ELSEVIER

Journal of Alloys and Compounds 311 (2000) 228–233

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Crystal structure of R_2Ni_2Pb (R=Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds

L.D. Gulay[a,*,1], Ya.M. Kalychak[b], M. Wołcyrz[a]

[a] *W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna Street 2, PO Box 1410, 50-950 Wroclaw, Poland*

[b] *Department of Inorganic Chemistry, L'viv Ivan Franko National University, Kyryla and Mefodia Street 6, 79005 L'viv, Ukraine*

Received 4 June 2000; accepted 20 June 2000

Abstract

The crystal structures of the R_2Ni_2Pb (R=Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds were determined using X-ray powder diffraction. The investigated compounds crystallize with Mn_2AlB_2 structure type (space group *Cmmm*, Pearson code *oC10*). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ternary intermetallic compounds; Crystal structure; X-ray diffraction

1. Introduction

Several series of the isostructural ternary compounds were found during a systematic investigation of the phase relations in the R–Ni–Pb (R is a rare earth metal) systems. The absence in literature of any information about the existence of the R_2Ni_2Pb ternary compounds have led us to study the crystal structure of these new ternary plumbides. The results of the crystal structure determination of the R_2Ni_2Pb (R=Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds are given in the present paper.

2. Experimental

The samples with total mass of about 1 g were prepared by arc melting of the pure metals (the purity of the ingredients was better than 99.9 wt.%) in a high-purity argon atmosphere. All alloys were remelted twice to ensure homogeneity. The losses after the melting were less than 1 wt.%. After melting, the samples were sealed in evacuated quartz ampoules. The ampoules with samples were annealed at 870 K for 720 h. After the annealing the ampoules were quenched in cold water.

X-ray powder diffraction patterns of the samples were recorded using a DRON-3M powder diffractometer (CuKα radiation, $15° \leq 2\Theta \leq 80°$, step scan mode with a step size of 0.05° and counting time of 6 s per data point). The phase analysis was carried out and lattice parameters were determined using these data. The diffraction data for the crystal structure determination were collected using a Siemens D5000 powder diffractometer (CuKα radiation, $10° \leq 2\Theta \leq 120°$, step scan mode with a step size of 0.02° and counting time of 19 s per data point).

Lattice parameters were calculated using least squares method. Crystal structure determination was performed using the DBWS-9411 program [1].

3. Results and discussion

Compounds with $R_{40}Ni_{40}Pb_{20}$ composition were found during the phase analysis of the samples in the R–Ni–Pb (R=Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) systems at 870 K. The crystal structures of the compounds were determined using X-ray powder diffraction. X-ray powder diffraction patterns were indexed assuming an orthorhombic unit cell with the lattice parameters listed in Table 1. The composition of the samples, intensities of reflections and calculated lattice parameters proved that these compounds

---

*Corresponding author.

E-mail address: damm@highscreen.int.pan.wroc.pl (L.D. Gulay).

[1] On leave from the Inorganic Chemistry Department, L'viv National University, L'viv, Ukraine.

0925-8388/00/$ – see front matter
PII: S0925-8388(00)01105-1

Table 1
Cell parameters and calculated density for the R_2Ni_2Pb (R=Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)	Calculated density (g/cm^3)
Y_2Ni_2Pb	4.019(1)	14.008(3)	3.679(1)	207.1(2)	8.056
Sm_2Ni_2Pb	4.087(1)	14.187(3)	3.716(1)	215.5(2)	9.638
Gd_2Ni_2Pb	4.0619(9)	14.107(2)	3.6942(9)	211.7(1)	10.026
Tb_2Ni_2Pb	4.043(1)	14.055(4)	3.670(1)	208.5(2)	10.230
Dy_2Ni_2Pb	4.026(1)	13.994(4)	3.651(1)	205.7(2)	10.487
Ho_2Ni_2Pb	4.0172(4)	13.9695(6)	3.6336(3)	203.91(5)	10.658
Er_2Ni_2Pb	4.008(1)	13.931(4)	3.617(1)	202.0(2)	10.838
Tm_2Ni_2Pb	3.9910(3)	13.8952(6)	3.5992(2)	199.60(3)	11.022
Lu_2Ni_2Pb	3.9844(9)	13.851(2)	3.5801(9)	197.6(1)	11.338

Table 2
Results of the crystal structure determination for the R_2Ni_2Pb (R=Ho, Tm) compounds

	Ho_2Ni_2Pb	Tm_2Ni_2Pb
Space group	*Cmmm*	*Cmmm*
a (Å)	4.0172(4)	3.9910(3)
b (Å)	13.9695(6)	13.8952(6)
c (Å)	3.6336(3)	3.5992(2)
V ($Å^3$)	203.91(5)	199.60(3)
Number of atoms in cell	10	10
Number of formula units per unit cell	2	2
Calculated density (g/cm^3)	10.658	11.022
Radiation and wavelength (Å)	Cu 1.54178	Cu 1.54178
Diffractometer	Siemens D5000	Siemens D5000
Mode of refinement	Full profile	Full profile
R_P	0.0382	0.0431
R_{wP}	0.0493	0.0566

are isostructural with the Mn_2AlB_2 structure type (space group *Cmmm*) [2]. The results of the crystal structure determination for the R_2Ni_2Pb (R=Ho, Tm) compounds are listed in Table 2, and atomic and thermal parameters are given in Table 3.

The projection of the crystal structure of the Tm_2Ni_2Pb compound on the *xy* plane and the coordination polyhedra of the Tm (a), Ni (b) and Pb (c) atoms are presented in Fig. 1. The Tm atoms form 17 vertices (c.n.=17), the Ni atoms form trigonal prisms with three additional atoms (c.n.=9) and the Pb atoms form distorted tetrahexahedrons (c.n.=14). Similar coordination polyhedra exist in the Ho_2Ni_2Pb compound.

Table 3
Atomic and thermal parameters for the R_2Ni_2Pb (R=Ho, Tm) compounds

Atom	Position	Ho_2Ni_2Pb	Tm_2Ni_2Pb
R	4(j) 0*y*1/2		
	y	0.3599(1)	0.3607(2)
	$B_{eq.}$ ($Å^2$)	1.33(8)	1.20(7)
Ni	4(i) 0*y*0		
	y	0.1986(6)	0.1964(5)
	$B_{eq.}$ ($Å^2$)	1.7(1)	1.6(1)
Pb	2(a) 000		
	$B_{eq.}$ ($Å^2$)	1.12(6)	0.93(5)

The interatomic distances (δ), Δ values ($\Delta=100(\delta-\Sigma_r)/\Sigma_r$, Σ_r is the sum of the respective atomic radii) and coordination numbers of the atoms for the R_2Ni_2Pb (R=Ho, Tm) compounds are listed in Table 4 (values of atomic radii are taken from [3]). Practically all R–Ni, R–Pb and Ni–Pb interatomic distances are significantly shorter than the sum of the respective atomic radii. The distances between the same sort of the atoms are close or longer than the sum of the atomic radii.

The Tm atoms form layers consisting of Ni centered trigonal [$NiTm_6$] prisms and Pb centered slightly distorted cubes [$PbTm_8$] (Fig. 2). Such a formation is very stable. The interactions between the Ni and Tm atoms in the trigonal prisms and the Pb and Tm atoms in the cubes are strong (the respective interatomic distances are significantly shorter than the sum of the atomic radii). Every cube is surrounded by two trigonal prisms and four another cubes. The interactions between the Ni and Pb atoms

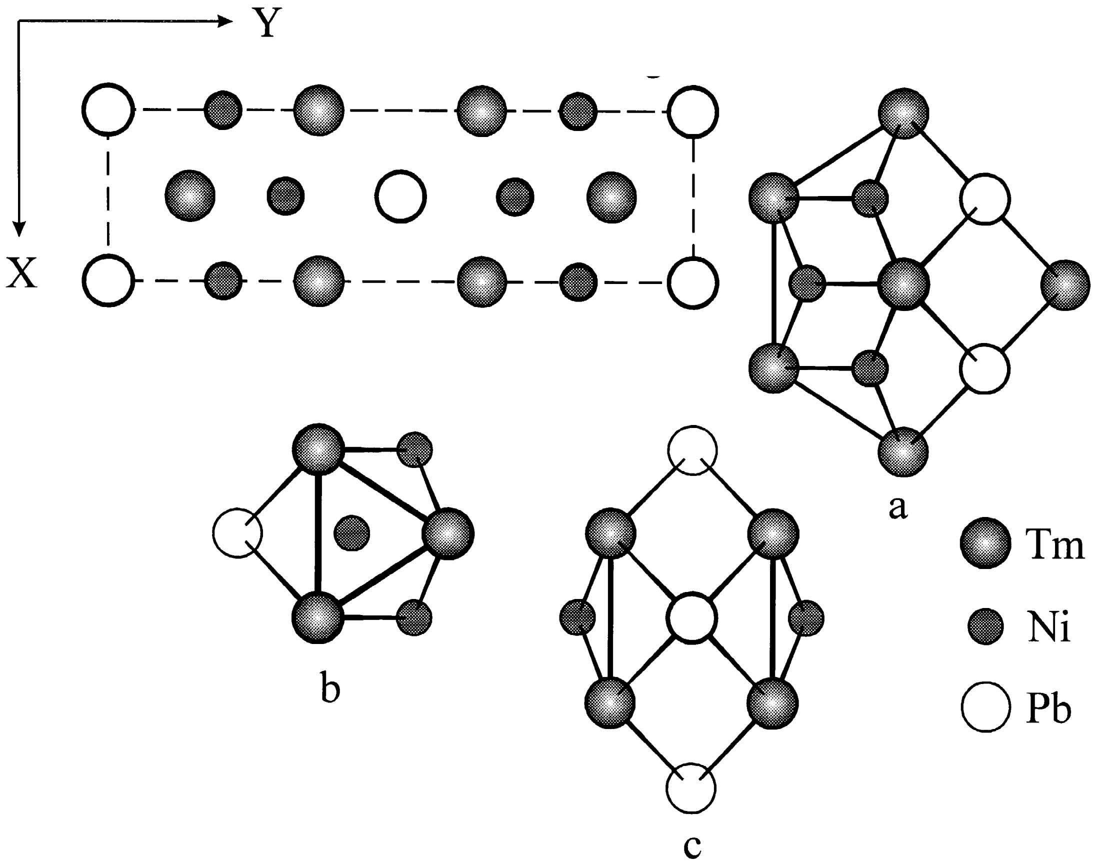

Fig. 1. Projection of the crystal structure of Tm_2Ni_2Pb on the *xy* plane and coordination polyhedra of the Tm (a), Ni (b) and Pb (c) atoms.

which centre trigonal prisms and cubes are strong ($\Delta = -8.73$). The Pb–Pb interactions are rather weak ($\Delta = +2.83$ and $+14.03$ along *z* and *x* axes, respectively). Every trigonal prism is surrounded by two trigonal prisms and one cube. The Ni–Ni interaction is not significant in the *xy* plane ($\Delta = +0.41$) and absent along the *z* axis (the Ni–Ni distances are significantly longer than the sum of the atomic radii in this direction).

Table 4
Interatomic distances (δ, Å), Δ values ($\Delta = 100(\delta - \Sigma_r)/\Sigma_r$, Σ_r is the sum of the respective atomic radii) and coordination numbers of the atoms for the R_2Ni_2Pb (R = Ho, Tm) compounds

Atoms		R = Ho		R = Tm		c.n.
		δ (Å)	Δ	δ (Å)	Δ	
R–	4Ni	2.829(3)	−5.70	2.802(2)	−5.98	17
	2Ni	2.894(7)	−3.52	2.907(6)	−2.45	
	4Pb	3.3415(9)	−4.80	3.312(2)	−5.11	
	2R	3.6336(3)	+3.23	3.5992(2)	+3.43	
	2R	3.669(2)	+4.24	3.667(3)	+5.37	
	1R	3.914(2)	+11.20	3.871(4)	+11.24	
	2R	4.0172(4)	+14.13	3.9910(3)	+14.68	
Ni–	2Ni	2.469(7)	−0.44	2.490(6)	+0.41	9
	1Pb	2.774(8)	−7.21	2.729(7)	−8.73	
	4R	2.829(3)	−5.70	2.802(2)	−5.98	
	2R	2.894(7)	−3.52	2.907(6)	−2.45	
Pb–	2Ni	2.774(8)	−7.21	2.729(7)	−8.73	14
	8R	3.3415(9)	−4.80	3.312(2)	−5.11	
	2Pb	3.6336(3)	+3.82	3.5992(2)	+2.83	
	2Pb	4.0172(4)	+14.78	3.9910(3)	+14.03	

The crystal structure of the Tm_2Ni_2Pb compound can be described as a packing of the columns of the Tm-centered distorted pentagonal $[TmNi_6Pb_4]$ prisms along *z* axis (Fig. 3). Such a formation is very stable. All Tm–Ni and Tm–Pb distances are shorter than sum of the respective atomic radii (Δ values are equal to -5.98 and -2.45 for Tm–Ni and -5.11 for Tm–Pb distances). The interactions between the Tm atoms in the centered pentagonal prisms are not significant (all Tm–Tm distances are longer than the sum of the atomic radii).

The presented packings of trigonal prisms and cubes (Fig. 2) and pentagonal prisms (Fig. 3) are typical for ternary compounds with Mn_2AlB_2 structure type.

It is possible to describe the structure of the Tm_2Ni_2Pb compound as a packing of empty distorted $[ETm_4Ni_2]$ (a), $[ETm_4Ni_1Pb_1]$ (b), $[ETm_4Pb_2]$ (c) octahedrons (Fig. 4) or $[ETm_2Ni_4]$ (a), $[ETm_2Ni_2Pb_2]$ (b), $[ETm_2Pb_4]$ (c) octahedrons (Fig. 5). The distances between the atoms which form octahedrons are shorter than the sum of the respective atomic radii in all cases. Such two types of the packings of the empty octahedrons are stable.

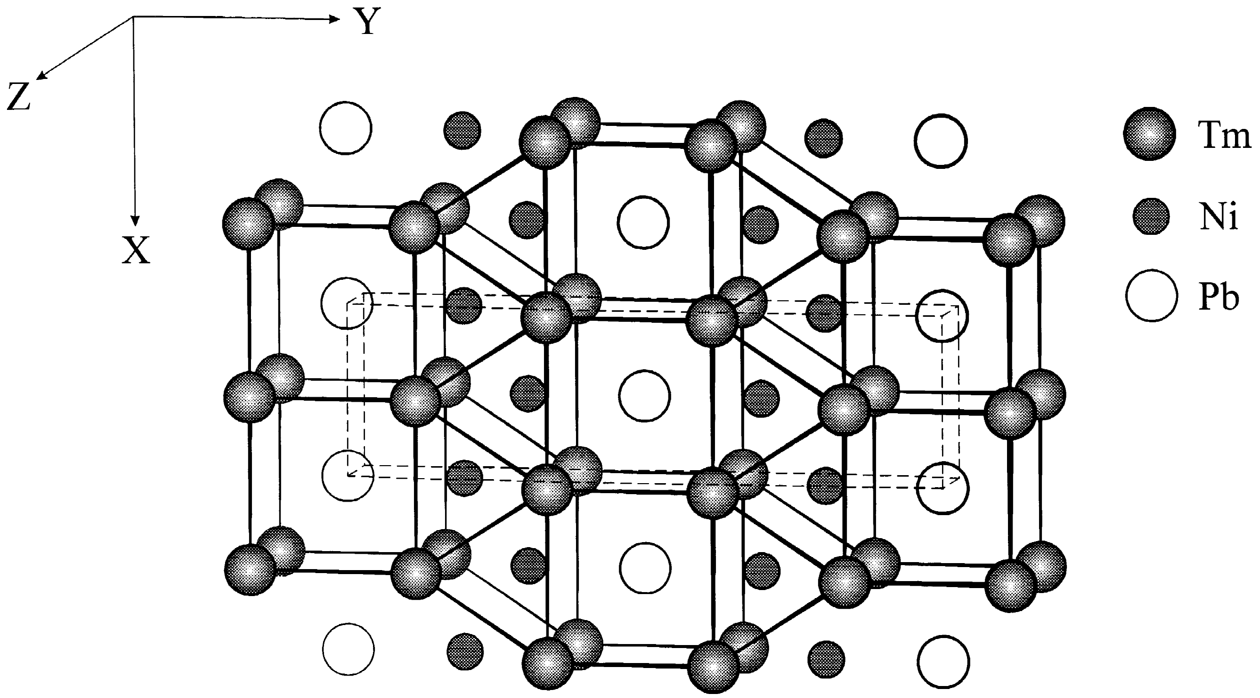

Fig. 2. Trigonal [$NiTm_6$] prisms and slightly distorted [$PbTm_8$] cubes in the Tm_2Ni_2Pb compound.

The unit cell volumes of the R_2Ni_2Pb (R=Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds are shown in Fig. 6. The decreasing values of the unit cell volumes are in good agreement with the decreasing atomic radii of the rare earth metals. The calculated density of the compounds are correlated with the atomic masses of the rare earth metals and cell volumes of the respective compounds.

The R_2Ni_2In compounds with Mn_2AlB_2 structure exist

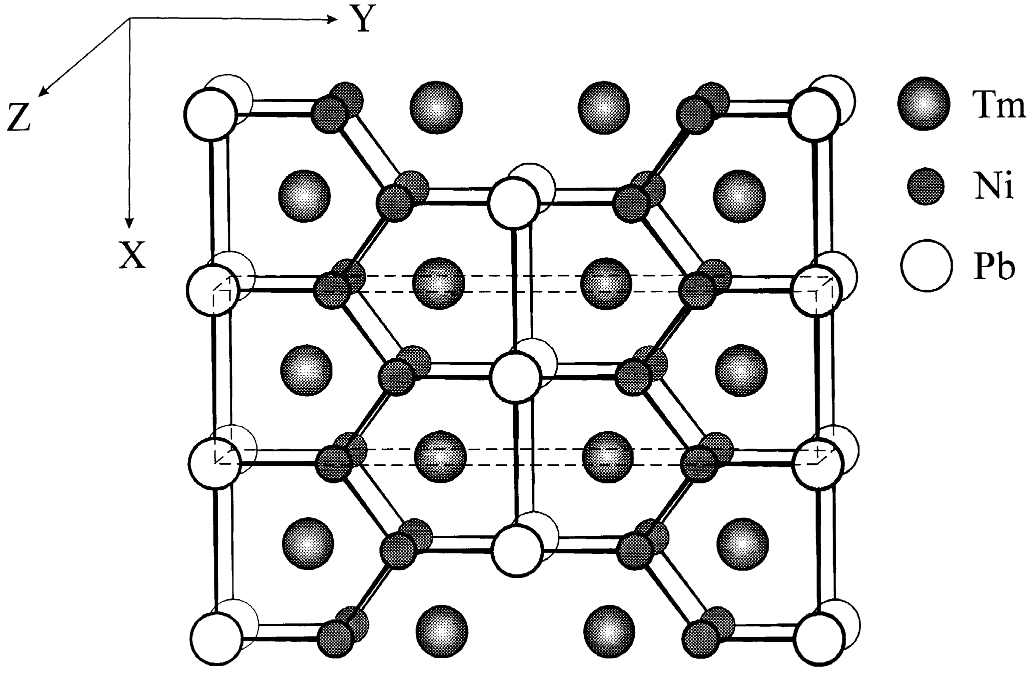

Fig. 3. Pentagonal [$TmNi_6Pb_4$] prisms in the Tm_2Ni_2Pb compound.

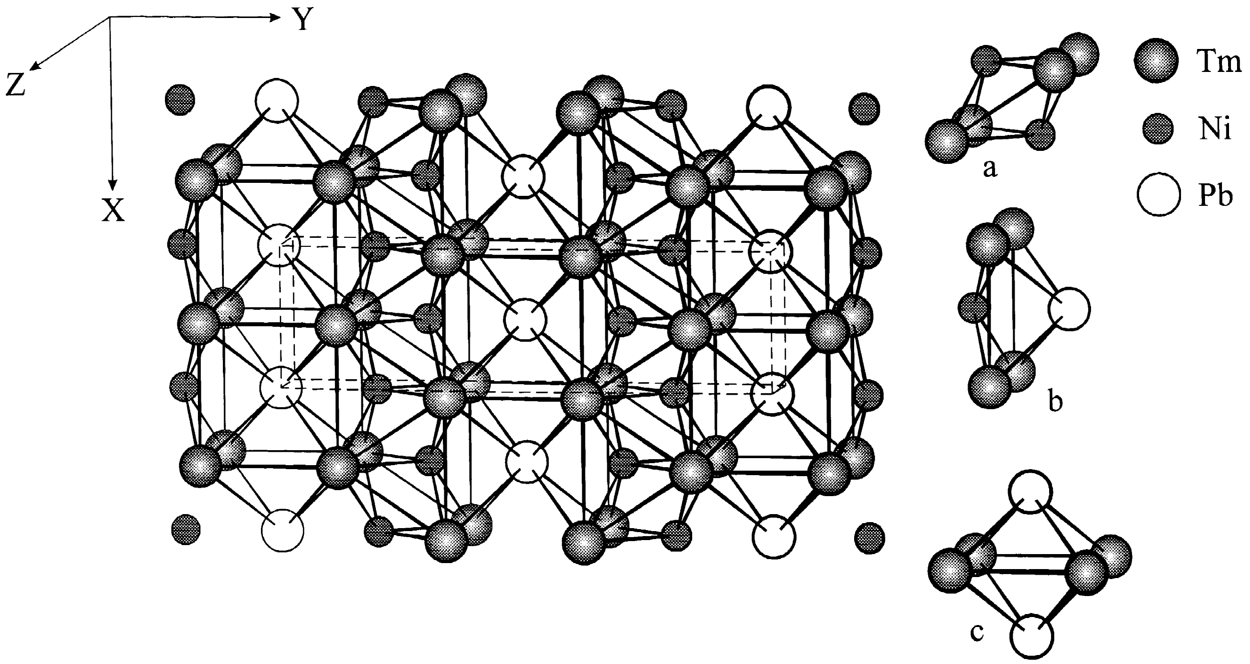

Fig. 4. Empty distorted [ETm_4Ni_2] (a), [ETm_4Ni_1Pb_1] (b) and [ETm_4Pb_2] (c) octahedrons in the Tm_2Ni_2Pb compound.

in the R–Ni–In systems [4]. The lattice parameters of the R_2Ni_2Pb compounds are close to the respective indium ones. The compounds with Mn_2AlB_2 structure are not formed in the R–Ni–Sn systems.

Acknowledgements

Dr. Lubomir Gulay is grateful to the Sniadecki Brothers Foundation for the financial support of his research project

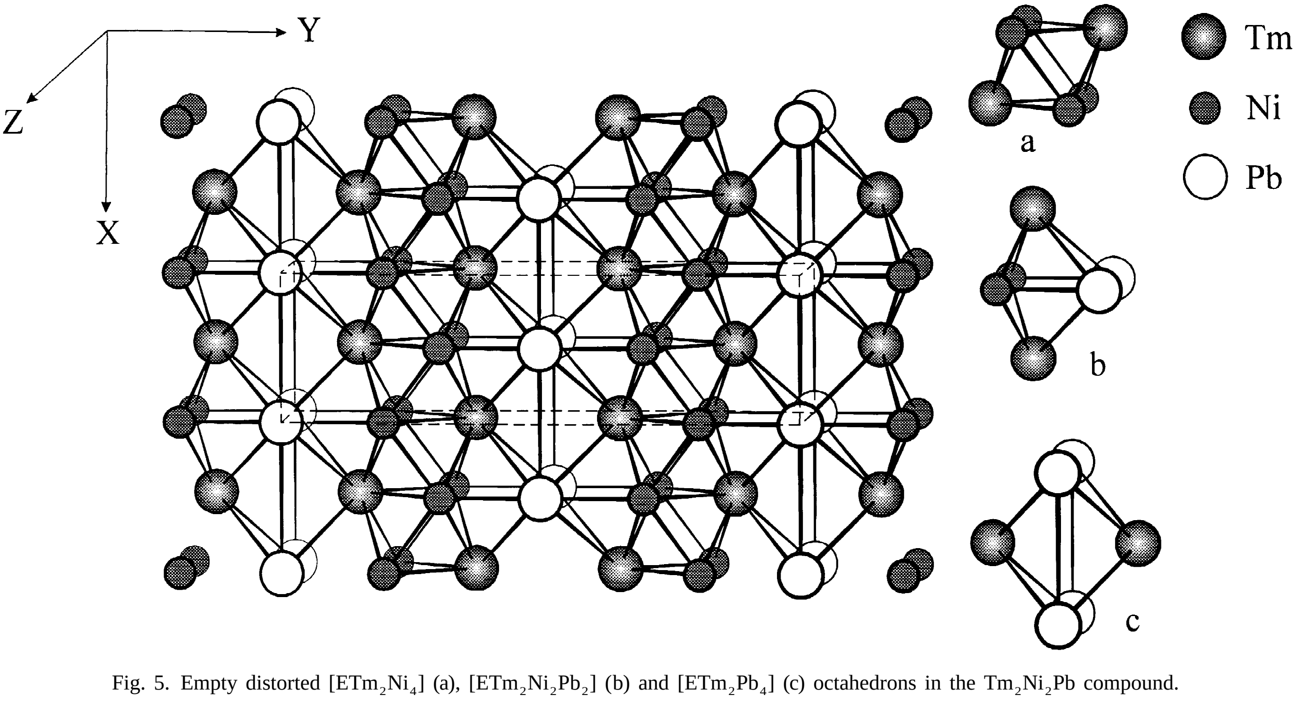

Fig. 5. Empty distorted [ETm_2Ni_4] (a), [ETm_2Ni_2Pb_2] (b) and [ETm_2Pb_4] (c) octahedrons in the Tm_2Ni_2Pb compound.

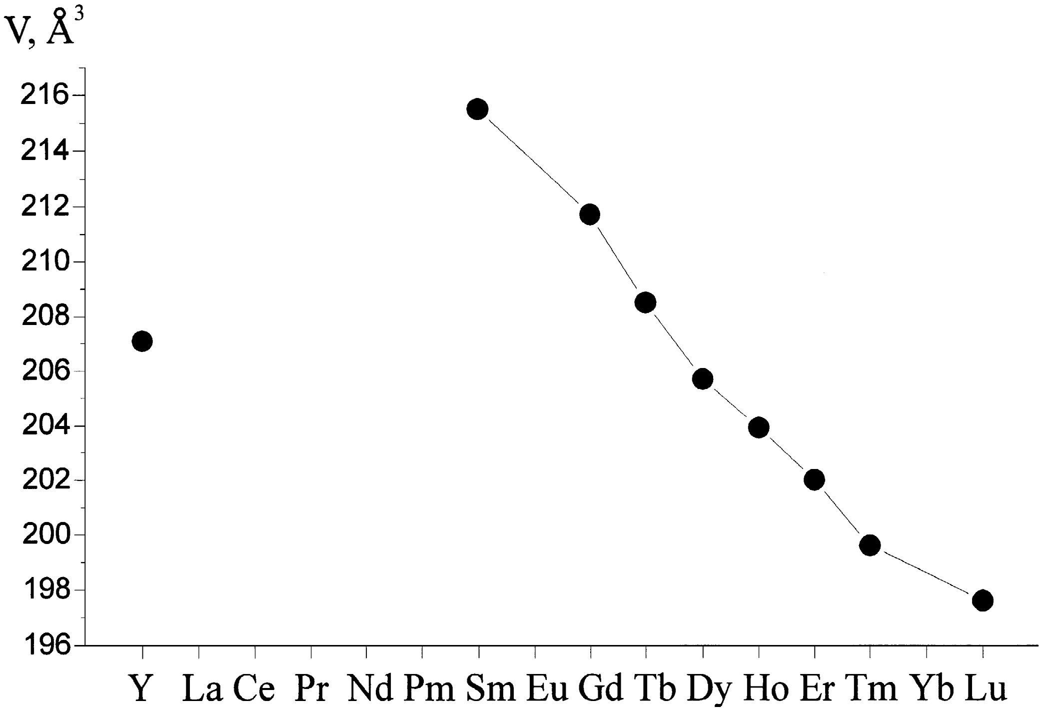

Fig. 6. Unit cell volumes for R_2Ni_2Pb (R = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) compounds.

in the W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences.

References

[1] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paria-Santos, Program DBWS-9411 for Rietveld analysis of the X-ray and neutron powder diffraction patterns, Georgia Inst. of Technology, Atlanta, 1995.

[2] H.I. Becher, K. Krogmann, E. Peisker, Z. Anorg. Chem. 344 (1966) 140.

[3] G.B. Bokij, Kristallokhimija, Nauka, Moskwa, 1971.

[4] Ya.M. Kalychak, V.I. Zaremba, V.M. Baraniak, P.Yu. Zavalij, V.A. Bruskov, L.V. Sysa, O.V. Dmytrah, Izvestija AN SSSR, Neorganicheskije Materialu 26 (1) (1990) 94.