

Crystal Structure of the Ternary Arsenide CeNi_{1.91}As_{1.94}

V. Babizhetskyy^{a,b}, E. Le Für^c, J. Y. Pivan^c, and R. Guérin^a

Institut de Chimie, Campus de Beaulieu, Avenue du Général Leclerc, F-35042 Rennes Cédex

^a Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511

^b Permanent address: Analytical Chemistry Department, Ivan Franko National University of L'viv, Kyrylo and Mefodij Str. 6, 79005 L'viv, Ukraine

^c Laboratoire de Physicochimie Analytique, ENSC Rennes

Reprint requests to Prof. Dr. R. Guérin. Fax: +33-2 99-63 57 04.

E-mail: roland.guerin@univ-rennes1.fr

Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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A new ternary intermetallic has been obtained in the Ce-Ni-As system, the composition of which is CeNi_{1.91}As_{1.94} from X-ray single crystal structure determination. The structure is derived from the CaBe₂Ge₂ type with the following relations between the vectors **a**, **b**, and **c** of the cell and **a**₀, **b**₀, and **c**₀ of the subcell: **a** = 2**a**₀ – 2**b**₀; **b** = 2**a**₀ + 2**b**₀ and **c** = 2**c**₀ (V = 16 V₀). The structure takes its origin from compositional and displacive mechanisms. The major structural modifications occur in the nickel-arsenic layers (two per cell) where the nickel atoms are in “square” pyramidal As sites. Moreover, the slight atomic displacements in these layers that develop in the *ab* plane, lead to As₈ clusters, each formed by a central part As₄ linked by four apical As ligands. These clusters constrain arsenic to adopt a valence state higher than –3 which in turn involves the lowering of the counterbalancing charge from the nickel substructure. The structure of CeNi_{1.91}As_{1.94} is compared in details with that of the previously reported URh_{1.6}As_{1.9}.

Introduction

A great number of ternary compounds LnM₂X₂ where Ln stands for a rare earth, M a transition metal and X a non metal atom (Si, Ge, As, P, Sb,...) have been synthesized during the last two decades. Most of them adopt the ThCr₂Si₂ or CaBe₂Ge₂-type structures [1, 2]. In some cases, these two BaAl₄-type derivative structures [3, 4] were reported as L. T. (ThCr₂Si₂-type) or H. T. (CaBe₂Ge₂-type) forms as for example for the silicides LaIr₂Si₂, YIr₂Si₂ and CeIr₂Si₂ [5 - 7]. Work was also focussed on the physical properties such as mixed or fluctuating valence, superconductivity... which occur for Ce, Eu, Yb and La-containing compounds.

In the course of our investigations on the Ln-Ni-As systems, we succeeded in preparing about ten years ago the ternary arsenides LnNi₂As₂ with Ln = La-Gd in their L. T. and H. T. modifications and the crystal structures of LaNi₂As₂ and CeNi₂As₂ were solved in the two forms [8]. In addition, a third polymorphic form was mentioned for NdNi₂As₂

when using the H.T. synthesis procedure (1450 - 1600 °C) [8]. Preliminary X-ray single crystal studies (Weissenberg, Buerger methods) indicated this third form to crystallize in tetragonal symmetry with possible space groups *I*4̄2*c*, *I*4*cm* or *I*4/*mcm* and lattice constants *a* = 11.178(2), *c* = 19.112(6) Å. This form was considered as a stacking variant (2*a*√2, 2*c*) of the CaBe₂Ge₂-type but no accurate structure determination could be performed at that time to support this hypothesis.

More recently, we isolated a new ternary phase, with orthorhombic symmetry and the approximate formula Ce₆Ni_{13.4}As₉ [9], when investigating the ternary Ce-Ni-As phase diagram. When attempting to improve the crystal growth of this arsenide by arc melting, small single crystals as platelets were picked from the molten block that were found to be tetragonal with lattice constants *a* = 11.6318(3), *c* = 19.2018(3) Å. These values were close to those of the third polymorphic form previously reported for NdNi₂As₂ (*vide supra*). All of this indicated that “CeNi₂As₂” and “NdNi₂As₂” may exist either as

ThCr₂Si₂-, as CaBe₂Ge₂- and as a third form likely related to the CaBe₂Ge₂-type through structural defaults.

The synthetic conditions, the characterization and the crystal structure determination of this third form are reported in detail in the present paper. As expected, the structure (true formula CeNi_{1.91}As_{1.94}) is derived from the CaBe₂Ge₂-type, by considering essentially partial occupancy and displacement of atomic positions on the nickel and arsenic substructures. The structural modifications between the true structure and the subcell of CaBe₂Ge₂-type are widely discussed as well as the relationship with the previously reported URh_{1.6}As_{1.9}.

Experimental Section

Polycrystalline samples of the ternary cerium nickel arsenide were prepared from pure elements: nickel and amorphous β -As as powders, cerium as ingots, all with minimum purity 99.9%.

Suitable amounts of powder and freshly filed chips of the constituents, in the nominal atomic percentage Ce : Ni : As = 23 : 42 : 35 were mixed together and pressed into pellets. A small excess of arsenic (1%) was added to compensate for evaporation losses during the arc melting process. Prior melting in a furnace under a Ti/Zr-gettered argon atmosphere using a non-consumable thoriated tungsten electrode, the pellets (about 2 g each) were pre-reacted in evacuated silica tubes, gradually heated up to 1070 K, held at this temperature for 2 d then slowly cooled down. To ensure homogeneity during arc melting, the samples were turned over and melted several times. The samples were recovered after treatment, as molten buttons with a metallic luster and were unreactive towards air. Small platelet-like single crystals were obtained after crushing the samples and could be extracted from the molten matrix.

Energy-dispersive analysis of these crystals using scanning electron microscopy confirmed cerium, nickel and arsenic as the only components. Single-crystal data were collected at ambient temperature using a Nonius Kappa CCD X-ray area-detector diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å).

Data collection strategy was performed with the help of the program COLLECT [10] and reflections were corrected using the program DENZO of the KappaCCD software package [11]. Absorption correction, taking into account the crystal morphology, was applied with the help of the program NUMABS [12]. Structures were solved by direct methods (SIR97 [13]) and least-squares refinements, difference Fourier syntheses were run with SHELXL-97 [14]. Crystal structure and refinement data

Table 1. Crystal data, intensity collection and refinement for CeNi_{1.91}As_{1.94}.

Crystal system	Tetragonal
Space group	<i>I4cm</i>
<i>a</i> [Å]	11.6318(3)
<i>c</i> [Å]	19.2018(5)
<i>V</i> [Å ³]	2597.98(12)
<i>Z</i> , calculated density [g·cm ⁻³]	32, 8.33
Crystal size [mm ³]	0.30 × 0.055 × 0.022
Linear absorption coeff. [mm ⁻¹]	45.18
Refinement limits:	
θ [°]	2 < θ < 38
<i>h</i> , <i>k</i> , <i>l</i>	-18 < <i>h</i> < 19, -20 < <i>k</i> < 19, -32 < <i>l</i> < 32
Collected reflections	18923
Independent reflections, <i>R</i> _{int}	3467, 0.064
Refls in refinement (<i>F</i> _o > 4 σ (<i>F</i> _o))	2584
Variable parameters	116
Absorption correction (<i>T</i> _{min} , <i>T</i> _{max})	0.030, 0.361
Refinement	<i>F</i> ²
<i>R</i> (<i>R</i> all data)	0.045 (0.074)
<i>wR</i> ₂ with <i>w</i> = 1/ σ^2 (<i>F</i> _o) ²	0.070
Extinction coefficient	3 × 10 ⁻⁶
Scale factor	0.513
Flack parameter	0.0(12)
Goodness of fit	1.43
Max. min (<i>e</i> /Å ³)	+4.9, -5.9

are given in Table 1. The drawings were done using the program DIAMOND [15].

Crystal structure determination

A single crystal of “CeNi₂As₂” with dimensions 0.30 × 0.055 × 0.022 mm³ was isolated for crystal structure determination. From the intensity data collection, it occurred immediately that the strongest reflections were consistent with a CaBe₂Ge₂-type structure, but numerous weak reflections were indicative of a new structure with lattice vectors **a**, **b**, and **c** that were combinations of the fundamental vectors **a**₀, **b**₀, and **c**₀ of the CaBe₂Ge₂-type subcell according to the relations: **a** = 2 **a**₀ - 2**b**₀; **b** = 2 **a**₀ + 2 **b**₀ and **c** = 2 **c**₀.

Subcell structure refinement

Using the 295 independent subcell reflections, the structure has been first refined in a CaBe₂Ge₂-type subcell (*a*₀ = 4.112 Å and *c*₀ = 9.601 Å, *V*₀ = 162.34 Å³). It is worthwhile to note that the volume of this subcell is smaller than that of the stoichiometric CeNi₂As₂ in its H. T. form (*a* = 4.222, *c* = 9.407 Å, *V* = 167.70 Å³) [8]. This result indicates that the title compound is a defective ternary compound. Moreover, it is important to note that the unit cell parameters are varying inversely for the defective and stoichiometric structures.

Table 2. Crystal data, atomic and isotropic displacement parameters of CeNi₂As₂ and their esd's.

CeNi _{1.91} As _{1.92} (defective subcell)						CeNi ₂ As ₂ (stoichiometric)					
$a = 4.112(3) \text{ \AA}$, $c = 9.601(3) \text{ \AA}$; $V = 162.3(1) \text{ \AA}^3$						$a = 4.222(1) \text{ \AA}$, $c = 9.407(1) \text{ \AA}$; $V = 167.70(3) \text{ \AA}^3$					
Independent Reflections: 295						Independent Reflections: 159					
Variable Parameters: 17; R , $wR2$: 0.042, 0.090						Variable Parameters: 15; R , $wR2$: 0.060, 0.069					
Atom	Occupancy	x	y	z	$U_{\text{eq}} (\text{\AA}^2)^a$	Atom	Occupancy	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Ce	1	1/4	1/4	0.25042(7)	0.009(3)	Ce	1	1/4	1/4	0.2520(1)	0.006(1)
Ni(1)	1	3/4	1/4	1/2	0.0128(4)	Ni(1)	1	3/4	1/4	1/2	0.0129(3)
Ni(2)	0.914(8)	3/4	3/4	0.1190(3)	0.0262(8)	Ni(2)	1	3/4	3/4	0.1166(3)	0.0086(3)
As(1)	1	1/4	1/4	0.6329(1)	0.0100(3)	As(1)	1	1/4	1/4	0.6295(2)	0.0077(2)
As(2)	0.920(8)	3/4	1/4	0	0.0383(8)	As(2)	1	3/4	1/4	0	0.0077(2)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Interatomic distances (\AA) and their esd's for defective subcell CeNi_{1.91}As_{1.92} and stoichiometric CeNi₂As₂ with the CaBe₂Ge₂ type.

CeNi _{1.91} As _{1.92} (def.subcell)		CeNi ₂ As ₂ (stoichiom.)	
Ce1: 4 As1	3.1159(6)	Ce1: 4 Ni1	3.146(1)
4 Ni1	3.1574(5)	4 As1	3.187(1)
4 As2	3.1635(5)	4 As2	3.174(1)
4 Ni2	3.169(1)	4 Ni2	3.246(1)
1 Ni2	3.547(3)	1 Ni2	3.467(2)
1 As1	3.672(2)	1 As1	3.555(2)
4 Ce1	4.112(3)	4 Ce1	4.222(1)
Ni1: 4 As1	2.4198(7)	Ni1: 4 As1	2.437(1)
4 Ni1	2.9076(2)	4 Ni1	2.985(1)
4 Ce1	3.1574(5)	4 Ce1	3.146(1)
Ni2: 4 As2	2.352(1)	Ni2: 4 As2	2.379(1)
1 As1	2.383(2)	1 As1	2.388(1)
4 Ce1	3.169(1)	4 Ce1	3.246(1)
As1: 1 Ni2	2.382(2)	As1: 1 Ni2	2.388(1)
4 Ni1	2.4198(7)	4 Ni1	2.437(1)
4 Ce1	3.1159(5)	4 Ce1	3.187(1)
As2: 4 Ni2	2.352(1)	As2: 4 Ni2	2.379(1)
4 As2	2.9075(2)	4 As2	2.985(1)
4 Ce1	3.1635(5)	4 Ce1	3.174(1)

The main crystallographic data for these two forms of CeNi₂As₂ are given for comparison in Table 2. As it can be readily seen, the Ni2 and As2 positions in the defective form are not fully occupied ($\tau = 0.92$) and the atoms exhibit large isotropic displacement parameters. This result indicates vacancies on both nickel and arsenic substructures and suggests slight atomic displacements from mean positions for these two elements. The final chemical formula from subcell refinement is CeNi_{1.91}As_{1.92}. Selected interatomic distances are summarized in Table 3.

In order to explain the structure of CeNi_{1.91}As_{1.92}, we need to recall the basic features of the CaBe₂Ge₂-type structure (Fig. 1a). The transition metals (B) and the metalloid atoms (X) form tetragonal pyramids which

share edges of the base to form two-dimensional sheets with composition B₂X₂. These sheets B₂X₂ are interspersed with layers of metal atoms A, and the final structure AB₂X₂ results. While the spatial distribution within the sheets B₂X₂ is always XBBX in the ThCr₂Si₂ type, alternating XBBX and BXXB sequences occur in the CaBe₂Ge₂ type [16]. As a result, the X coordination environment of metal atoms A is square antiprismatic and the atoms B occupy either regular tetrahedra (XBBX layer) or square pyramids (BXXB layer). When comparing the crystal structures of CeNi₂As₂ (stoichiometric) and CeNi_{1.91}As_{1.92} (deficient), it is obvious that the nickel deficit mainly affects the Ni2 atoms in pyramidal As-coordination (average Ni2-As distance = 2.358 \AA) within the layer BXXB. No deficit is observed for the Ni1 atoms in tetrahedral As-coordination ($d_{\text{Ni1-As}} = 2.420 \text{ \AA}$) in the layer XBBX. Moreover, it is worth noting that the arsenic deficit concerns the As2 atoms within the layer BXXB with As-As distances 2.908 \AA (As2-4As2). These As-As distances in the ab plane are significantly shorter than those observed in the stoichiometric CeNi₂As₂ (2.985 \AA) and explain the shortening of the a parameter for the title compound. Although these As-As distances are smaller in the subcell, they remain nevertheless too large to be considered as As-As bonds when comparing to the As-As pairs (2.627 \AA) found along the [001] direction for the L. T. form of CeNi₂As₂ with ThCr₂Si₂ type [8].

Structure refinement

Three space groups are consistent with all the observed reflections (hkl with $h + k + l = 2n$ and $h0l$ with $h(l) = 2n$) *i. e.* $I\bar{4}c2$, $I4cm$ and centrosymmetric $I4/mcm$. The best solution from direct methods was obtained for space group $I4cm$.

Four independent cerium atoms, fourteen independent positions corresponding to nickel and arsenic atoms were put progressively into the refinement steps. Refinement

Table 4. Positional and displacement parameters of the CeNi_{1.91}As_{1.94} structure and their esd's.

Atom	Position	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq} (Å ²) ^a
Ce1	8(c)	1	0.24560(3)	- <i>x</i> + 1/2	0.00417(4)	0.0081(2)
Ce2	16(d)	1	0.25029(3)	0.00196(4)	0.25360(3)	0.0076(2)
Ce3	4(a)	1	0	0	0	0.0074(2)
Ce4	4(b)	1	1/2	0	0.00740(4)	0.0077(2)
Ni1	4(a)	0.960(5)	0	0	0.3275(2)	0.0104(5)
Ni2	16(d)	1	0.25109(6)	0.0174(1)	0.9383(2)	0.0125(3)
Ni3	4(b)	0.302(5)	1/2	0	0.3069(4)	0.004(2)
Ni4	8(c)	1	0.23833(9)	- <i>x</i> + 1/2	0.3173(2)	0.0140(4)
Ni5	8(c)	1	0.6248(9)	0.1248(1)	0.12696(9)	0.0129(4)
Ni6	8(c)	1	0.37170(9)	- <i>x</i> + 1/2	0.12930(9)	0.0122(4)
Ni7	16(d)	1	0.12162(8)	0.12523(8)	0.12865(9)	0.0116(2)
As1	4(b)	0.964(5)	1/2	0	0.1908(2)	0.0090(4)
As2	16(d)	1	0.75073(5)	0.99663(7)	0.0616(2)	0.0085(3)
As3	8(c)	0.970(2)	0.40137(5)	- <i>x</i> + 1/2	0.8723(2)	0.0200(3)
As4	4(a)	1	0	0	0.1984(1)	0.0093(4)
As5	16(d)	0.981(2)	0.37814(4)	0.35424(4)	0.37987(8)	0.0118(2)
As6	8(c)	1	0.24767(8)	- <i>x</i> + 1/2	0.1942(2)	0.0090(3)
As7	8(c)	0.851(3)	0.37793(5)	- <i>x</i> + 1/2	0.3778(2)	0.0186(3)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

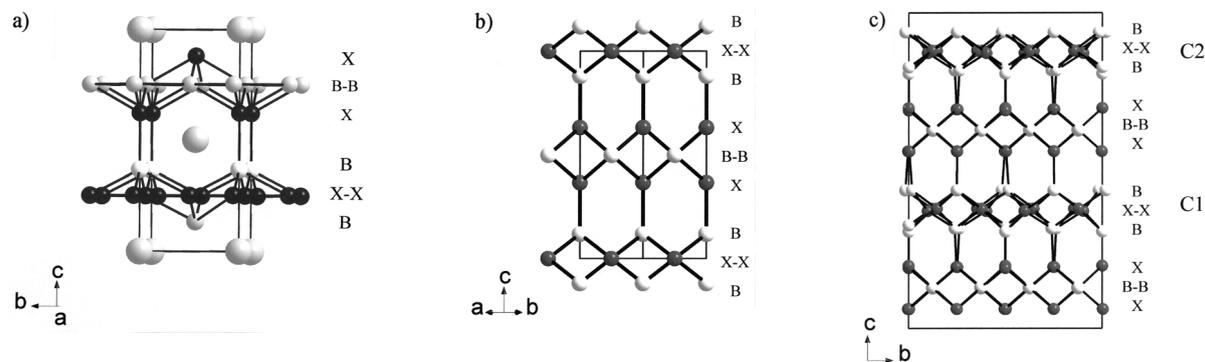


Fig. 1. Crystal structure of the defective compound CeNi₂As₂ derived from the CaBe₂Ge₂ type: 3D representation of the CaBe₂Ge₂-type structure (a) and projections onto the (100) plane of the subcell CeNi_{1.91}As_{1.92} (b) and the supercell CeNi_{1.91}As_{1.94} (c). For simplification, the cerium atoms have been omitted in (b) and (c). The nickel-arsenic layers, namely BXXB and XBBX layers, have been emphasized. White and black spheres correspond to the nickel and arsenic atoms, respectively. The labeling of the two different BXXB layers in the supercell corresponding to the C1 and C2 layers (doubling of the *c* parameter) is used also in (c).

cycles including displacement factors were run in order to make a correct attribution of the nickel and arsenic positions, with respect to the known interatomic distances. On refining the occupancy factors, the reliability factor converged to 6% and it became obvious that some atomic positions were more or less in deficit. As an example, the occupancy factor for Ni3 was found to be $\tau = 0.30$, and a slight deficit but with significant esd's was found for nickel (Ni1, $\tau = 0.96$) and arsenic (As1, As3 and As5, $0.96 < \tau < 0.98$; As7, $\tau = 0.85$) positions. Further refinements by including anisotropic displacement parameters

together with occupancy factors converged to the reliability factors given in Table 1. The final difference Fourier synthesis did not reveal any significant electronic density peaks. The formula CeNi_{1.91}As_{1.94} from the structure refinement is very close to the formula CeNi_{1.91}As_{1.92} obtained from subcell refinement (*vide supra*).

Atomic positional and displacement parameters are listed in Table 4 and selected interatomic distances in Table 5. Further details of the crystal structure investigation are available from the FIZ Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) under CSD-412610.

Table 5. Interatomic distances (Å) with their esd's for the CeNi_{1.91}As_{1.94} structure.

Ce1:	2	Ni2	3.034(2)	Ce3:	1	Ni1	3.313(3)	Ni5:	2	Ni7	2.908(1)	As2:	1	Ce1	3.122(1)
	2	As5	3.060(2)		4	Ce1	4.114(1)		2	Ni6	2.945(1)		1	Ce3	3.132(1)
	1	Ni5	3.083(2)	Ce4:	2	As3	3.060(2)		1	Ce4	3.080(2)	As3:	1	Ni3	2.052(5)
	2	As2	3.099(1)		2	Ni5	3.080(2)		1	Ce1	3.083(2)		2	Ni2	2.357(2)
	2	As2	3.122(1)		4	As2	3.097(1)		2	Ce2	3.193(2)		1	Ni4	2.529(2)
	1	As7	3.164(2)		2	Ni6	3.152(2)	Ni6:	1	As6	2.391(2)		2	As7	2.584(1)
	2	Ni7	3.170(2)		4	Ni2	3.192(2)		2	As2	2.414(2)		1	Ce4	3.060(2)
	1	Ni6	3.174(2)		2	As7	3.197(2)		1	As1	2.418(2)		2	Ce2	3.107(2)
	2	Ni2	3.311(2)		1	As1	3.522(3)		2	Ni7	2.909(2)	As4:	4	Ni7	2.432(2)
	1	Ce4	4.0410(5)		2	Ce1	4.0410(5)		2	Ni5	2.945(1)		1	Ni1	2.479(3)
	2	Ce3	4.114(1)	Ni1:	4	As5	2.428(2)		2	Ce2	3.139(2)		4	Ce2	3.099(1)
Ce2:	1	As5	3.050(2)		1	As4	2.479(3)		1	Ce4	3.152(2)	As5:	1	Ni4	2.291(2)
	1	Ni4	3.053(2)		4	Ce2	3.239(2)		1	Ce1	3.174(2)		1	Ni2	2.320(2)
	1	Ni3	3.079(3)	Ni2:	1	As5	2.320(2)	Ni7:	1	As2	2.419(2)		1	Ni2	2.397(2)
	1	As4	3.099(1)		1	As3	2.357(2)		1	As2	2.423(2)		1	Ni1	2.428(2)
	1	As3	3.106(2)		1	As2	2.374(2)		1	As4	2.432(2)		1	As7	2.701(1)
	1	As6	3.119(1)		1	As5	2.397(2)		1	As6	2.433(2)		1	Ce2	3.050(2)
	1	As6	3.127(1)		1	As7	2.481(2)	Ni7:	2	Ni7	2.872(1)		1	Ce1	3.060(2)
	1	As7	3.139(2)		1	Ce1	3.034(2)		1	Ni5	2.908(2)		1	Ce3	3.194(2)
	1	Ni6	3.139(2)		1	Ce3	3.159(1)		1	Ni6	2.909(2)		1	Ce2	3.326(2)
	1	As1	3.145(1)		1	Ce4	3.192(2)		1	Ce2	3.153(2)	As6:	1	Ni4	2.367(2)
	1	Ni7	3.153(2)		1	Ce1	3.311(2)		1	Ce1	3.170(2)		1	Ni6	2.391(2)
	1	Ni7	3.171(2)	Ni3:	2	As3	2.052(5)		1	Ce2	3.171(2)		1	Ni5	2.399(2)
	1	Ni5	3.193(2)		1	As1	2.229(6)		1	Ce3	3.198(2)		2	Ni7	2.434(2)
	1	Ni1	3.238(2)		2	As7	2.427(4)	As1:	1	Ni3	2.229(6)	As6:	2	Ce2	3.119(1)
	1	Ni4	3.262(2)		4	Ce2	3.079(2)		2	Ni5	2.391(2)		2	Ce2	3.127(1)
	1	As5	3.326(1)	Ni4:	2	As5	2.291(2)		2	Ni6	2.418(2)	As7:	1	Ni3	2.427(4)
	1	Ni2	3.553(3)		1	As6	2.367(2)		4	Ce2	3.145(1)		2	Ni2	2.481(2)
	1	Ce2	4.0754(8)		1	As3	2.529(2)	As2:	1	Ni2	2.374(2)		1	Ni4	2.575(2)
	2	Ce2	4.1174(4)		1	As7	2.575(2)		1	Ni6	2.414(2)		2	As3	2.584(1)
	1	Ce2	4.1400(8)		2	Ce2	3.053(2)		1	Ni7	2.419(2)		2	As5	2.701(1)
Ce3:	4	As2	3.132(1)		2	Ce2	3.262(2)		1	Ni7	2.423(2)		2	Ce2	3.139(2)
	4	Ni2	3.158(1)	Ni5:	1	As1	2.391(2)		1	Ni5	2.438(2)		1	Ce1	3.164(2)
	4	As5	3.194(1)		1	As6	2.399(2)		1	Ce4	3.097(1)		1	Ce4	3.196(2)
	4	Ni7	3.198(2)		2	As2	2.438(2)		1	Ce1	3.099(1)				

Structure Description and Discussion

A projection on the (100) plane of the CeNi_{1.91}As_{1.94} structure is given in Fig. 1c. As expected, the structure is strongly related to the CaBe₂Ge₂-type structure (Fig. 1b) and consists of four 2-dimensional B₂X₂ (*i.e.* Ni₂As₂) sheets per cell, stacked along the [001] direction.

The representation of the crystal structure shows immediately the alternating sequence of XBBX and BXXB layers and confirms that the XBBX layers are not distorted, contrary to the BXXB layers. Since the two BXXB layers are distorted in different ways, a doubling of the *c* parameter results. The projection of these two different BXXB layers, namely the C1 and C2 layers, is shown in Fig. 2a and 2b.

As it is readily seen, the atomic displacements in the *ab* plane from subcell positions mainly affect the nickel and arsenic sublattices in the C1 and C2 layers. The main structural feature is the occurrence of As-As bonding in the form of As₈ clusters involving 2As₃, 2As₇ and 4As₅ atoms. Each of these As₈ clusters consists of a central part As₄ (2As₃, 2As₇) with $d(\text{As3-As7}) = 2.584 \text{ \AA}$ and four apical As₅ ligands with $d(\text{As5-As7}) = 2.701 \text{ \AA}$ (Fig. 3a). It is worth noting that the As₈ clusters are not exactly planar and that they are rotated by 90° between the C1 and C2 layers. Therefore, it is clear that this new structure is compositional and displacive with most of the defaults located in the C1 and C2 layers.

Similar results have been found previously for URh_{1.6}As_{1.9} but not described accurately by the authors [17]. Indeed, the tetragonal structure of

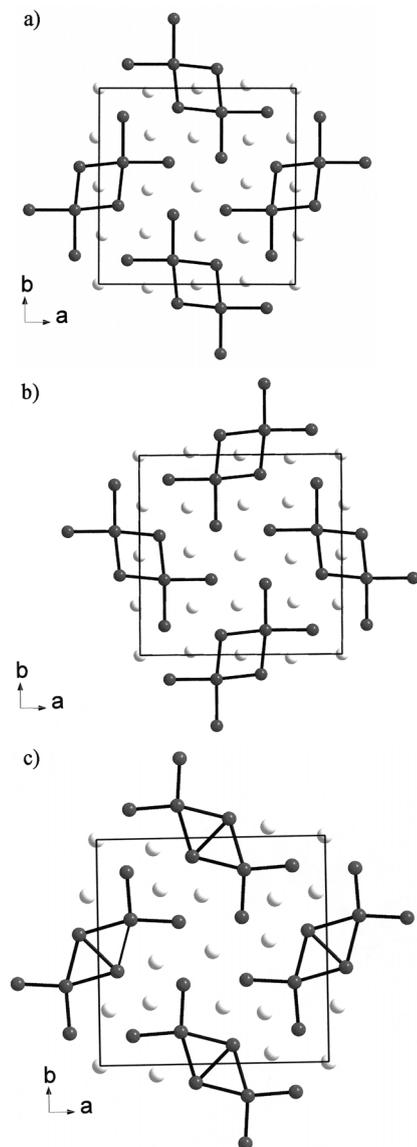


Fig. 2. Projection of the C1 and C2 layers onto the (001) plane for the structure $\text{CeNi}_{1.91}\text{As}_{1.94}$ (a, b) and equivalent C1 layer for $\text{URh}_{1.6}\text{As}_{1.9}$ (c). The clusters As_8 (full lines) have been emphasized.

$\text{URh}_{1.6}\text{As}_{1.9}$ with the unit cell parameters $a = 11.554(4)$, $c = 19.359(9)$ Å, is strongly related to that of $\text{CeNi}_{1.91}\text{As}_{1.94}$. However, an examination of the two structures shows that the occupancy factors are not exactly the same especially on the transition metal and arsenic substructures. The main structural difference is due to the partly filled Ni3 position ($\tau = 0.30$) in $\text{CeNi}_{1.91}\text{As}_{1.94}$ which has no corresponding Rh position in $\text{URh}_{1.6}\text{As}_{1.9}$. Accordingly, ordered

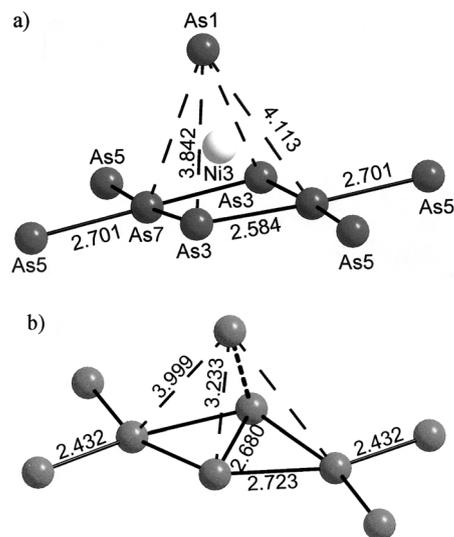


Fig. 3. Detailed representation of the As_8 cluster in the BXXB layer for $\text{CeNi}_{1.91}\text{As}_{1.94}$ (a) and $\text{URh}_{1.6}\text{As}_{1.9}$ (b). It is worth noting that the central part of the cluster is the basis of a pyramidal As site that is partly occupied by nickel ($\tau = 0.30$) in the cerium compound and vacant in the uranium compound.

metal vacancies occur on the rhodium sublattice for the uranium compound.

When describing the structure of $\text{URh}_{1.6}\text{As}_{1.9}$ using XBBX and BXXB layers, one can see that the same defaults as those found in $\text{CeNi}_{1.91}\text{As}_{1.94}$ occur in the layers BXXB (C1 and C2 layers) while the layers XBBX are not distorted. As found for $\text{CeNi}_{1.91}\text{As}_{1.94}$, As-As bonding occur in the layers BXXB of $\text{URh}_{1.6}\text{As}_{1.9}$ to form As_8 clusters that are strongly distorted as compared to those of $\text{CeNi}_{1.91}\text{As}_{1.94}$ (Fig. 2c). Indeed, the larger distortion of the central part As_4 of each cluster involves additional As-As bonding at 2.68 Å. As a consequence, this result generates a higher electronic deficit on the arsenic substructure which must be counterbalanced by the rhodium substructure, leading to the absence of rhodium atom on the position corresponding to Ni3 in $\text{CeNi}_{1.91}\text{As}_{1.94}$. As shown in Fig. 3, the central part of the As_8 cluster is the basis of a pyramidal site that is not suited for rhodium (metallic radius 1.34 Å) and not easily for nickel (1.24 Å, $\tau = 0.30$).

The occurrence of As-As bonding as As_8 clusters in the two structures of $\text{URh}_{1.6}\text{As}_{1.9}$ and $\text{CeNi}_{1.91}\text{As}_{1.94}$ lowers the overall charge for the metalloid substructure (formal valence for arsenic less than -3) and consequently from the charge equi-

librium criterion, the transition metal substructure has to be deficient as actually observed for the two structures. For URh_{1.6}As_{1.9}, uranium was considered to adopt the valence state 4+ leading to an excess of positive charge which is compensated by the occurrence of vacancies on the rhodium substructure [17]. In the case of CeNi_{1.91}As_{1.94}, the cerium atoms more likely adopt the valence state 3+ when recalling the magnetic results for the isostructural neodymium nickel arsenide ($a = 11.178(2)$, $c = 19.112(6)$ Å) [8]. To conclude, the fact that the arsenic contents are very close for the two structures together with the combined effect of valence state +4 for uranium and the lower formal charge from the arsenic substructure may explain the larger deficit on the rhodium substructure in case of URh_{1.6}As_{1.9}.

It can be noted that other deficient compounds derived from the CaBe₂Ge₂ type have been found with deficits occurring either on the transition metal or metalloid substructures, and were described in the usual unit cell with space group $P4/nmm$, as for example the ternaries CeCu₂Sn_{1.9} [18], LaNi_{1.51}Sb₂ [19] or ZrNi_{0.75}P₂ [16]. Also derivatives of the CaBe₂Ge₂ type are the variants SrZnBi₂ [20] or UCuP₂ [21].

Conclusion

The structure of the deficient arsenide CeNi_{1.91}As_{1.94} has been described. It is derived from the CaBe₂Ge₂ type with partial occupancy on both the nickel and arsenic substructures and offers a better understanding of the structural modifications

compared to the parent stoichiometric arsenide CeNi₂As₂ with CaBe₂Ge₂ type.

The new structure results from compositional and displacive mechanisms. The structural modifications affect mainly the Ni₂As₂ layers containing Ni atoms in “square” pyramidal As sites. In these layers (two different layers per cell), there is a slightly atomic deficit for both As and Ni positions. Moreover, As-As bonding as As₈ clusters occurs in these layers that do not exist in the stoichiometric CeNi₂As₂ with CaBe₂Ge₂ type. Such bonding reduces the electronic contribution from the metalloid substructure as compared to stoichiometric CeNi₂As₂ (CaBe₂Ge₂ type) and accordingly, the nickel substructure is deficient leading to the formula CeNi_{1.91}As_{1.94}. However, the question remains if the structure described herein is actually a third polymorphic form AB_{~2}X_{~2} related to the ThCr₂Si₂- and CaBe₂Ge₂-type structures? Due to the different composition, it is very unlikely. However, on the basis of As-As bonding as As₈ clusters, one can say that this new structure is intermediate between the ThCr₂Si₂ (As-As pairs) and CaBe₂Ge₂ types (no As-As bonding).

Finally, the structure described herein has been observed previously for the neodymium compound and it seems very likely that such a structure exists for other light rare earth elements (La → Gd).

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- [1] Z. Ban, M. Sikirica, *Acta Crystallogr.* **18**, 594 (1965).
 - [2] B. Eisenmann, N. May, W. Müller, H. Schäfer, *Z. Naturforsch.* **27b**, 1155 (1972).
 - [3] E. Parthé, B. Chabot, H. F. Braun, N. Engel, *Acta Crystallogr.* **39b**, 588 (1983).
 - [4] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cen-zual, R. Gladyshevskii, *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Springer, Berlin (1993).
 - [5] H. F. Braun; N. Engel, E. Parthé, *Phys. Rev.* **B28**, 1389 (1983).
 - [6] M. Sirjak, P. Lejay, B. Chevalier, J. Etourneau, P. Hagenmuller, *J. Less-Common Met.* **105**, 139 (1985).
 - [7] K. Hiebl, C. Horvath, P. Rogl, *J. Less-Common Met.* **117**, 375 (1986).
 - [8] E. H. El Ghadraoui, J. Y. Pivan, R. Guérin, O. Pena, J. Padiou, M. Sergent, *Mater. Res. Bull.* **23**, 1345 (1988).
 - [9] V. Babizhetskyy, C. Le Sénéchal, J. Bauer, S. Députier, R. Guérin, *J. Alloys Comp.* **287**, 174 (1999).
 - [10] COLLECT: KappaCCD software, Nonius BV, Delft, The Netherlands (1998).
 - [11] Z. Otwinoski, W. Minor, in C. W. Carter (Jr.), R. W. Sweet (eds): *Methods in Enzymology*, Vol. 276, Academic Press, New York (1997).
 - [12] P. Coppens, in F. R. Ahmed, S. R. Hall, C. P. Huber (eds): *Crystallographic Computing*, p. 255, Munksgaard Publishers Ltd, Copenhagen (1970).

- [13] G. Cascarano, A. Altomare, C. Giacovaggo, A. Guagliardi, A. G. G. Moliterni, D. Siliqi, M. C. Burla, G. Polidori, M. Camalli, *Acta Crystallogr.* **A5**, C-79 (1996).
- [14] G. M. Sheldrick: SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen (1997).
- [15] K. Brandenburg, DIAMOND, Version 2.0 (1998).
- [16] E. H. El Ghadraoui, J. Y. Pivan, R. Guérin, *J. Less-Common Met.* **136**, 303 (1988).
- [17] S. Zemni, J. Vicat, B. Lambert, R. Madar, P. Chaudouet, J. P. Sénateur, *J. Less-Common Met.* **143**, 113 (1988).
- [18] W. Jeitschko, W. K. Hoffmann, L. J. Terbüchte, *J. Less-Common Met.* **137**, 133 (1988).
- [19] G. Cordier, E. Czech, H. Schäfer, P. Woll, *J. Less-Common Met.* **110**, 327 (1985).
- [20] G. Cordier, B. Eisenmann, H. Schäfer, *Z. Anorg. Allg. Chem.* **426**, 205 (1976).
- [21] H. Noël, Z. Zolnierek, D. Kaczorowski, R. Troć, *J. Less-Common Met.* **132**, 327 (1987).