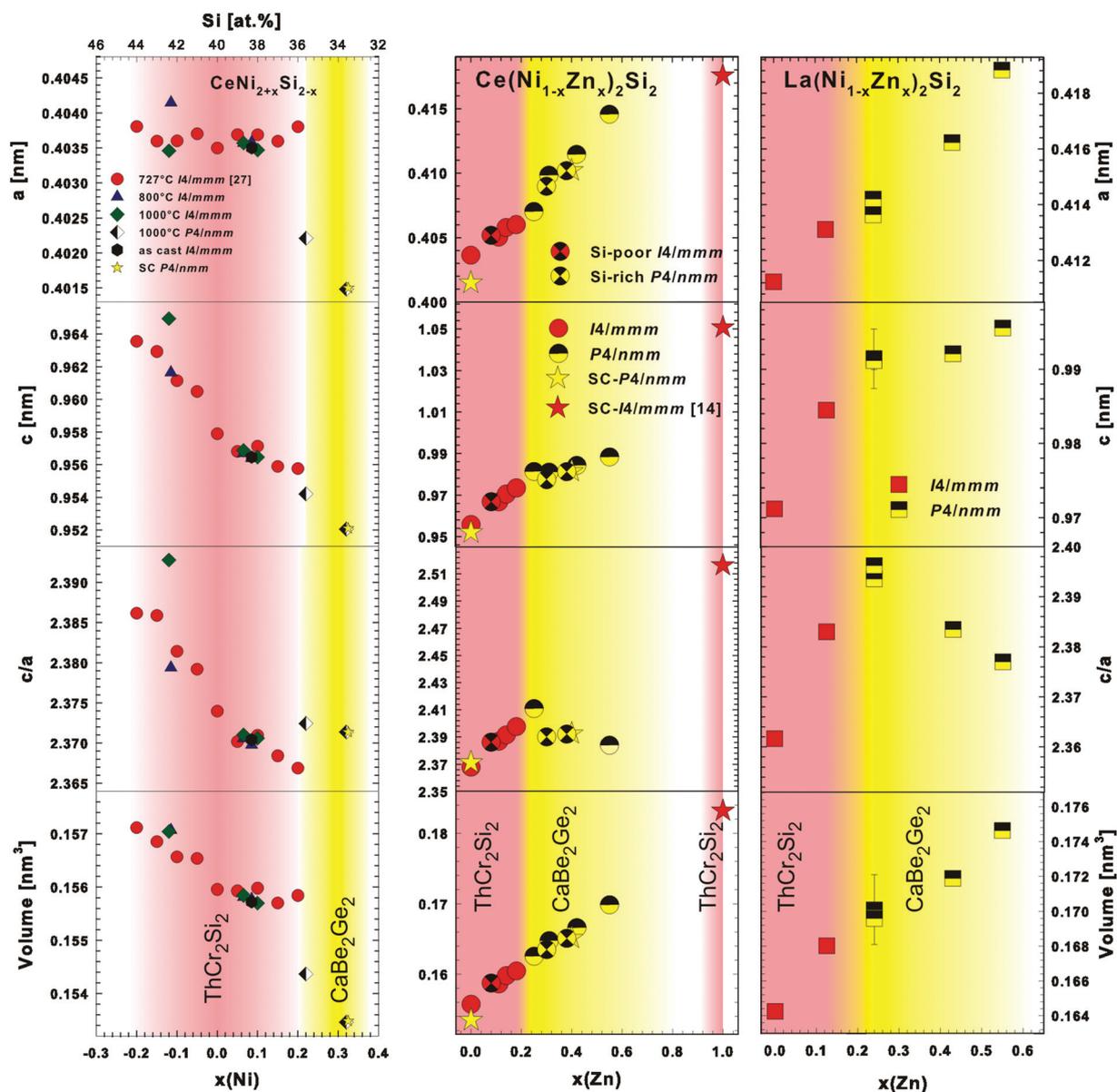


Fig. 1 Left column: compositional dependence of lattice parameters of $\text{CeNi}_{2+x}\text{Si}_{2-x}$. Right two columns: unit cell parameters vs. Zn-content in the BaAl_4 -type phases $\{\text{La,Ce}\}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$ (annealed at 800 °C) revealing a transition from the body centred to primitive symmetry as a consequence of Ni/Zn substitution (compositions from EPMA).



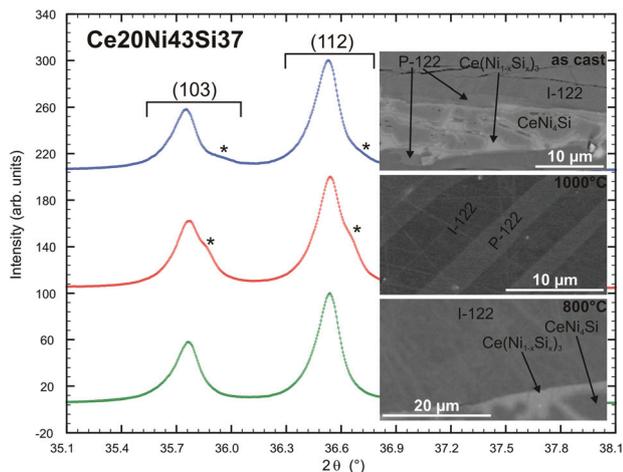


Fig. 2 The strongest $BaAl_4$ -type reflections and the micrograph of the $Ce_{20}Ni_{43}Si_{37}$ alloy in as-cast conditions, annealed at 1000 °C and at 800 °C. The asterisks represent the $CaBe_2Ge_2$ -type reflections (see section 3.1.1 for detailed explanation).

$Ce(Ni_{1-x}Si_x)_3$. Besides the main reflections arising from the $ThCr_2Si_2$ -type ($Ce_{20}Ni_{41}Si_{39}$), the X-ray powder pattern revealed a set of weak satellite reflections that correspond to a tetragonal lattice similar to $ThCr_2Si_2$ with smaller unit cell dimensions. At this point, it was not clear whether the Ni-rich phase $Ce_{20}Ni_{46}Si_{34}$ represents a new phase or the Ni-rich end of a homogeneity range of $ThCr_2Si_2$ -type $CeNi_2Si_2$. The amount of the Ni-rich phase $Ce_{20}Ni_{46}Si_{34}$ in the as-cast state increases as the alloy composition shifts towards the Ni-rich side at a constant Ce content, where at an alloy composition of $Ce_{20}Ni_{60}Si_{20}$ a single crystal suitable for X-ray structure analysis (see below) was selected.

3.1.1. The crystal structure of $CeNi_{2+x}Si_{2-x}$, $x = 0.33$ with the $CaBe_2Ge_2$ -type. A single crystal, extracted from an as-cast alloy with a nominal composition of $Ce_{20}Ni_{60}Si_{20}$ revealed unit cell parameters ($a = 0.40150(2)$ and $c = 0.95210(2)$ nm) consistent at first glance with a body centred $ThCr_2Si_2$ type, but additional weak reflections could be satisfactorily indexed on the basis of a primitive Bravais cell. Systematic extinctions suggested the space group type $P4/nmm$ for the highest crystal symmetry. Direct methods indicated Ce, Ni, Si atoms in positions typical for the $CaBe_2Ge_2$ -type, where the electropositive atom occupies the $2c$ site ($1/4, 1/4, \sim 0.75$), the transition metal atoms occupy a $2c$ site ($1/4, 1/4, \sim 0.1$) and a $2b$ site ($3/4, 1/4, 1/2$), and the tetrel atoms occupy the sites $2c$ ($1/4, 1/4, \sim 0.35$) and $2a$ ($3/4, 1/4, 0$). Refinement with anisotropic atom displacement parameters (ADPs) converged to $R_F = 0.0163$ and residual electron densities smaller than $\pm 1.53 e^- \text{ \AA}^{-3}$ with fully occupied metal sites but for a statistical occupation of $0.33Ni + 0.67Si$ in site $2a$ of $P4/nmm$, which was fixed after the EPMA value. Thus, a structure formula $CeNi_{2+x}Si_{2-x}$, $x = 0.33$, results, which corresponds to the composition $Ce_{20}Ni_{46.5}Si_{33.5}$ close to the $ThCr_2Si_2$ -type phase. Crystal data for $CeNi_{2+x}Si_{2-x}$ along with the ADPs are summarized in Table 1. Although attempts to refine the Ni/Si ratio at the $2a$ site yield a lower R_F of 0.011 and a residual electron density less than $0.87 e^- \text{ \AA}^{-3}$, the

resulting Ni content ($0.22(1)Ni + 0.78Si$) corresponds to the composition $Ce_{20}Ni_{44.5}Si_{35.5}$ deviating significantly from the EPMA derived composition. Thus we prefer the EPMA value and the corresponding formula $CeNi_{2+x}Si_{2-x}$, $x = 0.33$.

It is worth mentioning that although the primitive reflections in $CaBe_2Ge_2$ -type $CeNi_{2+x}Si_{2-x}$ are relatively small, they are still visible in the single-phase powder diffraction spectra. Interestingly, neither a Ni-rich composition nor primitive reflections could be observed at 800 °C in alloys at the Ni-rich side of the 1 : 2 : 2 stoichiometry. This strongly suggests that the primitive $CaBe_2Ge_2$ -type phase $CeNi_{2+x}Si_{2-x}$ is a high temperature phase. Alloys at the Ni-rich side of 1 : 2 : 2 annealed at 1000 °C indeed show the Ni-rich composition $Ce_{20}Ni_{46}Si_{34}$ in equilibrium with $CeNi_4Si$ and $Ce(Ni_{1-x}Si_x)_3$. Consequently, the X-ray powder diffraction spectra show two sets of $BaAl_4$ -type reflections (see Fig. 2). As the sample is multiphase, it is rather difficult to identify the primitive peaks, however, the lattice parameters of one of the $BaAl_4$ derivative phases show a shorter c -axis, which is closer to the value of $CeNi_{2+x}Si_{2-x}$ with the primitive $CaBe_2Ge_2$ -type as obtained from the single crystal data. The other set of $BaAl_4$ derivative reflections give similar unit cell parameters as for $CeNi_2Si_2$ with the $ThCr_2Si_2$ -type. These observations, together with the fact that a single crystal was obtained from an as-cast alloy led us to conclude that $CeNi_{2+x}Si_{2-x}$ with the primitive $CaBe_2Ge_2$ -type is a high temperature phase ($1000 \text{ °C} \leq T_{\text{stability}} < 1615 \text{ °C}$).³⁶

Polymorphism between $ThCr_2Si_2$ - and $CaBe_2Ge_2$ -types is often encountered in various systems, particularly for ternary rare earth silicides containing Ir and Pt.¹² In some cases, *e.g.* in the La–Ir–Si system,³⁷ the $CaBe_2Ge_2$ -type is the high temperature form, whilst the $ThCr_2Si_2$ -type is stable at lower temperatures. Therefore $CeNi_{2+x}Si_{2-x}$ with the primitive $CaBe_2Ge_2$ -type is hitherto the first example of $ThCr_2Si_2$ – $CaBe_2Ge_2$ polymorphism found in ternary rare earth silicides with 3d transition metal elements. The slight flattening of the unit cell, *i.e.* the shorter length of the c -axis observed in $CeNi_{2+x}Si_{2-x}$ ($CaBe_2Ge_2$ -type), is also commonly found in many systems exhibiting such polymorphism.¹²

Besides the temperature effect, the substitution of Si by Ni at the $2a$ -site may act as a driving force for the structural change from a body centred to a primitive atom arrangement in terms of a group–subgroup relation. This idea comes from the fact that an alloy with stoichiometric composition $CeNi_2Si_2$ does not show any changes in the powder diffraction spectra in the as-cast state, and after annealing at 1000 °C for 4 days. An example of structural evolution at a constant temperature can be found in the Sr–Au–Ge system³⁸ where at 700 °C, increasing the Ge content in $SrAu_{2-x}Ge_{2+x}$ led to a series of structural changes from the $ThCr_2Si_2$ -type to the $BaCu_2Sb_2$ -type and finally to the $CaBe_2Ge_2$ -type, where all structure types are variants of the $BaAl_4$ -type.

3.2. The quaternary solution phases $La(Ni_{1-x}Zn_x)_2Si_2$ and $Ce(Ni_{1-x}Zn_x)_2Si_2$

As neither stoichiometric $CeZn_2Si_2$ nor off-stoichiometric $CeZn_{2+x}Si_{2-x}$ ($x \sim 0.5$) exists in the Ce–Zn–Si system at 800 °C,



Table 1 X-ray single crystal data^a for CeNi_{2+x}Si_{2-x}, *x* = 0.33 and X-ray powder diffraction data for CeNi₂Si₂ and LaNi₂Si₂ (samples annealed at 800 °C)

Compound	CeNi _{2+x} Si _{2-x} , <i>x</i> = 0.33	CeNi ₂ Si ₂	LaNi ₂ Si ₂
EMPA composition [at.%]	Ce _{20.1} Ni _{46.5} Si _{33.4}	Ce _{20.4} Ni ₃₈ Si _{41.6}	La _{20.3} Ni _{37.9} Si _{41.8}
Refinement composition [at.%]	Ce ₂₀ Ni _{46.5} Si _{33.5}	Ce _{20.0} Ni _{40.0} Si ₄₀	La _{20.4} Ni _{38.8} Si _{40.8}
Space group	<i>P4/nmm</i> ; no. 129, origin choice 2	<i>I4/mmm</i> , no. 139	<i>I4/mmm</i> , no. 139
Structure type	CaBe ₂ Ge ₂	ThCr ₂ Si ₂	ThCr ₂ Si ₂
Data collection	Nonius Kappa CCD	Guinier image plate	Guinier image plate
Radiation	MoK _α	CuK _{α1}	CuK _{α1}
θ range	2.14 < θ < 36.16	10 < 2 θ < 100	10 < 2 θ < 100
Crystal size [μ m]	40 × 50 × 50	—	—
<i>a</i> [nm]	0.40150(2)	0.40363(1)	0.41124(1)
<i>c</i> [nm]	0.95210(2)	0.95758(1)	0.97119(1)
Reflections in refinement	226 F_o > 4 $\sigma(F_o)$ of 262	38	39
<i>Z</i> , volume [nm ³]	2, 0.1535(1)	2, 0.156(1)	2, 0.164(1)
Number of variables	15	22	22
$R_F = \sum F_o - F_c / \sum F_o$	0.0163	$R_F = 0.024$	$R_F = 0.028$
R_{int}	0.0107	$R_I = 0.024$	$R_I = 0.028$
GOF	1.195	$\chi^2 = 1.72$	$\chi^2 = 3.09$
Extinction (Zachariasen)	0.044(2)	—	—
RE	Ce in 2c (1/4, 1/4, <i>z</i>); <i>z</i> = 0.75072(4);	Ce in 2a (0, 0, 0)	La in 2a (0, 0, 0)
Occ.; B_{iso} .	1.00(1); —	1.00(1); 0.14(2)	1.00(1); 0.95(2)
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0057(1); 0.0068(2)	—	—
Ni	Ni1 in 2c (1/4, 1/4, <i>z</i>); <i>z</i> = 0.1264(1);	Ni in 4d (0, 1/2, 1/4)	Ni in 4d (0, 1/2, 1/4)
Occ.; B_{iso} .	1.00(1); —	1.00(2); 0.60(5)	0.95(2); 0.19(3)
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0134(3); 0.0120(4)	—	—
Ni; Occ.	Ni2 in 2b (3/4, 1/4, 1/2); 1.00(1)	—	—
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0085(2); 0.0074(3)	—	—
Si	Si1 in 2c (1/4, 1/4, <i>z</i>);	Si in 4e (0, 0, <i>z</i>);	Si in 4e (0, 0, <i>z</i>);
Occ.; B_{iso} .	<i>z</i> = 0.3717(2);	<i>z</i> = 0.3804(3);	<i>z</i> = 0.3684(2);
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	1.00(1); —	1.00(1); 0.26(7)	1.00(1); 0.49(5)
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0056(4); 0.0077(7)	—	—
<i>M</i>	<i>M</i> in 2a (3/4, 1/4, 0);	—	—
Occ.	0.33(–) Ni3 + 0.67(–) Si2 ^c	—	—
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0163(4); 0.0102(6)	—	—
Residual electron density; max; min in [electrons/nm ³] × 1000	1.18; –1.53	—	—

^a Crystal structure data are standardized using the program Structure Tidy.³⁹ ^b Anisotropic atomic displacement parameters U_{ij} in [10^{–2} nm²].

^c Fixed after EPMA.

it is interesting to investigate the extent of solubility of Zn in the CeNi₂Si₂ phase at 800 °C. Stoichiometric body centred CeNi₂Si₂ is found to substitute for Ni up to 18% Zn, *i.e.* Ce(Ni_{1-x}Zn_x)₂Si₂, *x* = 0.18. The substitution of Zn for Ni is also reflected in the gradual increase of the unit cell parameters (Fig. 1). For further Zn substitution the Bravais lattice changes from body centred to primitive, as indicated by the appearance of additional weak reflections that violate the systematic extinction of a body-centred cell. The samples remain single phase up to *x* = 0.55 at 800 °C. On further Zn substitution the samples became multiphase, indicating that the solubility limit has been reached.

Since the primitive CaBe₂Ge₂-type phase also exists in the Ce–Ni–Si end member system at a high temperature in the Ni-rich side, and the body centred ThCr₂Si₂-type phase extends slightly to both the Ni- and Si-rich sides at 800 °C, we suspected that a slight deviation from the stoichiometric 1 : 2 : 2 composition could stabilize/destabilize one of these structure types with the incorporation of Zn. Such a situation is often found in various systems, *e.g.* in the Ce–Zn–Si system at 800 °C¹³ or Ce–Ag–Si at 500 °C⁴⁰ where two compositional polymorphic modifications of CeSi₂ with the α -ThSi₂ type and the α -GdSi₂ type dissolve transition metal elements, however,

the α -GdSi₂-based solid solutions end prematurely while the α -ThSi₂-based solid solutions extend further up to ~20 at.% transition metal content.

In order to check the possibility of such a scenario we prepared several alloys with off-stoichiometric compositions. Although the nominal compositions deviate far (~5 at.%) from the 1 : 2 : 2 composition, only a small variation (± 1 at.%) in the homogeneity range could be observed in the quaternary 122 phase. A variation of unit cell parameters of alloys in both the Si-poor and rich parts of the 122 stoichiometry shows good agreement with those from the stoichiometric 122 alloys. This suggests that there is no parallel solid solution running beside the one shown in Fig. 1.

3.2.1. The crystal structures of {La,Ce}(Ni_{1-x}Zn_x)₂Si₂ with the CaBe₂Ge₂-type. In order to get details on the primitive unit cell, a single crystal has been selected from the flux residuals of an alloy with the composition Ce₂Ni₄Si₈Zn₈₆ (in at.%), slowly cooled from 900 °C. A SEM analysis performed directly on the crystals separated from the flux (shown in Fig. 3), defined the composition as Ce_{19.4}Ni_{25.3}Zn_{16.1}Si_{39.2} (at.%). Unit cell, systematic extinctions (indicating *P4/nmm* as the space group type of highest symmetry) as well as the X-ray intensity pattern confirmed a structure solution in terms of



the CaBe_2Ge_2 -type. It should be mentioned, however, that six reflections with $I_{\text{obs}} > 4\sigma(I)$ violated the space group extinction rules: (010), (210), (210), (230), (230) and (340). In comparison with the highest intensity observed (12 000 counts), the (210),

(210), (230), (230) reflection intensities are below 2 counts and can be disregarded, whereas the (010) intensity (below 7 counts) may stem from a 'Renninger enhancement' effect.

Interestingly, the site occupation of the transition metal and tetrel atoms is exchanged, *i.e.* the tetrel atoms occupy sites 2c (1/4, 1/4, ~0.1) and 2b, whilst the transition metal atoms occupy sites 2c (1/4, 1/4, ~0.35) and 2a. This site exchange configuration gives rise to the intensity of the primitive reflections, therefore the CaBe_2Ge_2 -type phases can be identified easily in the quaternary system by X-ray powder diffraction.

Although the small differences in the X-ray scattering power of Ni and Zn make it difficult to unambiguously differentiate between these atom types, it was possible to define the site occupation of Zn by analyzing site ADPs. As the ADPs of the two Si sites did not show any anomalies, it was certain that Zn occupied one or both of the Ni sites. Among all remaining combinations of Zn site occupations, the lowest R_F was found when Zn substituted Ni at the 2a site. Although it was possible to refine the Ni/Zn occupancy at this site, the resulting value (0.48(3)Ni + 0.52Zn) deviates far from the value obtained by EPMA: 0.22Ni + 0.78Zn. Therefore, in the final refinement the Ni/Zn occupancy was fixed according to EPMA, resulting in the structure formula $\text{Ce}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$, $x = 0.39$ (*i.e.* $\text{Ce}_{20}\text{Ni}_{24.4}\text{Zn}_{15.6}\text{Si}_{40}$).

The final refinement converged to $R_F = 0.0134$ and residual electron densities were less than ± 1.48 electrons per \AA^3 for three metal and two Si positions with a Wyckoff sequence

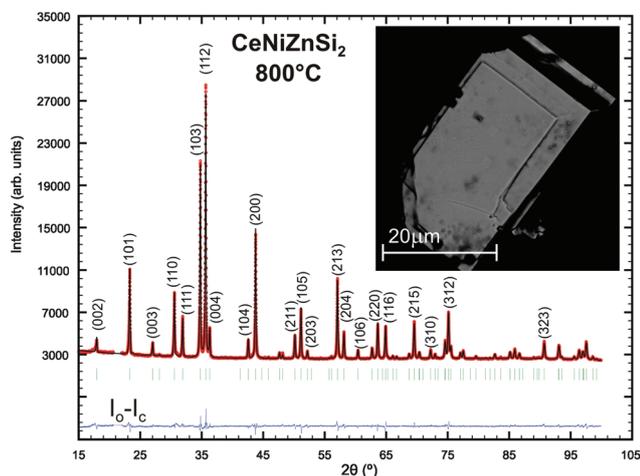


Fig. 3 Rietveld refinement pattern with hkl indexes of the alloy with the composition $\text{Ce}_{20}\text{Ni}_{20}\text{Zn}_{20}\text{Si}_{40}$ at.% showing $\text{Ce}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$ ($x = 0.39$) with CaBe_2Ge_2 -type (space group $P4/nmm$) and the micrograph of the single crystal obtained from the Zn flux (sample $\text{Ce}_2\text{Ni}_4\text{Si}_8\text{Zn}_{86}$ at.%). Note that the peak at $2\theta \sim 22^\circ$ is from the sample carrier foil.

Table 2 X-ray single crystal data for $\text{Ce}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$, $x = 0.39$ and Rietveld XRPD data for $\text{La}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$; $x = 0.44$ (space group $P4/nmm$; No. 129, origin at center)^a

Compound	$\text{Ce}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$, $x = 0.39$	$\text{La}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$, $x = 0.44$
EMPA composition [at.%]	$\text{Ce}_{19.4}\text{Ni}_{25.3}\text{Zn}_{16.1}\text{Si}_{39.2}$	$\text{La}_{19.9}\text{Ni}_{22.3}\text{Zn}_{17.2}\text{Si}_{40.7}$
Refinement composition [at.%]	$\text{Ce}_{20}\text{Ni}_{24.4}\text{Zn}_{15.6}\text{Si}_{40}$	$\text{La}_{20}\text{Ni}_{22.6}\text{Zn}_{17.4}\text{Si}_{40}$
Structure type	CaBe_2Ge_2	CaBe_2Ge_2
Data collection	Nonius Kappa CCD	Guinier-Huber IP
Radiation	$\text{MoK}\alpha$	$\text{CuK}\alpha_1$
θ range	$2.08 < \theta < 36.05$	$8 < 2\theta < 100$
Crystal size [μm]	$40 \times 50 \times 50$	—
a [nm]	0.41022(1)	0.41680(6) ^c
c [nm]	0.98146(4)	0.99213(7) ^c
Reflections in refinement	$266F_o > 4\sigma(F_o)$ of 272	72
Mosaicity	0.65	—
Z , density [gm cm^{-3}]	2, 6.44	2, 6.022
Number of variables	15	26
$R_F = \sum F_o - F_c / \sum F_o$	0.0134	$R_F = 0.043$
R_{int}	0.0135	$R_I = 0.025$
GOF	1.153	$\chi^2 = 2.78$
Extinction (Zachariasen)	0.024(1)	$R_w = 2.75$
RE in 2c (1/4, 1/4, z); Occ.	$z = 0.73977(3); 1.00(1)$	$z = 0.73833(7); 1.00(1)$
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0050(1); 0.0058(1)	$B_{\text{iso}} = 0.28(1)$
M in 2a (3/4, 1/4, 0); Occ.	$0.78(-)\text{Zn}1 + 0.22(-)\text{Ni}^d$	$0.87(-)\text{Zn}1 + 0.13(-)\text{Ni}1^d$
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0099(2); 0.0070(2)	$B_{\text{iso}} = 0.26(3)$
Ni2 in 2c (1/4, 1/4, z); Occ.	$z = 0.38514(6); 1.00(1)$	$z = 0.3883(1); 1.00(1)$
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0063(2); 0.0071(3)	$B_{\text{iso}} = 0.36(4)$
Si1 in 2b (3/4, 1/4, 1/2); Occ.	1.00(1)	1.00(1)
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0061(3); 0.0060(5)	$B_{\text{iso}} = 0.54(6)$
Si2 in 2c (1/4, 1/4, z); Occ.	$z = 0.1474(2); 1.00(1)$	$z = 0.1537(3); 1.00(1)$
$U_{11}^b = U_{22}; U_{33}; U_{23} = U_{13} = U_{12} = 0$	0.0106(4); 0.0096(6)	$B_{\text{iso}} = 0.68(7)$
Residual electron density; max; min in [$\text{electrons per nm}^3$] $\times 1000$	1.48; -0.97	

^a Crystal structure data are standardized using the program Structure Tidy.³⁹ ^b Anisotropic atomic displacement parameters U_{ij} in [10^{-2} nm^2]. ^c Ge standard. ^d Fixed after EPMA.



abc³. Crystal data for Ce(Ni_{1-x}Zn_x)₂Si₂, $x = 0.39$, with the CaBe₂Ge₂-type along with the ADPs are summarized in Table 2; interatomic distances are presented in Table 3; coordination polyhedra for all atom sites and a three-dimensional view on the crystal structure are presented in Fig. I of the ESI.†

The comparison of the structures of CeNi_{2+x}Si_{2-x} and Ce(Ni, Zn)₂Si₂ in Fig. 4 clearly reveals an atom site exchange in the tetrahedron-layers sandwiching the Ce-atoms: Ni- and Si-layers are exchanged. However, it is interesting to see that the random substitution of Ni/Si and Ni/Zn always occurs at the same site (2a site).

Several examples of such site exchange variants of the CaBe₂Ge₂-structure type can be found in the literature, particularly for ternary stannides and antimonides, e.g. Ce{Ni,Cu,Pd, Ir,Pt}₂Sn₂.¹² For ternary silicides, only the high temperature modification LaIr₂Si₂³⁷ is known to exhibit such a site exchange arrangement. A similar situation is also encountered in quaternary Ce(Cu_{1-x}Ag_x)_{2-y}Sb₂.⁴¹

In contrast to primitive Ce(Ni_{1-x}Zn_x)₂Si₂, where the occupation of Zn/Si sites is inverted with respect to primitive

CeNi_{2+x}Si_{2-x}, body centred Ce(Ni_{1-x}Zn_x)₂Si₂ as well as off-stoichiometric CeZn_{2+x}Si_{2-x} ($x \sim 0.5$) do not exhibit such a site exchange.

The Rietveld refinement performed on single-phase body centred Ce(Ni_{1-x}Zn_x)₂Si₂ ($x = 0.18$) shows that Zn substitutes Ni at the 4d site, while the 4e site remains fully occupied by Si. In the case of ternary CeZn_{2+x}Si_{2-x} ($x = 0.5$), due to the higher Zn-content, Zn and Si share the 4e site with a ratio of 3 : 7 whereas the 4d site is fully occupied by Zn.¹⁴ A detailed group-subgroup diagram relating the parent BaAl₄ structure to the ThCr₂Si₂ and CaBe₂Ge₂ for the various phases in the Ce–Ni–Zn–Si system is presented in terms of a Bärnighausen tree, depicted in Fig. II of the ESI.†

In analogy to the section Ce(Ni_{1-x}Zn_x)₂Si₂, phase relations have also been explored for the isopleth La(Ni_{1-x}Zn_x)₂Si₂ (see Fig. 1). Combined EPM and X-ray powder intensity data analyses revealed a solid solution with the ThCr₂Si₂-type for $0 \leq x \leq 0.125$, followed by a change to a primitive tetragonal symmetry typical for the CaBe₂Ge₂-type for $0.25 \leq x \leq 0.55$. The solid solution terminates at $x = 0.55$ as for higher Zn-concentrations multiphase X-ray spectra were observed. Rietveld refinement data for La(Ni_{0.56}Zn_{0.44})₂Si₂ are summarized in Table 2 and Fig. 5.

Table 3 Interatomic distances for Ce(Ni_{1-x}Zn_x)₂Si₂, $x = 0.39$ (*P4/nmm*; no. 129). Standard deviations <0.00007

Atom 1	Atom 2	$d_{1,2}$ [nm]
Ce1	Si2 (4×)	0.31047
	Si1 (4×)	0.31217
	Ni2 (4×)	0.31491
	M (4×)	0.32757
M	Si2 (4×)	0.25102
	M (4×)	0.29007
	Ce1 (4×)	0.32757
	Ni2 (1×)	0.23329
Ni2	Si1 (4×)	0.23405
	Ce1 (4×)	0.31491
	Si1 (4×)	0.23405
	Si1 (4×)	0.29007
Si1	Ce1 (4×)	0.31217
	Ni2 (1×)	0.23329
	M (4×)	0.25102
	Ce1 (4×)	0.31047

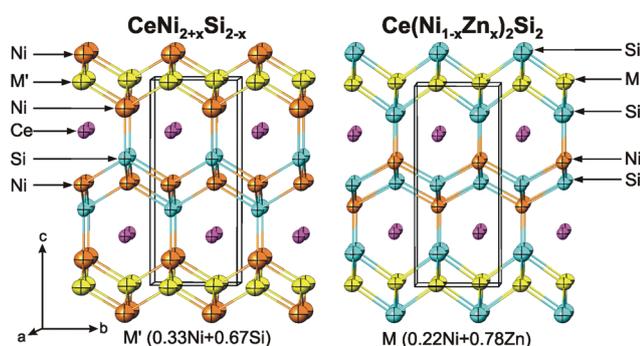


Fig. 4 Atom site distribution for ternary CeNi_{2+x}Si_{2-x} (CaBe₂Ge₂-type; left) and atom site exchange arrangement in isopointal quaternary Ce(Ni_{1-x}Zn_x)₂Si₂ (CaBe₂Ge₂-type; right). Atoms are presented with ADPs from single crystal refinement.

3.3. Physical properties of La(Ni_{1-x}Zn_x)₂Si₂ and Ce(Ni_{1-x}Zn_x)₂Si₂

Two samples, {La,Ce}(Ni,Zn)₂Si₂ were selected from the solid solution to check on the physical properties of this series.

3.3.1. La(Ni_{1-x}Zn_x)₂Si₂. La(Ni_{1-x}Zn_x)₂Si₂, $x = 0.44$ was studied down to 400 mK, but no phase transition, indicating e.g., superconductivity was observed. The temperature dependent heat capacity, C_p , of La(Ni_{0.56}Zn_{0.44})₂Si₂ is shown in Fig. 6(a) and plotted as C_p/T vs. T . Unexpectedly, $C_p/T(T)$ exhibits a minimum around 2.5 K below which the electronic con-

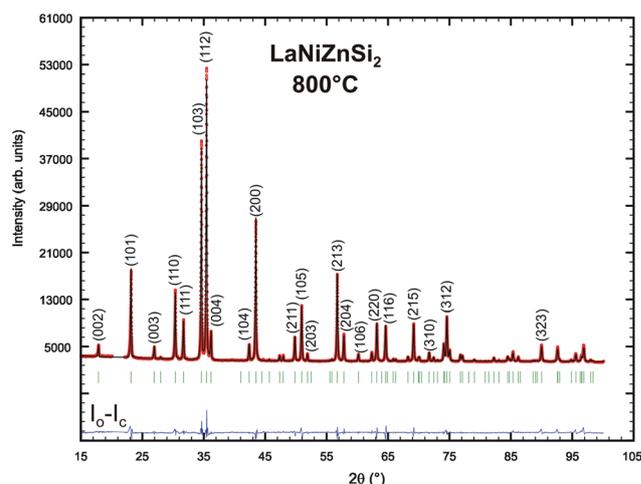


Fig. 5 Rietveld refinement pattern with hkl indexes of single phase La(Ni_{1-x}Zn_x)₂Si₂; $x = 0.44$ (CaBe₂Ge₂-type, space group *P4/nmm*) from the alloy with nominal composition La₂₀Ni₂₀Zn₂₀Si₄₀ at.%, annealed at 800 °C.



tribution tends towards $20 \text{ mJ mol}^{-1} \text{ K}^{-2}$ for $T \sim 0$, a value larger than what is likely for simple intermetallic compounds. The overall shape, however, reminds one of spin fluctuation systems like YCo_2 or UAl_2 .⁴² In order to prove such a proposition, the standard spin fluctuation ansatz, $C_p(T) = \gamma T + \beta T^3 + \delta T^3 \ln(T/T^*)$ is employed to the experimental data, revealing excellent agreement for $\gamma = 13 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $T^* = 8.7 \text{ K}$ (solid line, inset Fig. 6(a)). This agreement would suggest spin fluctuations in the nearly localized regime present in $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$. The fit parameter $\beta = 0.13 \text{ mJ mol}^{-1} \text{ K}^{-4}$ allows the estimation of a Debye temperature of about 460 K, referring to the rather stiff lattice of this system.

The resistivity, ρ , of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ was studied within the temperature range 4.2–300 K. At elevated temperatures ($T > 100 \text{ K}$) $\rho(T)$ behaves metallic-like. The almost linear slope of $\rho(T)$ refers predominantly to electron–phonon interactions. A shallow minimum is observed at about 25 K and below this temperature the resistivity increases with decreasing temperature (see Fig. 6(b)). A plot of the resistivity on a logarithmic temperature scale (inset, Fig. 6(b)) for various externally applied magnetic fields reveals, unexpectedly a logarithmic behaviour, indicating Kondo-type interactions, which might be attributed to a small amount of uncompensated Ni spins. These features were reproduced in several independently prepared samples and comply with the enhanced value of the Sommerfeld constant deduced from the specific heat experiment.

3.3.2. $\text{Ce}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$. Fig. 7–9 reveal experimental results regarding the magnetic properties of $\text{Ce}(\text{Ni}_{1-x}\text{Zn}_x)_2\text{Si}_2$, $x = 0.39$. Ce in its atomistic form possesses one electron in the 4f shell, constituting the $4f^1$ electronic configuration (EC) and thus carries a total angular momentum $j = 5/2$. This gives rise to a non-vanishing magnetic moment. In the case of cerium and ytterbium compounds, however, partial hybridisation with the conduction electron system is possible. Its degree depends

on the compound's specific electronic structure and in solid solutions on the local chemical environment, *i.e.*, Ce moments varying with the Ni/Zn random occupation in the title compound.

A simple proof of whether or not this EC is preserved in the solid state of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ can be obtained from temperature dependent magnetic measurements. The inverse magnetic susceptibility at 3 T is shown in Fig. 7(a). Phase transitions above 2.5 K are not obtained from this measurement. A quantitative description of the high temperature magnetic susceptibility (50–300 K) can be made by applying a modified Curie Weiss law, revealing a temperature independent Pauli susceptibility ($\chi_0 = 3.9 \times 10^{-4} \text{ emu mol}^{-1}$), an effective magnetic moment, which is related to the Curie constant ($\mu_{\text{eff}} = 2.20\mu_{\text{B}}/\text{Ce}$) and a paramagnetic Curie temperature ($\theta_{\text{p}} = -35 \text{ K}$) from a least squares fit of this model to the experimental data (solid line, Fig. 7(a)).

A negative paramagnetic Curie temperature, in general, refers to antiferromagnetic interactions between conduction electrons and the almost localized Ce 4f electrons. Crystalline electric field (CEF) effects, lifting the $2j + 1 = 6$ fold degenerate ground state, as well as the Kondo effect, modify, however, the absolute value of θ_{p} . The effective magnetic moment observed from the Curie Weiss law is below that ($2.54\mu_{\text{B}}$) expected for the free ion Ce^{3+} state (EC: $4f^1$). This reduction may be caused by the fraction of Ce ions in the Ni richer environments, whereas Zn tends to stabilise the Ce^{3+} local moment character.

The slight curvature observed in the $1/\chi$ vs. T data-set might result from CEF effects which are simply modelled here by adjusting the parameter χ_0 . At temperatures below about 2 K, the susceptibility, $\chi(T)$, displays a smooth cross-over from the high temperature Curie–Weiss behaviour towards a low temperature Kondo-like flattening of the susceptibility which reaches a value $\chi_{\text{LT}} = 0.054 \text{ emu mol}^{-1}$ at 0.7 K (see inset in Fig. 9b).

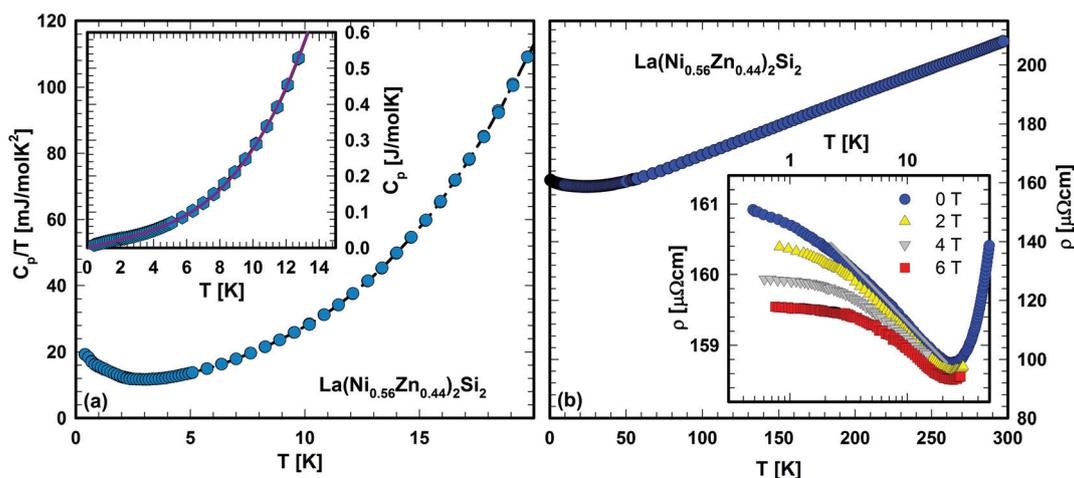


Fig. 6 (a) Temperature dependent specific heat C_p of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ plotted as C_p/T vs. T . The inset shows the data as C_p vs. T . The solid line is a least squares fit according to the spin fluctuation model (see text). (b) Temperature dependent electrical resistivity ρ of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$. The inset shows the low temperature resistivity data on the logarithmic temperature scale for various magnetic fields. The logarithmic temperature dependence is highlighted by the solid line.



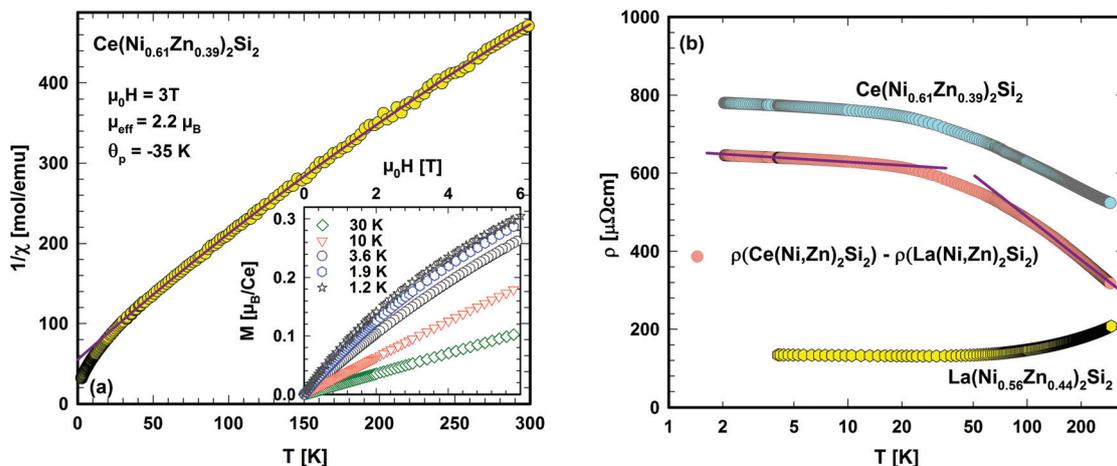


Fig. 7 (a) Temperature dependent magnetic susceptibility χ of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ plotted as $1/\chi$ vs. T . The solid line is the result of a least squares fit of the modified Curie Weiss law to the experimental data above 50 K. The inset shows the field dependent magnetization of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ for various temperatures. (b) Temperature dependent electrical resistivity ρ of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ and $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$. The magnetic contribution to the electrical resistivity, ρ_{mag} , of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ is shown as well. The solid lines are guides for the eyes.

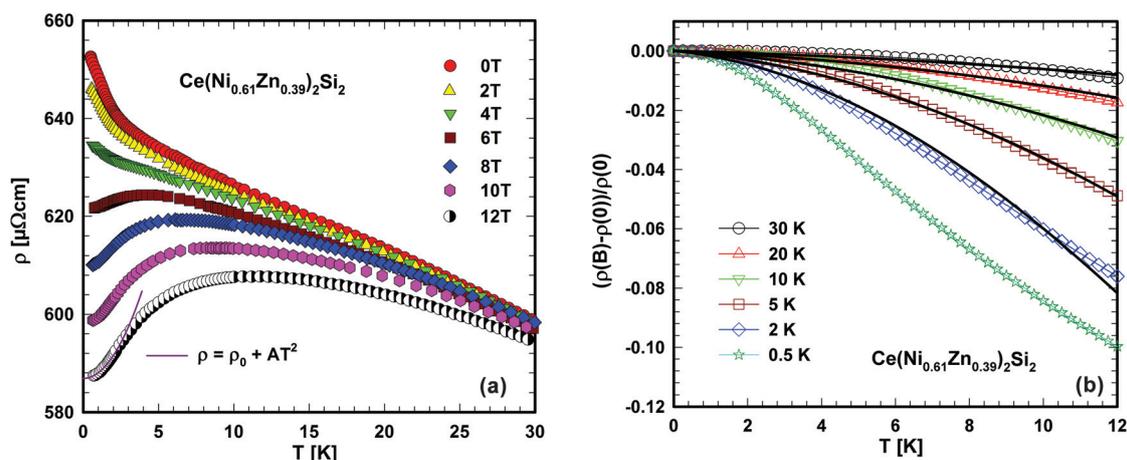


Fig. 8 (a) Low temperature electrical resistivity ρ of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ for various externally applied magnetic fields. The solid line is a least squares fit as explained in the text. (b) Field dependent magnetoresistance $(\rho(B) - \rho(0))/\rho(0)$ of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ for various temperatures. $\rho(B)$ and $\rho(0)$ are the field and the zero field resistivities. The solid lines correspond to numerical calculations according to Schlottmann's theory.⁴⁵

The inset in Fig. 7(a) shows isothermal magnetization curves, M , for $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ measured at temperatures ranging from 1.2 K to 30 K. Neither spontaneous magnetization nor metamagnetic-like features are obvious from these measurements, thus excluding long range magnetic order in the measured temperature range. A smooth, slightly curvilinear $M(H)$ dependence at low temperatures is observed with relatively small magnetization values near $0.3\mu_B/\text{Ce}$ at 1.2 K and 6 T. A combination of both, CEF splitting and the Kondo effect (see below) is expected to be responsible for the magnitude of the low temperature magnetic moment.

Fig. 7(b) shows the temperature dependent electrical resistivity, ρ , of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ in comparison with that of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$. In distinct contrast to $\rho(T)$ of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$, the electrical resistivity of

$\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ evidences a negative value of $d\rho/dT$ in the entire temperature range. Additionally, much larger $\rho(T)$ values are observed as a consequence of additional magnetic scattering processes. If $\rho(T)$ of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ is assumed to primarily derive from electron-phonon interactions, besides a constant residual resistivity, the magnetic scattering processes of electrons on the 4f moments of Ce can be isolated by simply subtracting the resistivity curve of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ from that of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$. Results are shown in Fig. 7(b) on a semi-logarithmic temperature scale. Obviously, two temperature ranges can be identified, where $\rho_{\text{mag}}(T)$ behaves in a negative-logarithmic manner (see the solid lines in Fig. 7(b) as a guide for the eyes). Such a behaviour is a hallmark of Kondo-type interactions, as present in a huge amount of cerium based compounds. Following the preposition of



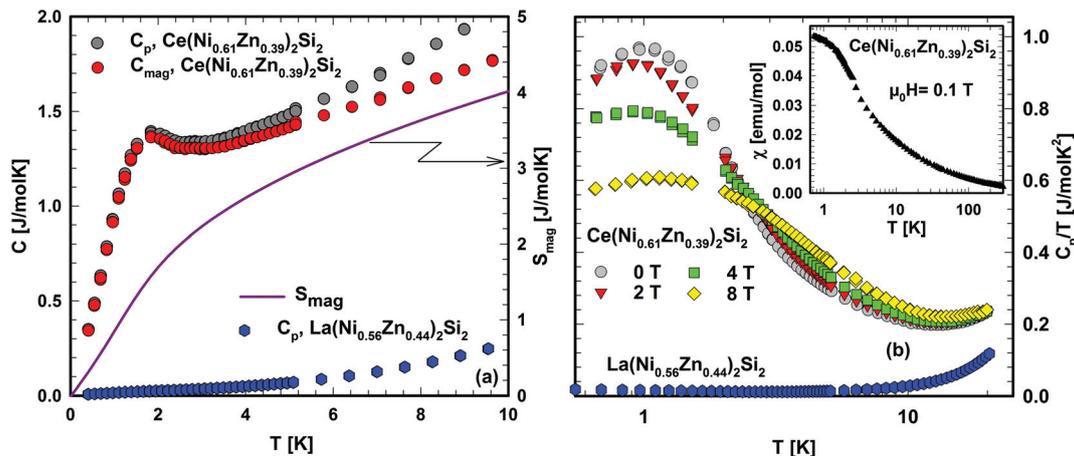


Fig. 9 (a) Temperature dependent specific heat C_p of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ and $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$. $C_{\text{mag}}(T)$ is derived by subtracting both data-sets. The temperature dependent magnetic entropy S_{mag} (solid line, referring to the right axis) originates from the integration of $C_{\text{mag}}/T(T)$. (b) Field and temperature dependent heat capacity data of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ plotted as C_p/T vs. $\log T$ for various externally applied magnetic fields. Data of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ are added for the purpose of comparison. The inset shows the low temperature magnetic susceptibility data measured at 0.1 T and temperatures down to 0.7 K.

Cornut and Coqblin⁴³ the logarithmic resistivity ranges at low and high temperatures can be understood as derived from the Kondo effect in the CEF ground state and in an excited CEF state, respectively. If these levels are well separated in energy, a pronounced maximum in $\rho_{\text{mag}}(T)$ would be expected as well. Overall, the present resistivity study strongly indicates a Kondo effect existing in $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$.

In general, a lattice of Kondo ions (*i.e.*, a Kondo lattice) is characterised by a drop of the electrical resistivity at lowest temperatures due to coherence. A distribution of Kondo temperatures due to random Ni/Zn occupation may inhibit the formation of a coherent state at low temperatures in the present system (compare Fig. 7b and 8a). Externally applied magnetic fields tend to suppress incoherent scattering processes. Accordingly, for fields above about 6 T, a smooth maximum forms in $\rho(T)$, which shifts continuously to higher temperatures. Such behaviour can be understood in terms of a Kondo lattice, where the maximum in $\rho(T)$ is a measure of the Kondo temperature.⁴⁴ At lowest temperatures, a Kondo lattice exhibits a Fermi liquid ground state documented by the T^2 behaviour of the electrical resistivity (solid line, Fig. 8(a)). Isothermal resistivity data at various external fields, as presented in Fig. 8(b), reveal a moderate negative magnetoresistance, amounting to about 10% at lowest temperatures and 12 T.

The overall negative magnetoresistance is in line with the Kondo behaviour, where increasing magnetic fields suppress Kondo interactions and as a result decrease resistivity. Although the field dependence of $(\rho(B) - \rho(0))/\rho(0)$ complies with numerical results employing Schlottmann's theory⁴⁵ (solid lines, Fig. 8(b)), the Kondo temperature inferred from such fits appears to be unphysically high (about 50 K) which may be a consequence of the aforementioned site-dependent hybridisation/Kondo interaction strength.

In Fig. 9 the heat capacity data of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$, measured down to 400 mK, are displayed as C_p vs. T . For com-

parison, $C_p(T)$ of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ is added, too. Below 2 K, the specific heat of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$ shows an anomaly, which is attributed to Kondo-type interactions and is in close correspondence with the smooth cross-over behaviour displayed by the low temperature magnetic susceptibility shown in the inset of Fig. 9b. In order to calculate the magnetic entropy, released at low temperatures, the specific heat data of $\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2$ are assumed to represent the phonon contribution to this quantity, *i.e.*, $C_{\text{mag}} = C(\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2) - C(\text{La}(\text{Ni}_{0.56}\text{Zn}_{0.44})_2\text{Si}_2)$. Results of this procedure are shown in Fig. 9(a) as well. Integrating C_{mag}/T from zero to the upper limit of the present measurements reveals the temperature dependent magnetic entropy, S , shown as a solid line in Fig. 9(a). At 3.9 K, the entropy reaches $0.45R \ln 2$ which according to Desgranges and Schotte,⁴⁶ corresponds to a Kondo temperature $T_K = 3.9$ K. As is obvious from Fig. 9(a), $S(T)$ continuously increases, finally reaching a value of $R \ln 2$ around 20 K. The response of the system to the application of magnetic fields is shown in Fig. 9(b), where the heat capacity data are plotted as C_p/T vs. $\log T$. The overall observation that C_p/T becomes reduced by magnetic fields, concomitant with an entropy transfer to higher temperatures, is in line with a typical Kondo scenario.

Comparing the absolute numbers of the low temperature Sommerfeld coefficient ($\gamma = C_p/T$) and of the susceptibility χ_{LT} , the value of the Wilson ratio, $R = \pi^2 k_B^2 \chi_{\text{LT}} / [g_1^2 J(J+1) \mu_B^2 \gamma] \sim 2$, provides a further proof that a Kondo screened ground-state CEF doublet dominates the low temperature physics of $\text{Ce}(\text{Ni}_{0.61}\text{Zn}_{0.39})_2\text{Si}_2$.

Finally, it is interesting to see that the substitution of Ni by Zn in CeNi_2Si_2 at 800 °C supports the ThCr_2Si_2 -type only up to $\text{Ce}(\text{Ni}_{0.82}\text{Zn}_{0.18})_2\text{Si}_2$, where a transition to an atom site occupation variant with the CaBe_2Ge_2 -type is observed extending up to a composition $\text{Ce}(\text{Ni}_{0.45}\text{Zn}_{0.55})_2\text{Si}_2$ and maintaining the stoichiometry $\text{Ce}(\text{Ni,Zn})_2\text{Si}_2$. At higher Zn contents the



ThCr₂Si₂-type reappears at temperatures below 800 °C in the form of CeZn₂(Si_{0.7}Zn_{0.3})₂ where Zn-atoms are found to enter the Si-site. It should be noted that Zn atoms in the Ni/Zn substitution enlarge the volume and concomitantly introduce a higher electron/atom ratio. Both facts provide the basis for a gradual change from the intermediate valent Ce in CeNi₂Si₂ with a characteristic Kondo-lattice temperature $T^* \sim 600$ K (ref. 21–26) towards a localised magnetic behaviour of Ce in CeZn₂(Si_{0.7}Zn_{0.3})₂ with a ground state close to trivalent Ce ($\mu_{\text{eff}} = 2.34\mu_{\text{B}}$).¹⁴ Intermediate compositions such as Ce(Ni_{0.61}Zn_{0.39})₂Si₂ exhibit a Kondo-type ground state.

4. Conclusions

Although the systems La–Zn–Si and Ce–Zn–Si at 800 °C do not contain a compound “{La,Ce}Zn₂Si₂”, solid solutions exist starting from CeNi₂Si₂ by the addition of Zn which substitutes Ni. This homogeneity range has been studied for {La,Ce}-(Ni_{1-x}Zn_x)₂Si₂, $0 \leq x \leq 0.55$. Single crystal X-ray diffraction data define the CaB₂Ge₂-type for the crystals of the compounds Ce(Ni_{0.61}Zn_{0.39})₂Si₂ ($P4/nmm$; $a = 0.41022(1)$ nm, $c = 0.98146(4)$ nm) and CeNi_{2+x}Si_{2-x}, $x = 0.33$ ($P4/nmm$; $a = 0.40150(2)$ nm, $c = 0.95210(2)$ nm). Whilst the quaternary CaB₂Ge₂-type phase is stable at 800 °C, a reinvestigation of the Ce–Ni–Si system near the stoichiometric composition 1:2:2 revealed that the CaB₂Ge₂-type phase exists only at high temperatures (≥ 1000 °C) in the Ni-rich side. Bravais lattice changes from body centered to primitive have been observed at 800 °C starting from Ce(Ni_{1-x}Zn_x)₂Si₂ ($0 \leq x \leq 0.18$) $I4/mmm$ to Ce(Ni_{1-x}Zn_x)₂Si₂, $0.25 < x \leq 0.55$, $P4/nmm$, however, on further Zn substitution the stability of the 1:2:2 phase is reduced (<695 °C) and it exists only with an excess amount of Zn as CeZn₂(Si_{1-x}Zn_x)₂ with the ThCr₂Si₂ type.

The effective paramagnetic moment of Ce in Ce(Ni_{0.61}Zn_{0.39})₂Si₂ suggests that the ground state of the Ce ions in this compound is close to trivalent. Enhanced values of the electronic contribution to the specific heat, a Curie–Weiss to Kondo-type cross-over behaviour of the low temperature susceptibility and pronounced ranges of negative logarithmic temperature dependences of the electrical resistivity reveal the presence of the Kondo effect in this cerium compound, in the context of a Wilson ratio, $R \sim 2$. Unexpectedly, La(Ni_{0.56}Zn_{0.44})₂Si₂ exhibits a spin fluctuation scenario at low temperatures together with a distinct minimum of the temperature dependent electrical resistivity which we, presumably, interpret as a Kondo effect due to a very low concentration of uncompensated nickel spins.

Acknowledgements

Z. Malik acknowledges the support from the Higher Education Commission of Pakistan (HEC) under the scholarship scheme “PhD in Natural & Basic Sciences from Austria”. F. Failamani is thankful for the support from the Austrian Federal Ministry

of Science and Research (BMWF) under the scholarship scheme: Technology Grant Southeast Asia (PhD) in the frame of the ASEA UNINET. We thank Dr S. Puchegger for his expert assistance in EPMA measurements and Dr N. Ponweiser and P. Wibner for their contributions to Ce–Ni–Si at the early stage of this work. Support by the FWF P24380 is acknowledged.

References

- 1 K. R. Andress and E. Alberti, *Z. Metallkd.*, 1935, 27.
- 2 Z. Ban and M. Sikirica, *Acta Crystallogr.*, 1965, 18, 594–599.
- 3 O. S. Zarechnyuk, P. I. Kripyakevich and E. I. Gladyshevskii, *Kristallografiya*, 1965, 9, 706–708.
- 4 B. Eisenmann, N. May, W. Müller and H. Schäfer, *Z. Naturforsch., B*, 1972, 27, 1155–1157.
- 5 W. Dörrscheidt and H. Schäfer, *J. Less-Common Met.*, 1978, 58, 209–216.
- 6 E. Parthé, B. Chabot, H. F. Braun and N. Engel, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1983, 39, 588–595.
- 7 O. I. Bodak and E. I. Gladyshevskii, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1969, 5, 2060–2065.
- 8 O. I. Bodak, M. G. Mis'kiv, A. T. Tyvanchuk, O. I. Kharchenko and E. I. Gladyshevskii, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1973, 9, 864–866.
- 9 B. Chabot and E. Parthé, *J. Less-Common Met.*, 1984, 97, 285–290.
- 10 E. R. Hovestreydt, *J. Less-Common Met.*, 1984, 102, L27–L29.
- 11 F. Merlo, M. L. Fornasini and M. Pani, *J. Alloys Compd.*, 2005, 387, 165–171.
- 12 P. Villars and K. Cenzual, *Pearson's Crystal Data—Crystal Structure Database for Inorganic Compounds, release 2014/15*, ASM International, Materials Park, OH, USA, 2014.
- 13 Z. Malik, A. Grytsiv, P. Rogl and G. Giester, *Intermetallics*, 2013, 36, 118–126.
- 14 F. Failamani, A. Grytsiv, R. Podloucky, H. Michor, E. Bauer, P. Brož, G. Giester and P. Rogl, *RSC Adv.*, 2015, 5, 36480–36497.
- 15 F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz and H. Schäfer, *Phys. Rev. Lett.*, 1979, 43, 1892–1896.
- 16 M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes and R. Pöttgen, *Phys. Rev. B: Condens. Matter*, 2008, 78, 020503.
- 17 M. Rotter, M. Tegel and D. Johrendt, *Phys. Rev. Lett.*, 2008, 101, 107006.
- 18 A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, D. J. Singh and D. Mandrus, *Phys. Rev. Lett.*, 2008, 101, 117004.
- 19 E. Bauer, R. T. Khan, H. Michor, E. Royanian, A. Grytsiv, N. Melnychenko-Koblyuk, P. Rogl, D. Reith, R. Podloucky, E.-W. Scheidt, W. Wolf and M. Marsman, *Phys. Rev. B: Condens. Matter*, 2009, 80, 064504.
- 20 F. Kneidinger, E. Bauer, I. Zeiringer, P. Rogl, C. Blaas-Schenner, D. Reith and R. Podloucky, *Phys. C*, 2015, 514, 388–398.



- 21 G. Knebel, M. Brando, J. Hemberger, M. Nicklas, W. Trinkl and A. Loidl, *Z. Phys. B: Condens. Matter*, 1999, **259**–261, 399–400.
- 22 E. V. Sampathkumaran and R. Vijayaraghavan, *Phys. Rev. Lett.*, 1986, **56**, 2861–2864.
- 23 M. Koterlyn, I. Shcherba, R. Yasnitskii and G. Koterlyn, *J. Alloys Compd.*, 2007, **442**, 176–179.
- 24 T. Toliński, K. Synoradzki, M. Koterlyn, G. Koterlyn and R. Yasnitskii, *J. Alloys Compd.*, 2013, **580**, 512–516.
- 25 R. K. Singhal, N. L. Saini, K. B. Garg, J. Kanski, L. Ilver, P. O. Nilsson, R. Kumar and L. C. Gupta, *J. Phys.: Condens. Matter*, 1993, **5**, 4013.
- 26 M. Bertin Tchoula Tchokonté, P. de Villiers du Plessis, A. M. Strydom, T. B. Doyle, S. Ghosh and D. Kaczorowski, *J. Phys. Chem. Solids*, 2015, **77**, 56–61.
- 27 E. M. Levin, O. I. Bodak, E. I. Gladyshevskii and V. G. Sinyushko, *Phys. Status Solidi A*, 1992, **134**, 107–117.
- 28 J. Rodriguez-Carvajal, *FULLPROF, a program for Rietveld refinement and pattern matching analysis*, Abstract of the satellite meeting on powder diffraction of the XV congress, Int. Union of Crystallography, Talence, France, 1990, p. 127; see also: J. Rodriguez-Carvajal, *Physica B*, 1993, **55**, 192–194.
- 29 *Nonius Kappa CCD Program Package COLLECT, DENZO, SCALEPACK, SORTAV*, Nonius Delft, The Netherlands, 1998.
- 30 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2007, **64**, 112–122.
- 31 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
- 32 M. Falmbigl, F. Kneidinger, A. Grytsiv, H. Michor, H. Müller, P. Rogl, E. Bauer, G. Hilscher and G. Giester, *Intermetallics*, 2013, **42**, 45–51; see also: F. Kneidinger, H. Michor, A. Sidorenko, E. Bauer, I. Zeiringer, P. Rogl, C. Blaas-Schenner, D. Reith and R. Podloucky, *Phys. Rev. B: Condens. Matter*, 2013, **88**, 104508.
- 33 H. Zhou, Q. Yao, S. Yuan, J. Liu and H. Deng, *J. Alloys Compd.*, 2004, **366**, 161–164.
- 34 O. I. Bodak, E. I. Gladyshevskii and P. I. Kripyakevich, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1966, **2**, 2151–2155.
- 35 A. V. Morozkin, A. V. Knotko, V. O. Yapaskurt, F. Yuan, Y. Mozharivskiy and R. Nirmala, *J. Solid State Chem.*, 2013, **208**, 9–13.
- 36 A. V. Morozkin, Y. D. Seropegin, A. V. Gribanov, I. A. Sviridov, J. M. Kurenbaeva and A. L. Kurenbaev, *J. Alloys Compd.*, 1998, **264**, 190–196.
- 37 H. F. Braun, N. Engel and E. Parthé, *Phys. Rev. B: Condens. Matter*, 1983, **28**, 1389–1395.
- 38 I. Zeiringer, A. Grytsiv, E. Bauer, G. Giester and P. Rogl, *Z. Anorg. Allg. Chem.*, 2015, **641**, 1404–1421.
- 39 L. M. Gelato and E. Parthé, *J. Appl. Crystallogr.*, 1987, **20**, 139–143.
- 40 B. Belan, O. Bodak, R. Gladyshevskii, I. Soroka, B. Kuzhel, O. Protsyk and I. Stets, *J. Alloys Compd.*, 2005, **396**, 212–216.
- 41 A. Guzik and E. Talik, *J. Alloys Compd.*, 2002, **346**, 10–16.
- 42 K. Ikeda, S. K. Dhar, M. Yoshizawa and K. A. Gschneidner Jr., *J. Magn. Magn. Mater.*, 1991, **100**, 292–321.
- 43 B. Cornut and B. Coqblin, *Phys. Rev. B: Solid State*, 1972, **5**, 4541–4561.
- 44 D. L. Cox and N. Grewe, *Z. Phys. B: Condens. Matter*, 1988, **71**, 321–340.
- 45 P. Schlottmann, *Phys. Rev. B: Condens. Matter*, 1982, **25**, 4815–4827, see also: P. Schlottmann, *Phys. Rev. B: Condens. Matter*, 1982, **25**, 4828, and P. Schlottmann, *Phys. Rev. B: Condens. Matter*, 1982, **25**, 4838.
- 46 H.-U. Desgranges and K. D. Schotte, *Phys. Lett. A*, 1982, **91**, 240–242.

