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Rhombohedral Ce₂Ni₅Zn₂ and Hexagonal CeNi₂Zn: the First Ternary Compounds from the Ce–Ni–Zn System

VOLODYMYR VASYL'OVYCH PAVLYUK,
IGOR MYCHAJLOVYCH OPAINYCH AND
OKSANA IVANIVNA BODAK

Department of Inorganic Chemistry, L'viv University,
6 Lomonosova Street, 290005 L'viv 5, Ukraine

RADOVAN  ERNY AND KLAUS YVON

Laboratoire de Cristallographie, Universit  de
Gen ve, 24 quai Ernest-Ansermet, CH-1211
Geneva 4, Switzerland

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Abstract

Dicerym pentanickel dizinc, Ce₂Ni₅Zn₂, crystallizes as a new ordered substitution variant of the Er₂Co₇ structure type. Cerium dinickel zinc, CeNi₂Zn, crystallizes with the YRh₂Si structure type. Both structures contain MgZn₂- and CaCu₅-type slabs which occur in ratios of 1:2 in Ce₂Ni₅Zn₂ and 1:1 in CeNi₂Zn.

Comment

No ternary phases have been reported in R–Ni–Zn systems (where R is a rare earth element). Our investigations of the phase equilibria in the Ni-rich region of the Ce–Ni–Zn system at 470 K have revealed the following compounds: rhombohedral Ce₂Ni₅Zn₂ form-

ing with the nominal compositions Ce₂₅Ni₅₅Zn₂₀ and Ce_{22.5}Ni₅₅Zn_{22.5}, and hexagonal CeNi₂Zn forming with the nominal compositions Ce₂₅Ni₃₅Zn₄₀, Ce₂₅Ni₄₀Zn₃₅, Ce₂₅Ni₅₀Zn₂₅ and Ce₂₂Ni₅₀Zn₂₈.

Ce₂Ni₅Zn₂ crystallizes as an ordered substitution variant of the Gd₂Co₇ structure type (Bertaut, Lemaire & Schweizer, 1965), also known as the Er₂Co₇ structure type (Ostertag, 1967). Ni and Zn occupy the Co positions 6(c) and 18(h), and 3(b) and 9(e), respectively, in space group *R* $\bar{3}m$. Another ordered substitution variant of this structure type is Y₄Rh₉Si₅ (Paccard, Paccard, Moreau & Gomez Sal, 1985), in which Rh and Si occupy the positions 9(e) and 18(h), and 3(b) and 6(c), respectively.

The distribution of Ni and Zn in the structure of Ce₂Ni₅Zn₂ could not be determined from X-ray data alone because of a lack of scattering contrast. The following two arguments support the proposed distribution. Firstly, the composition of the model is close to the nominal compositions of the alloys for which crystals of Ce₂Ni₅Zn₂ were found. A model with Y₄Rh₉Si₅-type distribution would correspond to the nominal compositions of the alloys for which crystals of CeNi₂Zn were found. Secondly, the bond distances associated with the positions 3(b) and 9(e) are longer than those associated with the 6(c) and 18(h) positions. This is in accordance with the larger atomic radius of Zn compared to that of Ni. As shown in Fig. 1, the structure contains the following coordination polyhedra: Ce1 [Ni₁₂Zn₆Ce₂], Ce2 [Ni₉Zn₃Ce₄], Ni1 [Ni₆ZnCe₅], Ni2 and Ni3 [Ni₆Zn₃Ce₃], Zn1 [Ni₄Zn₄Ce₄], Zn2 [Ni₆Ce₆].

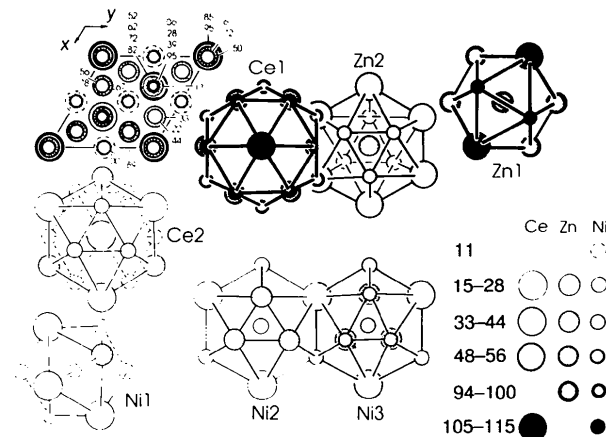


Fig. 1. Structural projection of rhombohedral Ce₂Ni₅Zn₂ along [001] showing the coordination polyhedra.

CeNi₂Zn crystallizes with the YRh₂Si structure type (Paccard & Paccard, 1985), which is an ordered substitution variant of the CeNi₃ structure type (Cromer & Olsen, 1959). Its structural projection is shown in Fig. 2. The structure contains the following coordina-

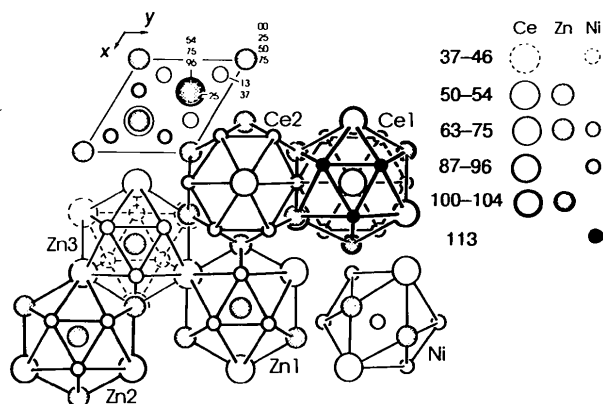


Fig. 2. Structural projection of hexagonal CeNi_2Zn along [001] showing the coordination polyhedra.

tion polyhedra: Ce1 [$\text{Ni}_9\text{Zn}_3\text{Ce}_4$], Ce2 [$\text{Ni}_{12}\text{Zn}_6\text{Ce}_2$], Ni [$\text{Ni}_4\text{Zn}_3\text{Ce}_5$], Zn1 and Zn2 [$\text{Ni}_6\text{Zn}_3\text{Ce}_3$], Zn3 [Ni_6Ce_6].

The structures of $\text{Ce}_2\text{Ni}_5\text{Zn}_2$ and CeNi_2Zn both contain MgZn_2 - and CaCu_5 -type slabs, which occur in a ratio of 1:2 in $\text{Ce}_2\text{Ni}_5\text{Zn}_2$ and a ratio of 1:1 in CeNi_2Zn .

Experimental

$\text{Ce}_2\text{Ni}_5\text{Zn}_2$ and CeNi_2Zn were prepared by arc melting and annealing at 470 K for 400 h.

$\text{Ce}_2\text{Ni}_5\text{Zn}_2$

Crystal data

$\text{Ce}_2\text{Ni}_5\text{Zn}_2$

$M_r = 704.45$

Rhombohedral

$R\bar{3}m$

$a = 4.945(2) \text{ \AA}$

$c = 36.78(1) \text{ \AA}$

$V = 778.8(9) \text{ \AA}^3$

$Z = 6$

$D_x = 9.02 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 12

reflections

$\theta = 8-14^\circ$

$\mu = 43.737 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Flake

$0.112 \times 0.080 \times 0.016 \text{ mm}$

Metallic

Data collection

Philips PW1100 diffractometer

$\omega-2\theta$ scans

Absorption correction:

analytical by integration
from crystal shape

$T_{\min} = 0.040$, $T_{\max} = 0.487$

2615 measured reflections

336 independent reflections

283 observed reflections

$[F > 3\sigma(F)]$

$R_{\text{int}} = 0.146$

$\theta_{\text{max}} = 29.92^\circ$

$h = 0 \rightarrow 6$

$k = 0 \rightarrow 6$

$l = 0 \rightarrow 51$

2 standard reflections

frequency: 60 min

intensity decay: 0.6 and
0.7%

Refinement

Refinement on F

$R = 0.055$

Extinction correction:

Zachariasen (1968)

$wR = 0.050$

$S = 1.785$

277 reflections

26 parameters

Weighting scheme based

on measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 4.63 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -3.43 \text{ e \AA}^{-3}$

Extinction coefficient:

745 (275)

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Tables

2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{Ce}_2\text{Ni}_5\text{Zn}_2$

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

		x	y	z	U_{eq}
Ce1	6(c)	0	0	0.05011 (3)	0.0108 (4)
Ce2	6(c)	0	0	0.14652 (3)	0.0119 (4)
Ni1	18(h)	0.5003 (3)	$-x$	0.10972 (3)	0.0106 (6)
Ni2	6(c)	0	0	0.27812 (6)	0.0112 (7)
Ni3	6(c)	0	0	0.38828 (7)	0.0134 (7)
Zn1	9(e)	1/2	0	0	0.0145 (7)
Zn2	3(b)	0	0	1/2	0.0152 (9)

Table 2. Interatomic distances up to 4 \AA in $\text{Ce}_2\text{Ni}_5\text{Zn}_2$

Ce1	—Ni3	2.86 (3) \times 3	Ce2	—Ni1	2.82 (2) \times 6
	—Ni2	2.86 (3) \times 3		—Zn2	2.95 (3) \times 3
	—Zn1	3.08 (2) \times 6		—Ni1	3.17 (3) \times 3
	—Ni1	3.30 (2) \times 6		—Ce2	3.22 (2) \times 3
	—Ce2	3.55 (4)		—Ce1	3.55 (4)
	—Ce1	3.69 (4)			
Ni1	—Ni2	2.46 (2)	Ni2	—Ni1	2.46 (2) \times 3
	—Ni3	2.47 (2)		—Zn1	2.48 (2) \times 3
	—Ni1	2.47 (3) \times 4		—Ni3	2.86 (3) \times 3
	—Zn2	2.54 (2)		—Ce1	2.86 (3) \times 3
	—Ce2	2.82 (2) \times 2			
	—Ce2	3.17 (3)			
	—Ce1	3.30 (2) \times 2			
Ni3	—Ni1	2.47 (2) \times 3			
	—Zn1	2.47 (2) \times 3			
	—Ni2	2.86 (3) \times 3			
	—Ce1	2.86 (3) \times 3			
Zn1	—Zn1	2.47 (3) \times 4	Zn2	—Ni1	2.54 (2) \times 6
	—Ni3	2.47 (2) \times 2		—Ce2	2.95 (3) \times 6
	—Ni2	2.48 (2) \times 2			
	—Ce1	3.08 (2) \times 4			

CeNi_2Zn

Crystal data

CeNi_2Zn

$M_r = 322.88$

Hexagonal

$P6_3/mmc$

$a = 5.045(3) \text{ \AA}$

$c = 16.434(7) \text{ \AA}$

$V = 362.2(4) \text{ \AA}^3$

$Z = 6$

$D_x = 8.881 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 12

reflections

$\theta = 7-12.5^\circ$

$\mu = 43.233 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Flake

$0.100 \times 0.064 \times 0.010 \text{ mm}$

Metallic

Data collection

Philips PW1100 diffractometer	176 observed reflections
ω -2 θ scans	[$F > 3\sigma(F)$]
Absorption correction:	$R_{\text{int}} = 0.137$
analytical by integration	$\theta_{\text{max}} = 29.94^\circ$
from crystal shape	$h = 0 \rightarrow 6$
$T_{\text{min}} = 0.095$, $T_{\text{max}} = 0.646$	$k = 0 \rightarrow 6$
	$l = 0 \rightarrow 23$
968 measured reflections	2 standard reflections
243 independent reflections	frequency: 60 min
	intensity decay: 0.8 and 1.87%

Refinement

Refinement on F	Extinction correction:
$R = 0.066$	Zachariasen (1968)
$wR = 0.034$	Extinction coefficient:
$S = 2.512$	500.00
170 reflections	Atomic scattering factors
18 parameters	from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2B and 2.3.1)
Weighting scheme based on measured e.s.d.'s	
$(\Delta/\sigma)_{\text{max}} = 0.0007$	
$\Delta\rho_{\text{max}} = 3.28 \text{ e } \text{\AA}^{-3}$	
$\Delta\rho_{\text{min}} = -4.06 \text{ e } \text{\AA}^{-3}$	

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for CeNi₂Zn

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ce1	4(f)	1/3	2/3	0.53984 (7)
Ce2	2(d)	1/3	2/3	0.0215 (7)
Ni	12(k)	0.1674 (3)	2x	0.12571 (7)
Zn1	2(c)	1/3	2/3	1/4
Zn2	2(b)	0	0	1/4
Zn3	2(a)	0	0	0.016 (1)
				0.012 (1)

Table 4. Interatomic distances up to 4 \AA in CeNi₂Zn

Ce1		Ce2	
—Ni	2.890 (4) \times 6	—Zn1	2.912 (1) \times 3
—Zn3	2.985 (1) \times 3	—Zn2	2.912 (1) \times 3
—Ni	3.083 (2) \times 3	—Ni	3.246 (4) \times 12
—Ce1	3.193 (1) \times 3	—Ce1	3.454 (2) \times 2
—Ce1	3.454 (2)		
Ni		Zn1	
—Zn1	2.505 (2)	—Ni	2.505 (2) \times 6
—Zn2	2.512 (2)	—Ce2	2.912 (1) \times 2
—Ni	2.512 (3) \times 2	—Zn2	2.912 (1) \times 3
—Zn3	2.531 (2)	—Ce2	2.9132 (9)
—Ni	2.533 (4) \times 2		
—Ce1	2.890 (4) \times 2		
—Ce1	3.083 (2)		
—Ce2	3.246 (4) \times 2		
Zn2		Zn3	
—Ni	2.512 (2) \times 6	—Ni	2.531 (2) \times 6
—Zn1	2.912 (1) \times 3	—Ce1	2.985 (1) \times 6
—Ce2	2.912 (1) \times 3		

The *Xtal3.2* package (Hall, Flack & Stewart, 1992) was used for cell refinement and data reduction. Structure solution was by *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). *Xtal3.2* was used for least-squares refinement based on $|F|$ values, varying a scale factor, isotropic extinction, atomic positional and anisotropic displacement parameters.

The absorption correction was performed using *LSABS* (Blanc, Schwarzenbach & Flack, 1991). The atomic coordinates were standardized by *STRUCTURE TIDY* (Gelato & Parthé, 1987)

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Acid Terbium(III) Cerium(IV) Sulfate Hydrate, H₉Tb₇Ce₆(SO₄)₂₇·72.2H₂O

JOHN C. BARNES

Department of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland

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Abstract

Hexagonal crystals of H₉Ln₇Ce₆(SO₄)₂₇·72H₂O are known for Ln = La–Tb. The Tb compound is isomorphous with the Nd compound described previously. Tb—O (2.55 \AA average) is unusually long compared with a typical literature value of 2.43 \AA and, in spite of the lanthanide contraction, is longer than the corresponding Nd—O distance although the Ce—O distances are identical. Since the quality of the crystals and hence the data is not as good for the Tb compound, and since this phase has not been reported for Ln = Dy–Lu, it may be that the size of the Ln^{III} site is fixed by the Ce^{IV}–SO₄²⁻ network.