Crystal chemical peculiarities of rare earth (R) rich magnesium intermetallic compounds in R–T–Mg (T = transition element) systems

Pavlo SOLOKHA^{1,2*}, Serena DE NEGRI¹, Volodymyr PAVLYUK^{2,3}, Adriana SACCONI¹

¹ Dipartimento di Chimica e Chimica Industriale, Università di Genova,
Via Dodecaneso 31, I-16146 Genova, Italy

² Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

³ Institute of Chemistry and Environment Protection, Jan Dlugosz University,
Al. Armii Krajowej 13/15, 42200 Czestochowa, Poland

* Corresponding author. Tel.: +39-0103536159; fax: +39-0103625051; e-mail: solokha_pavlo@yahoo.com

Received March 20, 2009; accepted June 3, 2009; available on-line November 16, 2009

The rare earth rich compounds $R_{23}Ni_7Mg_4$ (R = Ce, Pr) and R_4NiMg (R = La, Tb, Dy, Ho, Er) were synthesized by slow thermal treatment in a resistance furnace, starting from element pieces enclosed in sealed Ta crucibles. SEM-EDXS analyses were performed for monitoring the phase composition. The crystal structures of the majority of these intermetallics were investigated by X-ray diffraction on single crystals. The $R_{23}Ni_7Mg_4$ compounds crystallize in the $Pr_{23}Ir_7Mg_4$ structure type: $P6_3mc$, $hP68$, $Z = 2$, for Ce $a = 0.99742(1)$, $c = 2.25206(4)$ nm, $wR_2 = 0.0686$, 1483 F^2 values, 74 variables; for Pr $a = 0.99249(4)$, $c = 2.24460(9)$ nm, $wR_2 = 0.0735$, 1395 F^2 values, 74 variables; for La $a = 1.01234(8)$, $c = 2.2887(2)$ nm, $R_B = 7.3\%$ and $R_F = 5.1\%$. The series of isostructural R_4NiMg compounds belongs to the Gd_4RhIn structure type, $F\bar{4}3m$, $cF96$, $Z = 16$. Crystal chemical relations of $R_{23}Ni_7Mg_4$ with other rare earth rich intermetallics are discussed. The cubic R_4NiMg structures are described in terms of nested polyhedra units and relations with some other cubic structures are shown on the basis of group-subgroup relations.

Crystal structure / Group-subgroup relation / Mg-containing alloys

Introduction

Constitutional properties of R–T–Mg (R = rare earth metal; T = transition metal) ternary systems are being systematically investigated by our research groups [1–3]. During the study of the La–Ni–Mg isothermal section at 500 °C [1] two intermetallic phases were found with approximate compositions $La_{67}Ni_{16.5}Mg_{16.5}$ and $La_{67}Ni_{21}Mg_{12}$. Afterwards, in order to facilitate the crystal structure determination of these compounds, the synthesis of homologous phases with other rare earth metals (R) was attempted; the existence of two series of isostructural phases with general formulae R_4NiMg and $R_{23}Ni_7Mg_4$, respectively, was therefore established, and their crystal structures solved. The same isostructural series were in the meantime investigated by Tuncel *et al.* [4,5]. In this paper we report our crystal structure data on some of these phases, mainly obtained by single crystal X-ray diffraction analysis. Crystal chemical relations of R_4NiMg and $R_{23}Ni_7Mg_4$ with other binary and ternary intermetallic phases are discussed.

Experimental

Synthesis

Starting materials for the preparation of the samples were compact metals, all with nominal purities >99.9 wt.%. Alloys were prepared in two ways: *via* induction melting of metal mixtures sealed in Ta crucibles, or by thermal treatment of arc-welded Ta crucibles containing element pieces placed into evacuated quartz vials, which were then located in a resistance furnace with a thermal cycle controller. The heating process was carried out at a rate of 5 °C/min up to $T = 850$ °C and this temperature was held for 15–20 minutes. The sample was then slowly (0.1 °C/min) cooled down to 350 °C, and finally the furnace was switched off. After cooling to room temperature, the samples could easily be extracted from the tantalum container. No side-reaction of the samples with the crucible was detected. Single crystals, mainly of prismatic form, exhibiting metallic luster, were isolated by mechanical fragmentation from the samples prepared by the second method.

Table 1 Crystallographic data for the Ce₂₃Ni₇Mg₄ and Pr₂₃Ni₇Mg₄ crystals and experimental details of the structure determination.

Empirical formula	Ce ₂₃ Ni ₇ Mg ₄	Pr ₂₃ Ni ₇ Mg ₄
Structure type	Pr ₂₃ Ir ₇ Mg ₄	Pr ₂₃ Ir ₇ Mg ₄
Formula weight, M_r	3730.97	3749.14
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3mc$ (# 186)	$P6_3mc$ (# 186)
Pearson symbol, Z	$hP68$, 2	$hP68$, 2
Crystal dimensions, mm ³	0.24×0.13×0.08	0.16×0.11×0.09
Unit cell dimensions:		
a , nm	0.99742(1)	0.99249(4)
c , nm	2.25206(4)	2.24460(9)
V , nm ³	1.94029(4)	1.91479(13)
Calculated density (D_x , g·cm ⁻³)	6.39	6.50
Absorption coefficient (μ , mm ⁻¹)	29.68	32.00
Scan mode	ω	ω
Theta range for data collection, deg.	2.4 ÷ 26.3	2.4 ÷ 26.4
$F(000)$	3156	3202
Range in $h\ k\ l$	$-12 \leq h \leq 11$, $-10 \leq k \leq 12$, $-28 \leq l \leq 23$	$-12 \leq h \leq 11$, $-12 \leq k \leq 11$, $-23 \leq l \leq 28$
Absorption correction: analytical	$T_{\min} = 0.015$; $T_{\max} = 0.091$	$T_{\min} = 0.021$; $T_{\max} = 0.054$
Total no. reflections	12135	12012
Independent reflections	1483 ($R_{\text{int}} = 0.0302$)	1466 ($R_{\text{int}} = 0.0301$)
Reflections with $I > 2\sigma(I)$	1413 ($R_{\text{sigma}} = 0.0156$)	1395 ($R_{\text{sigma}} = 0.0156$)
Weighting scheme	$1/[\sigma(F_o)^2 + (0.0286 \times P)^2 + 35.9319 \times P]$	$1/[\sigma(F_o)^2 + (0.0343 \times P)^2 + 36.7470 \times P]$
Data/parameters	1483/74	1395/74
Goodness-of-fit on F^2	1.172	1.165
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0244$; $wR_2 = 0.0660$	$R_1 = 0.0248$; $wR_2 = 0.0694$
R indices (all data)	$R_1 = 0.0272$; $wR_2 = 0.0686$	$R_1 = 0.0281$; $wR_2 = 0.0735$
Extinction coefficient	0.00025(2)	0.00024(3)
$\Delta\rho_{\text{fin}}$ (max/min), e·Å ⁻³	1.21 and -2.32	1.16 and -2.47

Microstructure and phase analysis

All samples were characterized by means of light optical microscopy (*DM4000M*, Leica Microsystems, Wetzlar, Germany), scanning electron microscopy and energy-dispersive X-ray spectroscopy (*Stereoscan 200*, Cambridge Instruments, Cambridge, UK and *EVO 40*, Carl Zeiss SMT Ltd, Cambridge, UK) with the purpose to examine the microstructure and phase composition. Smooth surfaces of the specimens were prepared by using SiC papers and diamond pastes down to 1 μm grain size. Cobalt standard was used for calibration. X-ray spectra were processed by the software package INCA Energy (Oxford Instruments, Analytical Ltd., Bucks, UK).

Crystal structure determination

Single crystal data sets for R₂₃Ni₇Mg₄ (R = Ce, Pr) and R₄NiMg (R = Tb, Dy, Ho, Er) were collected at room temperature by using a four-circle diffractometer (*Xcalibur Oxford Diffraction*) with CCD detector (graphite monochromatized Mo K α radiation, $\lambda = 0.071073$ nm). Scans were taken in the ω mode, analytical absorption corrections were made by *CrysAlisRed* [6]. Relevant crystallographic details for

the data collection and determination of the structures are listed in **Tables 1, 2**.

The crystal structure of Ce₂₃Ni₇Mg₄ was successfully solved by direct methods using SHELX-97 package programs [7]. Analysis of the systematic absences in the Ce₂₃Ni₇Mg₄ data set indicated $P31c$ (# 159), $P31c$ (# 163), $P6_3mc$ (# 186), $P62c$ (# 190), and $P6_3/mmc$ (# 194) as possible space groups. A statistical test of the distribution of E values [8] suggested that the structure is centrosymmetric with 81.33 % probability. Nevertheless, satisfactory results were obtained neither in $P31c$ nor in $P6_3/mmc$. Following recommendations by Marsh [9] the structure solution and refinement were also performed in non-centrosymmetric groups. In fact, an acceptable structural model was found in space group $P6_3mc$. The occupancy parameters were checked for deviation from the ideal ones in separate series of least-squares cycles. As far as they did not diverge significantly from those corresponding to full occupation, in the final cycles the ideal values were assumed and anisotropic displacement parameters were refined for all atoms. Finally, the ADDSYM algorithm implemented in PLATON [10] was used to search for possibly

Table 2 Crystallographic data for the R_4NiMg (R=Gd, Tb, Dy, Ho, Er) crystals and experimental details of the structure determination.

Empirical formula	Gd ₄ NiMg	Tb ₄ NiMg	Dy ₄ NiMg	Ho ₄ NiMg	Er ₄ NiMg
Structure type	Gd ₄ RhIn	Gd ₄ RhIn	Gd ₄ RhIn	Gd ₄ RhIn	Gd ₄ RhIn
Formula weight, M_r	712.02	718.70	733.02	742.74	752.06
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	$F\bar{4}3m$ (# 216)	$F\bar{4}3m$ (# 216)	$F\bar{4}3m$ (# 216)	$F\bar{4}3m$ (# 216)	$F\bar{4}3m$ (# 216)
Pearson symbol, Z	$cF96$, 16	$cF96$, 16	$cF96$, 16	$cF96$, 16	$cF96$, 16
Crystal dimensions, mm ³	0.18×0.12×0.06	0.17×0.11×0.09	0.23×0.10×0.08	0.15×0.11×0.08	0.20×0.11×0.07
Unit cell dimensions:					
<i>a</i> , nm	1.37472(1)	1.36216(7)	1.35801(2)	1.35227(1)	1.34686(1)
<i>V</i> , nm ³	2.59802(3)	2.5275(2)	2.50443(6)	2.47281(3)	2.44325(3)
Calculated density (D_x , g·cm ⁻³)	7.28	7.555	7.776	7.980	8.178
Absorption coefficient (μ , mm ⁻¹)	43.07	47.057	50.046	53.533	57.324
Scan mode	ω	ω	ω	ω	ω
Theta range for data collection, deg.	2.6 ÷ 26.2	2.6 ÷ 24.0	2.6 ÷ 26.4	2.6 ÷ 26.2	2.6 ÷ 26.4
$F(000)$	4736	4800	4864	4928	4992
Range in $h\ k\ l$	-17 ≤ h ≤ 13, -16 ≤ k ≤ 17, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -14 ≤ k ≤ 15, -13 ≤ l ≤ 15	-15 ≤ h ≤ 16, -16 ≤ k ≤ 16, -14 ≤ l ≤ 16	-16 ≤ h ≤ 16, -13 ≤ k ≤ 16, -16 ≤ l ≤ 16	-16 ≤ h ≤ 14, -16 ≤ k ≤ 16, -12 ≤ l ≤ 16
Absorption correction: analytical	$T_{min} = 0.003$; $T_{max} = 0.075$	$T_{min} = 0.003$; $T_{max} = 0.014$	$T_{min} = 0.002$; $T_{max} = 0.018$	$T_{min} = 0.001$; $T_{max} = 0.014$	$T_{min} = 0.001$; $T_{max} = 0.014$
Total no. reflections	4208	2849	4054	4101	4015
Independent reflections	308	223	299	296	296
($R_{int} = 0.0303$)		($R_{int} = 0.0890$)	($R_{int} = 0.0886$)	($R_{int} = 0.0430$)	($R_{int} = 0.0558$)
Reflections with $I > 2\sigma(I)$	305	195	294	293	293
($R_{sigma} = 0.0111$)		($R_{sigma} = 0.0418$)	($R_{sigma} = 0.0315$)	($R_{sigma} = 0.0153$)	($R_{sigma} = 0.0191$)
Weighting scheme	$1/[\sigma(F_o)^2 + (0.0106 \times P)^2 + 111.549 \times P]$	$1/[\sigma(F_o)^2 + (0.0479 \times P)^2 + 1477.625 \times P]$	$1/[\sigma(F_o)^2 + (0.0309 \times P)^2 + 654.330 \times P]$	$1/[\sigma(F_o)^2 + (0.0129 \times P)^2 + 152.270 \times P]$	$1/[\sigma(F_o)^2 + (0.0294 \times P)^2 + 229.332 \times P]$
Data/parameters	308/20	223/20	299/20	296/20	296/20
Goodness-of-fit on F^2	1.197	1.207	1.999	1.173	1.166
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0144$; $wR_2 = 0.0337$	$R_1 = 0.0493$; $wR_2 = 0.1092$	$R_1 = 0.0406$; $wR_2 = 0.0843$	$R_1 = 0.0163$; $wR_2 = 0.0392$	$R_1 = 0.0219$; $wR_2 = 0.0588$
R indices (all data)	$R_1 = 0.0145$; $wR_2 = 0.0337$	$R_1 = 0.0664$; $wR_2 = 0.1280$	$R_1 = 0.0410$; $wR_2 = 0.0845$	$R_1 = 0.0164$; $wR_2 = 0.0392$	$R_1 = 0.0223$; $wR_2 = 0.0590$
Extinction coefficient	0.000087(6)	0.00006(2)	0.000110(17)	0.000067(6)	0.000113(13)
$\Delta\rho_{fin}$ (max/min), e·Å ⁻³	1.01 and -0.92	4.36 and -2.45	3.01 and -1.64	1.33 and -1.11	1.70 and -1.24

Table 3 EDXS results for the R-Ni-Mg alloys prepared in this work.

R-Ni-Mg alloys	Gross composition (EDXS) R; Ni; Mg	Phase	Phase composition (EDXS) R; Ni; Mg
La	66.0; 23.6; 10.4	La ₂₃ Ni ₇ Mg ₄	67.0; 21.4; 11.6
Ce	65.4; 13.9; 20.7	Ce ₂₃ Ni ₇ Mg ₄	68.6; 20.4; 11.1
Pr	62.9; 17.1; 20.0	Pr ₄ NiMg	63.1; 19.2; 17.7
Gd	69.3; 16.4; 14.3	Gd ₄ NiMg	65.5; 16.2; 18.3
Tb	66.9; 16.4; 16.7	Tb ₄ NiMg	65.5; 18.4; 16.1
Dy	63.9; 16.3; 19.8	Dy ₄ NiMg	62.1; 17.1; 20.8
Ho	62.4; 15.3; 22.3	Ho ₄ NiMg	62.7; 14.3; 23.0
Er	65.9; 16.4; 17.7	Er ₄ NiMg	65.3; 16.0; 18.7

Table 4 Crystal structure data and experimental details of the refinement for La₄NiMg and La₂₃Ni₇Mg₄.

Empirical formula	La ₄ NiMg	La ₂₃ Ni ₇ Mg ₄
Structure type	Gd ₄ RhIn	Pr ₂₃ Ir ₇ Mg ₄
Crystal system	Cubic	Hexagonal
Space group	<i>F</i> $\bar{4}3m$ (# 216)	<i>P</i> 6 ₃ <i>mc</i> (# 186)
Pearson symbol, Z	<i>cF</i> 96, 16	<i>hP</i> 68, 2
2 θ range, deg.; number of points	8.0–100.0; 18401	10.0–100.0; 3001
Step size, deg.	0.005	0.03
Number of generated reflections	111	468
Unit cell parameters:		
<i>a</i> , nm	1.43088(1)	1.01230(8)
<i>c</i> , nm	1.43088(1)	2.28866(21)
<i>V</i> , nm ³	2.92959(3)	2.0311(3)
Number of refined parameters	24	29
Reliability factors, %:		
<i>R</i> _F	0.89	5.10
<i>R</i> _B	1.10	7.34
<i>R</i> _P	1.32	8.30
<i>R</i> _{wp}	1.83	10.6
χ^2	1.53	1.96

missed higher crystallographic symmetry in the tested model, but none was revealed. The crystal structure of Pr₂₃Ni₇Mg₄ was refined taken as starting model the Ce₂₃Ni₇Mg₄ one. The final difference Fourier syntheses were flat in both cases and revealed no significant residual peaks.

The R₄NiMg (R = Tb, Dy, Ho, Er) data sets were compatible with the noncentrosymmetric space group *F* $\bar{4}3m$, in agreement with the investigation on the R₄NiMg series carried out by Tuncel [4]. The atomic parameters of the praseodymium compound were taken as starting model and the structure was refined using SHELX-97 package programs [7] (full-matrix least-squares on *F*_o²) with anisotropic displacement parameters for all atom positions. The sites of all atoms were assumed to be fully occupied.

The atomic positions for all structures reported here were standardized with the *STRUCTURE TIDY* program [11]. X-ray diffraction on powdered samples was performed using Philips X'Pert MPD and STOE STADI P diffractometers (Cu K α radiation, step-by-step scan mode) in order to confirm the crystal structures of the phases. The crystal structure of

La₄NiMg was refined from X-ray powder diffraction data by using the program FULLPROF [12].

Results and discussion

Results of the SEM-EDXS characterization of the R–Ni–Mg samples are listed in Table 3. No impurity elements were detected in the alloys and their measured gross compositions correspond well to the nominal ones. All samples show R₂₃Ni₇Mg₄ or R₄NiMg as main phase.

The La₄NiMg phase, the crystal structure of which has not been reported in the literature, belongs to the R₄NiMg (*cF*96–Gd₄RhIn) isostructural series; crystal structure data and experimental details concerning the Rietveld refinement performed on this compound, together with data for La₂₃Ni₇Mg₄, are listed in Table 4. For details on the crystal chemistry and hydrogenation behavior of R₄NiMg phases we refer to the literature [4].

The hexagonal unit cell of Ce₂₃Ni₇Mg₄ consists of 68 atoms occupying 14 sites. The majority of

Table 5 Atomic coordinates and anisotropic displacement parameters ($\text{nm}^2 \times 10^5$) for the $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ and $\text{Pr}_{23}\text{Ni}_7\text{Mg}_4$ single crystals.

Atom	Wyckoff position	x/a	y/b	z/c	U_{11}	U_{33}	U_{13}	U_{12}	U_{eq}^a
$\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$									
Ce1	6c	0.12942(5)	$\bar{x}$	0.36550(8)	17.8(3)	16.9(5)	0.06(2)	8.5(4)	17.7(2)
Ce2	6c	0.20519(5)	$\bar{x}$	0.21656(8)	17.9(3)	17.0(5)	-0.07(2)	9.9(4)	17.2(2)
Ce3	6c	0.20659(5)	$\bar{x}$	0.05096(8)	19.7(3)	15.0(5)	-0.10(2)	11.2(4)	17.6(2)
Ce4	2a	0	0	0.00000(7)	19.2(5)	13.7(7)	0.0	9.6(3)	17.4(3)
Ce5	6c	0.78679(7)	$\bar{x}$	0.00566(9)	30.9(4)	28.9(7)	-0.19(2)	12.7(5)	31.5(5)
Ce6	6c	0.53904(5)	$\bar{x}$	0.41409(9)	16.6(3)	17.8(5)	-0.05(2)	6.6(3)	17.7(2)
Ce7	6c	0.54305(5)	$\bar{x}$	0.14146(9)	20.7(4)	20.7(5)	-0.05(2)	10.1(4)	20.8(2)
Ce8	6c	0.79287(5)	$\bar{x}$	0.27923(8)	16.3(3)	17.3(5)	0.05(2)	7.9(4)	16.8(2)
Ce9	2b	1/3	2/3	0.3548(1)	18.4(5)	17.2(8)	0.0	9.2(2)	18.0(3)
Ni1	6c	0.47817(12)	$\bar{x}$	0.28905(12)	21.2(8)	25.0(12)	-0.28(4)	11.5(9)	28.9(1)
Ni2	2b	1/3	2/3	0.13537(19)	23.1(12)	15.1(17)	0.0	11.6(6)	20.4(8)
Ni3	6c	0.85636(13)	$\bar{x}$	0.43429(12)	23.9(9)	24.5(12)	0.13(4)	15.7(10)	22.4(5)
Mg1	6c	0.8940(3)	$\bar{x}$	0.1351(3)	13.6(16)	14(2)	-0.06(11)	5(2)	14.6(10)
Mg2	2a	0	0	0.2493(5)	16(3)	19(5)	0.0	7.8(14)	16.7(19)
$\text{Pr}_{23}\text{Ni}_7\text{Mg}_4$									
Pr1	6c	0.12941(5)	$\bar{x}$	0.36544(9)	17.3(3)	16.6(5)	0.06(2)	8.3(4)	17.7(2)
Pr2	6c	0.20520(5)	$\bar{x}$	0.21655(8)	17.5(4)	16.5(5)	-0.06(2)	9.7(4)	16.7(2)
Pr3	6c	0.20659(5)	$\bar{x}$	0.05092(9)	19.3(4)	14.5(5)	-0.09(2)	10.9(4)	17.1(2)
Pr4	2a	0	0	0.00000(7)	18.6(5)	13.3(8)	0.0	9.3(3)	16.8(3)
Pr5	6c	0.78682(7)	$\bar{x}$	0.00565(9)	30.2(5)	28.5(7)	0.18(3)	12.3(5)	30.9(3)
Pr6	6c	0.53905(5)	$\bar{x}$	0.41405(9)	16.2(3)	17.0(5)	-0.05(2)	6.6(4)	17.2(2)
Pr7	6c	0.54307(6)	$\bar{x}$	0.14143(9)	20.4(4)	20.2(6)	-0.05(2)	9.9(4)	20.4(2)
Pr8	6c	0.79286(5)	$\bar{x}$	0.27921(9)	16.1(3)	16.4(5)	0.05(2)	7.7(4)	16.4(2)
Pr9	2b	1/3	2/3	0.35476(10)	18.1(5)	16.5(8)	0.0	9.0(2)	17.6(4)
Ni1	6c	0.47824(13)	$\bar{x}$	0.28898(12)	19.2(8)	23.4(13)	-0.27(4)	10.5(10)	20.2(5)
Ni2	2b	1/3	2/3	0.1353(2)	21.0(12)	13.2(18)	0.0	10.5(6)	18.4(8)
Ni3	6c	0.85630(13)	$\bar{x}$	0.43429(13)	22.0(9)	22.6(13)	0.14(4)	14.8(10)	20.5(5)
Mg1	6c	0.8940(3)	$\bar{x}$	0.1349(3)	10.9(17)	14(3)	-0.05(12)	4(2)	12.8(10)
Mg2	2a	0	0	0.2495(5)	15(3)	15(5)	0.0	7.3(15)	14.6(19)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$, $U_{11} = U_{22}$; $U_{23} = -U_{13}$.

the atom sites display $.m.$ site symmetry, whereas two Ce, one Ni and one Mg atom occupy $3m.$ positions. Standardized atomic positions and anisotropic displacement parameters for $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ and $\text{Pr}_{23}\text{Ni}_7\text{Mg}_4$ are listed in **Table 5**.

Unit cell projections of $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ together with the coordination polyhedra of the atoms are shown in **Fig. 1**. The number of adjacent atoms of the largest atom, Ce, varies from 14 to 15, the polyhedra being always Frank-Kasper or distorted Frank-Kasper polyhedra: $[\text{Ce1Ce}_{10}\text{Ni}_4\text{Mg}]$, $[\text{Ce2Ce}_9\text{Ni}_3\text{Mg}_2]$, $[\text{Ce3Ce}_{10}\text{Ni}_2\text{Mg}_2]$, $[\text{Ce4Ce}_9\text{Ni}_3\text{Mg}_3]$, $[\text{Ce5Ce}_{13}\text{Mg}]$, $[\text{Ce6Ce}_{11}\text{Ni}_3]$, $[\text{Ce7Ce}_{10}\text{Ni}_2\text{Mg}_2]$, $[\text{Ce8Ce}_{10}\text{Ni}_3\text{Mg}_2]$, and $[\text{Ce9Ce}_{12}\text{Ni}_3]$. All the Ni atoms have the same coordination of equatorially tri-capped trigonal prisms of cerium atoms. Both Mg sites are surrounded by icosahedrons of compositions $[\text{Mg1Ce}_9\text{Mg}_3]$ and $[\text{Mg2Ce}_9\text{Mg}_3]$.

Interatomic distances in the $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ compound are listed in **Table 6**. The Mg atoms in $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ form slightly distorted tetrahedra. The

Mg–Mg contacts are 0.315–0.317 nm and correspond well to 0.320 nm in *hcp* elementary Mg. Due to the high cerium content, the Ni atoms appear to be “isolated” in the Ce- and Mg_4 -framework. As a result, the Ni–Ni and Ni–Mg distances exceed by far the sum of metallic radii. All the Ce–Mg contacts match well with the sum of single bond metallic radii (the shortest one is 0.341 nm) [13]. Numerous Ce–Ce distances exist in a broad range up to 0.398 nm, but only the Ce1–Ce5 contacts of 0.347 nm are noticeably shorter than the sum of metalloid radii. As for the R_4NiMg compounds, we can assume that the strongest chemical bonding corresponds to Ce–Ni interactions. The Ce–Ni distances within the NiCe_6 trigonal prisms range from 0.278 to 0.291 nm, that is closer to the sum of covalent radii (0.280 nm) than to the sum of metallic ones (0.307 nm).

The unit cell volume vs. the size of the R^{3+} ion according to Emsley [13] for the series of R_4NiMg and $\text{R}_{23}\text{Ni}_7\text{Mg}_4$ compounds is shown in **Fig. 2**. The difference between single crystal and powder

Table 6 Interatomic distances δ (nm) and coordination numbers (CN) of the atoms in $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$.

δ (nm)	δ (nm)		δ (nm)		δ (nm)		
<i>Frank-Kasper (CN 15)</i>	2Ce5	0.3768(1)	<i>Distorted Frank-Kasper (CN 14)</i>		Ce6	0.3006(3)	
Ce1– 2Ni3	0.2830(2)	2Ce6			0.3785(2)	Ce7	0.3508(3)
Mg2	0.3442(9)	2Ce3			0.3792(1)	2Ce1	0.3581(2)
Ce5	0.3473(3)	<i>Frank-Kasper (CN 15)</i>			<i>Tri-capped trigonal prism (CN 9)</i>		
Ce9	0.3530(1)	Ce4– 3Ni3	0.2889(1)	Ni2– 3Ce2			0.2871(3)
2Ni1	0.3581(2)	3Mg1	0.3551(6)	3Ce3			0.2900(3)
Ce2	0.3601(2)	3Ce5	0.3686(0)	3Ce7			0.3625(0)
2Ce8	0.3685(1)	3Ce3	0.3749(1)	2Ce5	0.3713(2)	<i>Tri-capped trigonal prism (CN 9)</i>	
2Ce6	0.3704(1)	3Ce1	0.3765(1)	2Ce3	0.3761(2)		
Ce4	0.3765(1)	<i>Distorted Frank-Kasper (CN 14)</i>		2Ce8	0.3780(2)		
2Ce1	0.3873(1)			<i>Frank-Kasper (CN 15)</i>			
<i>Frank-Kasper (CN 15)</i>	Ce5– Mg1	0.3454(6)	Ce8– 2Ni1	0.2882(1)	Ni3– 2Ce1	0.2830(2)	
Ce2– Ni2	0.2871(3)	Ce1	0.3473(3)	Mg2	0.3641(2)	Ce3	0.2844(3)
2Ni1	0.2879(2)	2Ce5	0.3594(1)	Ni3	0.3660(3)	Ce4	0.2889(2)
2Mg1	0.3577(4)	2Ni3	0.3629(2)	2Ce1	0.3685(1)	2Ce6	0.2930(2)
2Ce7	0.3587(1)	Ce4	0.3686(1)	Mg1	0.3686(6)	2Ce5	0.3629(2)
Ce1	0.3601(2)	2Ce7	0.3713(2)	2Ce6	0.3746(2)	Ce8	0.3660(3)
Mg2	0.3621(2)	2Ce6	0.3717(2)	2Ce8	0.3776(1)	<i>Icosahedron (CN 12)</i>	
Ce3	0.3729(3)	2Ce3	0.3768(1)	2Ce7	0.3780(2)		
Ce9	0.3820(2)	Ce9	0.3981(3)	2Ce2	0.3831(1)	Mg1– Mg2	0.3157(9)
2Ce8	0.3831(1)	<i>Distorted Frank-Kasper (CN 14)</i>		<i>Frank-Kasper (CN 15)</i>		2Mg1	0.3172(4)
2Ce2	0.3834(1)					Ce6– 2Ni3	0.2930(1)
<i>Distorted Frank-Kasper (CN 14)</i>	Ni1	0.3006(3)	Ce9– 3Ni1	0.2907(2)	Ce5	0.3454(6)	
Ce3– Ni3	0.2844(3)	2Ce1	0.3704(1)	3Ce1	0.3530(1)	Ce4	0.3551(6)
Ni2	0.2899(3)	2Ce5	0.3717(2)	3Ce6	0.3796(1)	2Ce2	0.3577(4)
2Mg1	0.3626(4)	2Ce8	0.3746(2)	3Ce2	0.3820(2)	2Ce3	0.3626(4)
Ce2	0.3729(3)	2Ce3	0.3785(2)	3Ce5	0.3981(3)	Ce8	0.3686(6)
Ce4	0.3749(1)	Ce9	0.3797(1)	<i>Tri-capped trigonal prism (CN 9)</i>		<i>Icosahedron (CN 12)</i>	
2Ce7	0.3761(2)	2Ce6	0.3819(1)				
				2Ce8	0.2882(1)	Mg2– 3Mg1	0.3157(9)
				Ce9	0.2908(2)	3Ce1	0.3442(9)
						3Ce2	0.3621(2)
						3Ce8	0.3641(2)

data is negligible and was not distinguished in the plot. The graph confirms the effect of the lanthanide contraction. Ignoring Y_4NiMg , the volume exhibits an approximately linear increase. Our results match perfectly those taken from the literature.

A careful analysis of the crystal structure of $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ (taken as representative of the $\text{R}_{23}\text{Ni}_7\text{Mg}_4$ series) revealed interesting relations with other binary and ternary phases.

For example the $\text{Ce}_{24}\text{Co}_{11}$ structure type (*hP70*) [14], with $\text{Nd}_{24}\text{Co}_{11}$ as only known isostructural binary phase [15], is an interstitial variant of the $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ structure. The site of the interstitial Ce10 atom corresponds to tetrahedral voids in Mg_4 fragments. Due to the similarity in the cerium content and the crystal structure, the unit cell parameters of the two phases are similar and the atomic parameters can be

easily compared (Table 7). All nine Ce positions in $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ correspond to Ce ones in $\text{Ce}_{24}\text{Co}_{11}$, whereas the Ni and Mg atoms have Co analogues.

The cerium richest Ce-Ni compound is Ce_7Ni_3 (*P6₃mc*, *hP20*, $a = 0.992(2)$, $c = 0.633(2)$ nm) [16]. It appears that $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ contains fragments corresponding to the Ce_7Ni_3 unit cell, as shown in Fig. 3a. In other words, the $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ structure can be interpreted as an inhomogeneous linear intergrowth of Ce_7Ni_3 slabs that alternate with slabs of “ Ce_9NiMg_4 ” composition. The combination of these constitutive fragments can be represented by the equation $2 \text{Ce}_{14}\text{Ni}_6 + 2 \text{“Ce}_9\text{NiMg}_4\text{”} = 2 \text{Ce}_{23}\text{Ni}_7\text{Mg}_4$.

The existence of the $\text{Yb}_{23}\text{Cu}_7\text{Mg}_4$ intermetallic phase with hexagonal symmetry (*P6₃/mmc*, *hP68*) was recently reported [17]; the lattice parameters of this phase ($a = 1.1866(2)$; $c = 2.34371(5)$ nm) are similar

Fig. 1 Unit cell projections of the $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ structure. The coordination polyhedra of the atoms are shown; symmetries of the central atoms are indicated in parentheses.

Table 7 The atoms distribution in the $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ phase and in its interstitial variant $\text{Ce}_{24}\text{Co}_{11}$.

$\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ (hP68)					$\text{Ce}_{24}\text{Co}_{11}$ (hP70)				
Atom	Wyck.	x/a	y/b	z/c	Atom	Wyck.	x/a	y/b	z/c
Ce1	6c	0.12942(5)	$\bar{x}$	0.36550(8)	Ce7	6c	0.1245(6)	$\bar{x}$	0.3528(6)
Ce2	6c	0.20519(5)	$\bar{x}$	0.21656(8)	Ce1	6c	0.2011(7)	$\bar{x}$	0.2070
Ce3	6c	0.20659(5)	$\bar{x}$	0.05096(8)	Ce2	6c	0.2016(8)	$\bar{x}$	0.0442(6)
Ni1	6c	0.47817(12)	$\bar{x}$	0.28905(12)	Co3	6c	0.4819(16)	$\bar{x}$	0.2780(12)
Ce6	6c	0.53904(5)	$\bar{x}$	0.41409(9)	Ce5	6c	0.5420(6)	$\bar{x}$	0.4013(6)
Ce7	6c	0.54305(5)	$\bar{x}$	0.14146(9)	Ce6	6c	0.5414(5)	$\bar{x}$	0.1322(6)
Ce5	6c	0.78679(7)	$\bar{x}$	0.00566(9)	Ce4 ^a	6c	0.7935(8)	$\bar{x}$	-0.0021(6)
Ce8	6c	0.79287(5)	$\bar{x}$	0.27923(8)	Ce3	6c	0.7971(6)	$\bar{x}$	0.2656(6)
Ni3	6c	0.85636(13)	$\bar{x}$	0.43429(12)	Co1	6c	0.8544(19)	$\bar{x}$	0.4308(12)
Mg1	6c	0.8940(3)	$\bar{x}$	0.1351(3)	Co2	6c	0.8497(21)	$\bar{x}$	0.1189(15)
Ni2	2b	1/3	2/3	0.13537(19)	Co4	2b	1/3	2/3	0.1225(27)
Ce9	2b	1/3	2/3	0.3548(1)	Ce8	2b	1/3	2/3	0.3423(8)
Ce4	2a	0	0	0.00000(7)	Ce9	2a	0	0	0.0000(10)
Mg2	2a	0	0	0.2493(5)	Co5	2a	0	0	0.2744(22)
<i>inclusion</i>					Ce10	2a	0	0	0.1544(12)

^a atom coordinates were not standardized for clearness

Fig. 2 Unit cell volume of cubic R_4NiMg and hexagonal $R_{23}Ni_7Mg_4$ phases vs. size of R^{3+} ions.

Fig. 3 a) 2D intergrowth of Ce_7Ni_3 and " Ce_9NiMg_4 " slabs in $Ce_{23}Ni_7Mg_4$; b) packing of trigonal prisms in the structures of $Yb_{23}Ni_7Mg_4$ and $Ce_{23}Ni_7Mg_4$.

Fig. 4 a) Gd₄NiMg as a 3D intergrowth of nested polyhedra units; b) Group-subgroup relation in the Bärnighausen formalism for Ti₂Ni and Gd₄NiMg together with the W₃Fe₃C and AuSTa₅ structures. The index of the *translationengleiche* transition (*t*₂), the evolution of the atomic parameters, and the origin shift are given.

to those of Ce₂₃Ni₇Mg₄. In order to show the crystal chemical relation between these two structures, the packing of trigonal prisms (TP) around Cu/Ni was emphasized (Fig. 3b). In both structures one may distinguish layers of single prisms, whose axes are parallel to the [001] direction; the prisms of each layer are rotated by 60° with respect to those belonging to the subsequent layer. These layers are separated by

twinned TP slabs, which are different in the two structures. Each TP slab may be viewed as an intergrowth of two sub-layers of trigonal prisms. The building blocks of each sub-layer are triple trigonal prisms (three trigonal prisms that share base edges so that a tetrahedral void is formed at the center), which are condensed in two dimensions via vertices. In Yb₂₃Cu₇Mg₄ these sub-layers are stacked two by two

by sharing TP faces; alternating twinned trigonal prism slabs are related by a mirror plane. Differently, in $\text{Ce}_{23}\text{Ni}_7\text{Mg}_4$ the sub-layers form pairs by sharing vertices of the triple trigonal prisms and each sub-layer is screwed by 60° with respect to the other one. A 3D network with similar triple trigonal prisms has been described also for R_4TMg compounds [4,5], so this feature appears to be common to all rare earth rich ternaries discussed in this report.

The cubic unit cell of the R_4NiMg compounds contains 96 atoms and is thus relatively large. This is the reason why we decided to describe the structure according to the idea developed in Chabot *et al.* [18] as a combination of nested polyhedra units (3D intergrowth series). In [18], seven different polyhedral units were proposed as basic ones. With respect to the spatial arrangement of the nested polyhedra units, selected cubic structures were divided into two groups, with isolated and linked units, respectively. The linked building blocks of Gd_4NiMg have been outlined in Fig. 4a: unit A (22 atoms, $\text{Gd}_6\text{Mg}_4\text{Gd}_{12}$) and unit B (26 atoms, $\text{Gd}_4\text{Ni}_4\text{Gd}_6\text{Gd}_{12}$) correspond to Ti_2Ni and γ -brass units, following Chabot *et al.* Unit A contains the following concentric geometrical elements starting from its centre: octahedron, tetrahedron, cubooctahedron; unit B: inner tetrahedron, outer tetrahedron, octahedron and cubooctahedron. The Ti_2Ni structure type ($Fd\bar{3}m$, $cF96$) has the same packing of units [19]. This fact indicates that a group-subgroup relation [20,21] may exist between the Ti_2Ni and R_4NiMg structures. The relations between the Wyckoff positions were checked with the aid of the computer program *POWDER CELL* [22].

The reduction of the symmetry on passing from Ti_2Ni to R_4NiMg corresponds to the loss of the 3 axis, caused by the ordered occupation of the Ni positions ($32e$) by different atoms. The space group symmetry is lowered from $F4_1/d\bar{3}2/m$ to $F\bar{4}3m$ by a *translationengleiche* reduction of index 2 (t2). The resulting two 16-multiplicity positions ($16e$) are occupied by nickel and magnesium atoms (see scheme in Fig. 4b), respectively. The Ti positions in the “parent” Ti_2Ni structure ($48f$, $16c$) correspond to rare earth atoms locations ($24g$, $24f$, $16e$) in R_4NiMg . In these structures a number of octahedral voids exist, among which those corresponding to $16d$ and $16e$ positions. Inclusion variants of the Ti_2Ni and Gd_4RhIn types are $\text{W}_3\text{Fe}_3\text{C}$ [23] and AuSTa_5 [24], respectively, where carbon and sulfur atoms occupy the $16d$ and $16e$ sites. The group-subgroup relations for the latter structures (also shown in Fig. 4b) are identical to those discussed above.

References

[1] S. De Negri, M. Giovannini, A. Saccone, *J. Alloys Compd.* 397 (2005) 126-134.

[2] S. De Negri, M. Giovannini, A. Saccone, *J. Alloys Compd.* 439 (2007) 109-113.
 [3] S. De Negri, M. Giovannini, A. Saccone, *J. Alloys Compd.* 427 (2007) 134-141.
 [4] S. Tuncel, J.G. Roquefère, C. Stan, J.L. Bobet, B. Chevalier, E. Gaudin, R.D. Hoffmann, U.Ch. Rodewald, R. Pöttgen, *J. Solid State Chem.* 182 (2009) 229-235.
 [5] S. Tuncel, W. Hermes, B. Chevalier, U.Ch. Rodewald, R. Pöttgen, *Z. Anorg. Allg. Chem.* 634 (2008) 2140-2144.
 [6] *CrysalisRed, CCD data reduction GUI, version 1.171.29.2*, Oxford Diffraction Poland Sp., 2005.
 [7] G.M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement and SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997.
 [8] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837-838.
 [9] R.E. Marsh, *Acta Crystallogr. B* 51 (1995) 897-907.
 [10] A.L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2002.
 [11] L. Gelato, E. Parthé, *J. Appl. Crystallogr.* 20 (1987) 139-143.
 [12] J. Rodriguez-Carvajal, *FULLPROF SUITE*, LLB Saclay and LCSIM Rennes, France, 2003.
 [13] J. Emsley, *Elements*, Mir, Moscow, 1993, 256 p. (in Russian, translated).
 [14] A.C. Larson, D.T. Cromer, *Acta Crystallogr.* 15 (1962) 1224-1227.
 [15] P.P. Singh, A. Raman, *Mater. Res. Bull.* 3 (1968) 843-854.
 [16] R.B. Roof Jr, A.C. Larson, D.T. Cromer, *Acta Crystallogr.* 14 (1961) 1084-1087.
 [17] S. De Negri, A. Saccone, P. Rogl, G. Giester, *Intermetallics* 16 (2008) 1285-1291.
 [18] B. Chabot, K. Cenzual, E. Parthé, *Acta Crystallogr. A* 37 (1981) 6-11.
 [19] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Vols. 1-4, 2nd Ed., ASM International, Materials Park, OH, 1991.
 [20] H. Bärnighausen, *Commun. Math. Comput. Chem.* 9 (1980) 139-175.
 [21] Th. Hahn (Ed.), *International Tables for Crystallography*, 2nd Ed., Kluwer Academic Publishers, Dordrecht, 1989.
 [22] G. Nolze, *POWDER CELL, Computer program for the calculation of X-ray powder diagrams*, Bundesanstalt für Materialforschung, Berlin, 1996.
 [23] Z. Bojarski, J. Leciejewicz, *Arch. Hutn.* 12 (1967) 255-263.
 [24] B. Harbrecht, V. Wagner, C. Pietzonka, *J. Solid State Chem.* 139 (1998) 45-51.