Chemistry of
Metals and Alloys

Chem. Met. Alloys 5 (2012) 142-147
Ivan Franko National University of Lviv
www.chemetal-journal.org

$Zr_6Cu_4Al_3$ – a new ternary disordered derivative with the rhombohedral W_6Fe_7 structure type

Yuriy VERBOVYTSKYY[1,2,3]*

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
[2] *M. Smoluchowski Institute of Physics, Jagiellonian University,*
Reymonta 4, 30-059 Kraków, Poland
[3] *Departamento de Química, Instituto Tecnológico e Nuclear/CFMC-UL,*
Estrada Nacional 10, P-2686-953 Sacavém Codex, Portugal
* *Corresponding author. E-mail: yuryvv@bigmir.net*

Received October 11, 2012; accepted December 26, 2012; available on-line July 5, 2013

The ternary aluminide $Zr_6Cu_4Al_3$ was prepared by arc melting. Its crystal structure was studied by X-ray powder diffraction for the first time. The above mentioned intermetallic compound crystallizes with the rhombohedral W_6Fe_7 structure type (space group *R*-3*m*, Pearson symbol *hR*39, *Z* = 3). Isostructural phases were observed in the systems Hf–Cu–Al, Nb–Cu–Al, Ta–Cu–Al, Zr–Ag–Al, and Hf–Ag–Al.

Zirconium / Ternary aluminides / X-ray diffraction / Crystal structure

Introduction

The ternary Zr–Cu–Al system is well explored among the glass-forming systems. Zr-based bulk-metallic glasses are of interest due to their unique properties, such as high strength, low coefficients of friction, high wear resistance, low shrinkage during cooling, and almost perfect as-cast surfaces, making them promising materials for industrial applications [1,2].

Special attention has been devoted to the investigation of the phase diagram of the Zr–Cu–Al system at different temperatures, and to the synthesis and characterization of ternary intermetallic phases [3]. The isothermal sections at 400°C and 500°C in the Al-rich part were reported in [4] and [5], respectively. A determination of the isothermal section at 800°C in the whole concentration range was also reported in [5] and [6]. Recent studies of the Zr–Cu–Al system were performed at 1000°C and 1100°C [7]. Seven ternary compounds with established structures are known so far. The compounds $ZrCu_{0.5}Al_{2.5}$ [4], $ZrCu_{0.4-1.0}Al_{1.6-1.0}$ [5], $ZrCu_{5.5-6.7}Al_{6.5-5.3}$ [5], $Zr_6Cu_{16}Al_7$ [5], $ZrCu_2Al$ [8], and Zr_3Cu_2Al [8] belong to the structure types $AuCu_3$, $MgCu_2$, $ThMn_{12}$, $Mg_6Cu_{16}Si_7$, $MnCu_2Al$, and Ti_2Ni, respectively. The compound $ZrCu_{1-x}Al_4$ ($x = 0.144$) crystallizes in a unique structure type [9]. The crystal structures of the ternary phases with composition $Zr_{12}Cu_{51}Al_{37}$ (800°C) [5], $Zr_{15}Cu_{71}Al_{14}$ (800°C) [5], $Zr_{51}Cu_{28}Al_{21}$ (800°C) [5], $Zr_{73}Cu_{14}Al_{13}$ (800°C) [5], $Zr_{48-50}Cu_{30-20}Al_{22-30}$ (1000/1100°C) [7] and $Zr_{62-64}Cu_{22-26}Al_{16-10}$ (1000/1100°C) [7] are still unknown. The crystal structure determination of the $Zr_6Cu_4Al_3$ phase is the subject of the present work.

Experimental

The starting materials for the preparation of the alloys were ingots, all with purities better than 99.95 wt.%. The samples were prepared directly from the elements by arc-melting under an argon atmosphere on a water-cooled copper hearth. The products were turned over and re-melted at least three times in order to ensure the homogeneity. Finally, fragments of the alloys were sealed in evacuated quartz tubes and annealed at 800°C for two weeks and 900°C for three days. After the heat treatment, the samples were quenched by submerging the silica tubes in cold water.

X-ray phase analysis was performed using a Siemens D500 diffractometer (Cu *K*α-radiation). A PANalytical X'Pert Pro diffractometer (Cu *K*α-radiation) was used for the X-ray structural studies. The scans were taken in the $\theta/2\theta$ mode within a 2θ region of 15-120° (step scan, 0.02/0.03°; counting time per step, 20 s). Theoretical powder patterns were calculated with the help of the PowderCell program [10] and used for the identification of the synthesized phases. The lattice parameters were obtained by leastsquares fitting using the Latcon program [11]. The FullProf program [12] was used for the Rietveld fittings. A pseudo-Voigt profile shape function was assumed. The background was refined with a polynomial function.

Results and discussion

A series of as-cast and annealed samples containing between 40 and 60 at.% Zr were analysed. Al-rich samples usually contained $ZrCu_xAl_{2-x}$ ($MgCu_2$-type) and $Zr_4Cu_xAl_{3-x}$ (Zr_4Al_3-type) phases. In the as-cast Cu-rich samples with 50 at.% Zr, the Zr_3Cu_2Al (Ti_2Ni-type) compound was recognized, but the annealed alloys mainly consisted of the ternary $ZrCu_xAl_{2-x}$ ($MgCu_2$-type) and binary ZrCu (CsCl-type) and/or Zr_2Cu (Zr_2Cu-type). The existence of the earlier reported ternary phase with unknown structure close to the composition $Zr_{50}Cu_{30}Al_{20}$ was confirmed in the as-cast, as well as in the annealed samples. The average composition of this phase, $Zr_{48}Cu_{30}Al_{22}$, obtained from SEM/EDX analyses, is in good agreement with the literature data.

A crystal structure determination of the above mentioned phase was conducted on the base of powder X-ray diffraction data obtained for the as-cast $Zr_{51}Cu_{28}Al_{21}$ sample. Almost all of the intense peaks were well indexed in a hexagonal unit cell with lattice parameters a ~ 5.28 Å and c ~ 29.0 Å. Having generated different models based on known structures of ternary {Zr, Hf, Nb, Ta}–{Cu, Ag, Au}–Al compounds, and taking into account the characteristic intensities of the peaks, our attention was drawn to the W_6Fe_7 structure type. A secondary phase with Ti_2Ni-type structure was detected. The Rietveld method was applied for the crystal structure refinement.

In the W_6Fe_7 structure (space group R-3m, Pearson symbol $hR39$, $Z = 3$), the large tungsten atoms (atomic radius $r_W = 1.40$ Å) occupy three 6c sites, while the smaller iron atoms ($r_{Fe} = 1.26$ Å) are positioned in 3b and 18h sites [13]. The crystal structure was initially refined for a model in which the Zr atoms ($r_{Zr} = 1.60$ Å) were placed at the positions of the W atoms, while a statistical mixture of Cu ($r_{Cu} = 1.28$ Å) and Al ($r_{Al} = 1.43$ Å) atoms was distributed over the Fe sites. In spite of the low reliability factors, the occupation and thermal parameters were out of reasonable values; the refined composition of the phase was also incorrect. Taking in account the atomic radii of the Zr, Cu and Al atoms, it was suggested that Zr/Al substitution could occur in this compound. Several examples of structures of binary and ternary phases with Zr/Al substitution are known from the literature [8]. It should also be noted that α-Zr (Mg-type) and β-Zr (W-type) dissolve up to 11 at.% Al at 940°C and 26 at.% Al at 1350°C, respectively. Several structural models were tested. Reasonable results were obtained for a disordered model. Here, Zr or Zr/Al atoms occupy the three 6c and the 3b sites, and the Cu/Al mixture is located in the 18h site. Details of the refinement are given in Table 1. The X-ray diffraction pattern is presented in Fig. 1.

A projection of the structure along the c-axis and the coordination polyhedra of the atoms are shown in Fig. 2. The M1, M2 and M3 atoms are located inside of 14-, 15- and 16-vertex Frank-Kasper polyhedra. The atoms surrounding M4 and M5 form icosahedra. The interatomic distances (see Table 2) are, in general, close to the sum of the atomic radii of the respective atoms [14]. Significantly shorter distances are formed between M1 atoms: 2.73 Å (~14 % reduction). This can indicate multiple bonding character. Such interaction can be seen in other compounds with the W_6Fe_7, Zr_4Al_3 and Nb_2Al structure types [8]. Distances considerably shorter than the sum of the average radii of the atoms, pointing to strong bonding, are also observed for M1-M2, M2-M4, M3-M3, M4-M5, and M5-M5.

Preliminary investigations of Hf-rich alloys in the Hf–Cu–Al system revealed the formation of a new isostructural phase with approximate composition $Hf_{48}Cu_{26}Al_{26}$. The lattice parameters refined to a = 5.2250(3) Å, c = 28.8688(18) Å, V = 682.54(7) Å^3. X-ray phase analysis of annealed $Nb_{50}Cu_{25}Al_{25}$ and $Ta_{50}Cu_{25}Al_{25}$ alloys confirmed the formation of rhombohedral phases also in these systems. The refined cell parameters (a = 5.0276(7) Å, c = 27.361(5) Å, V = 598.97(17) Å^3 and a = 5.0126(6) Å, c = 27.527(3) Å, V = 598.97(13) Å^3) are close to those reported in the literature [15,16].

Table 1 Atom coordinates, occupation and isotropic displacement parameters of the $Zr_6Cu_4Al_3$ phase (a = 5.2751(2) Å, c = 29.0290(15) Å, V = 699.58(6) Å^3, R_B = 3.36 %).

Atom	Site	x	y	z	B_{iso} (Å^2)	G
M1	6c	0	0	0.04702(15)	0.84(16)	5.37(12)Zr+0.63(12)Al
M2	6c	0	0	0.15197(13)	0.75(18)	5.24(15)Zr+0.76(15)Al
M3	6c	0	0	0.33457(11)	1.16(19)	6Zr
M4	3b	0	0	½	1.44(35)	1.70(8)Zr+1.30(8)Al
M5	18h	0.5016(7)	1-x	0.09282(17)	1.28(15)	11.66(34)Cu+6.34(34)Al

Refined composition: $Zr_{6.10}Cu_{3.89}Al_{3.01}$.

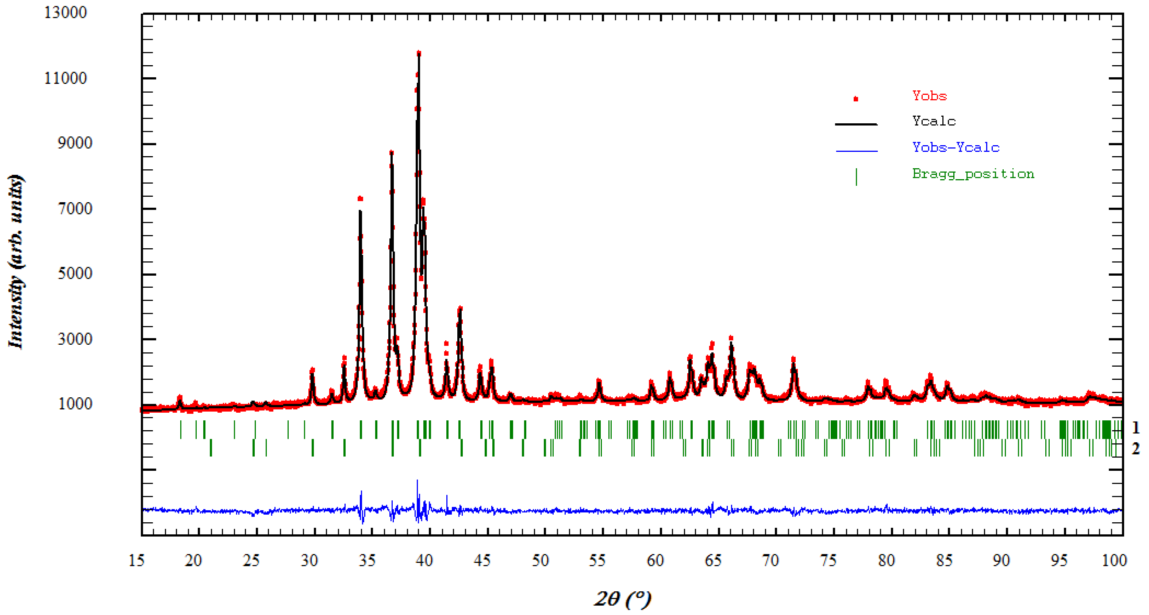

Fig. 1 Rietveld refinement of the sample $Zr_{51}Cu_{28}Al_{21}$ (1 – $Zr_6Cu_4Al_3$, R_B = 3.36 %; 2 – Zr_3Cu_2Al, R_B = 5.76 %) (Cu $K\alpha$-radiation, R_p = 3.02 %, R_{wp} = 3.85 %, χ = 1.43)

Table 2 Interatomic distances (*d*), sums of the average radii of the *M* mixtures (d_M), the relative increase/decrease (d - d_M)/d_M (Δ) and the coordination numbers of the atoms (CN) in the structure of the $Zr_6Cu_4Al_3$ phase.

Atom	Atom	*d* (Å)	d_M (Å)	Δ (%)	CN
*M*1	-1*M*1	2.730(6)	3.16	–13.6	14
	-6*M*5	2.954(4)	2.91	+1.5	
	-1*M*2	3.047(6)	3.16	–3.6	
	-3*M*3	3.323(2)	3.18	+4.5	
	-3*M*3	3.352(2)	3.18	+5.4	
*M*2	-3*M*5	2.980(5)	2.91	+2.4	16
	-1*M*1	3.047(6)	3.16	–3.6	
	-3*M*4	3.075(1)	3.11	–1.1	
	-6*M*5	3.147(4)	2.91	+8.1	
	-3*M*2	3.163(1)	3.16	+0.1	
*M*3	-3*M*3	3.046(1)	3.20	–4.8	15
	-3*M*5	3.071(5)	2.93	+4.8	
	-3*M*5	3.119(5)	2.93	+6.5	
	-3*M*1	3.323(2)	3.18	+4.5	
	-3*M*1	3.352(2)	3.18	+5.4	
*M*4	-6*M*5	2.638(4)	2.86	–7.8	12
	-6*M*2	3.075(1)	3.11	–1.1	
*M*5	-2*M*5	2.612(5)	2.66	–1.8	12
	-1*M*4	2.638(5)	2.86	–7.8	
	-2*M*5	2.663(5)	2.66	+0.1	
	-2*M*1	2.954(4)	3.11	+1.5	
	-1*M*2	2.980(6)	3.11	+2.4	
	-1*M*3	3.071(6)	2.93	+4.8	
	-1*M*3	3.119(6)	2.93	+6.5	
	-2*M*2	3.147(4)	3.11	+8.1	

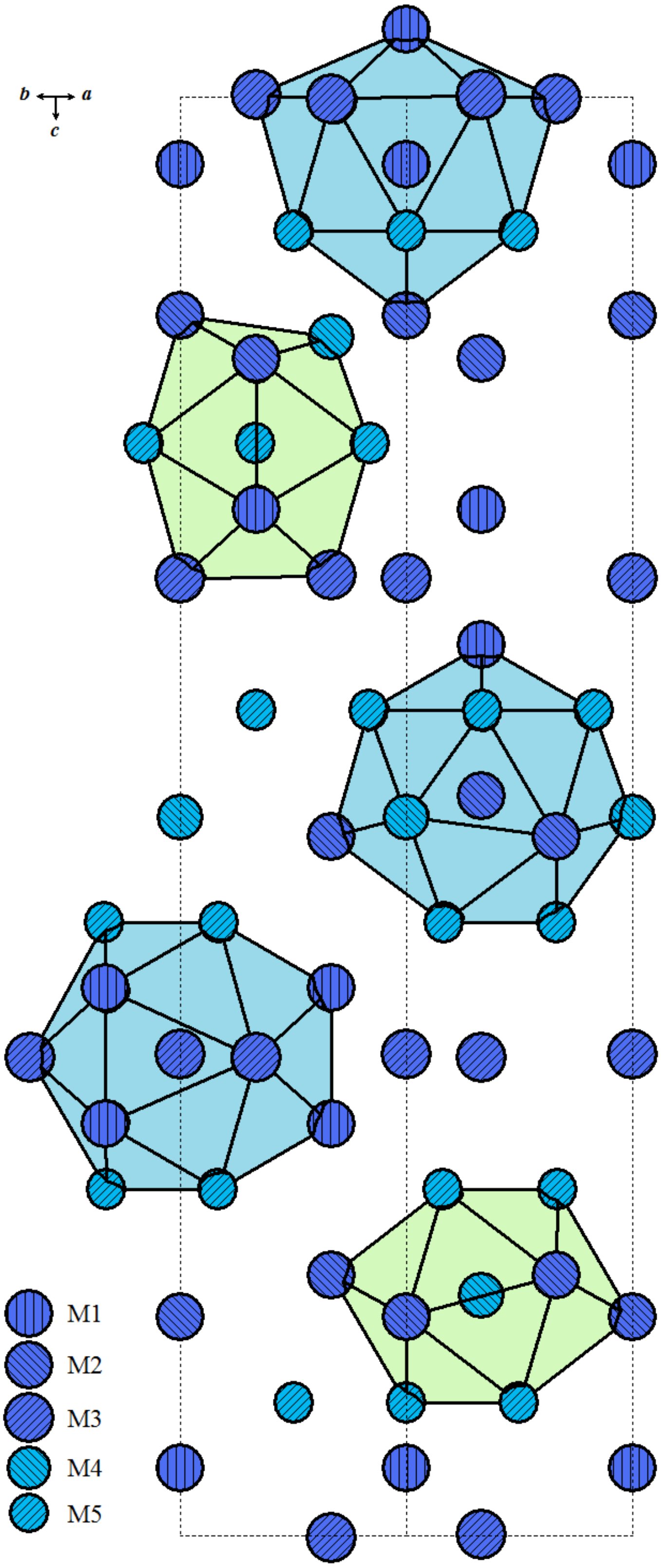

Fig. 2 Unit cell and coordination polyhedra of the atoms in the structure of $Zr_6Cu_4Al_3$.

Table 3 Atom coordinates, occupations and isotropic displacement parameters of the Hf_6AgAl_6 phase (a = 5.3386(1) Å, c = 29.1811(7) Å, V = 720.26(3) Å^3, R_B = 6.50 %).

Atom	Site	x	y	z	B_{iso} (Å^2)	G
$M1$	6c	0	0	0.04571(5)	1.08(4)	6Hf
$M2$	6c	0	0	0.14941(6)	0.92(4)	6Hf
$M3$	6c	0	0	0.33413(5)	0.62(4)	6Hf
$M4$	3b	0	0	½	1.58(22)	0.93(3)Ag+2.07(3)Al
$M5$	18h	0.5005(6)	1-x	0.09085(20)	1.32(12)	1.42(7)Ag+16.58(7)Al

Refined composition: $Hf_6Ag_{0.78}Al_{6.22}$.

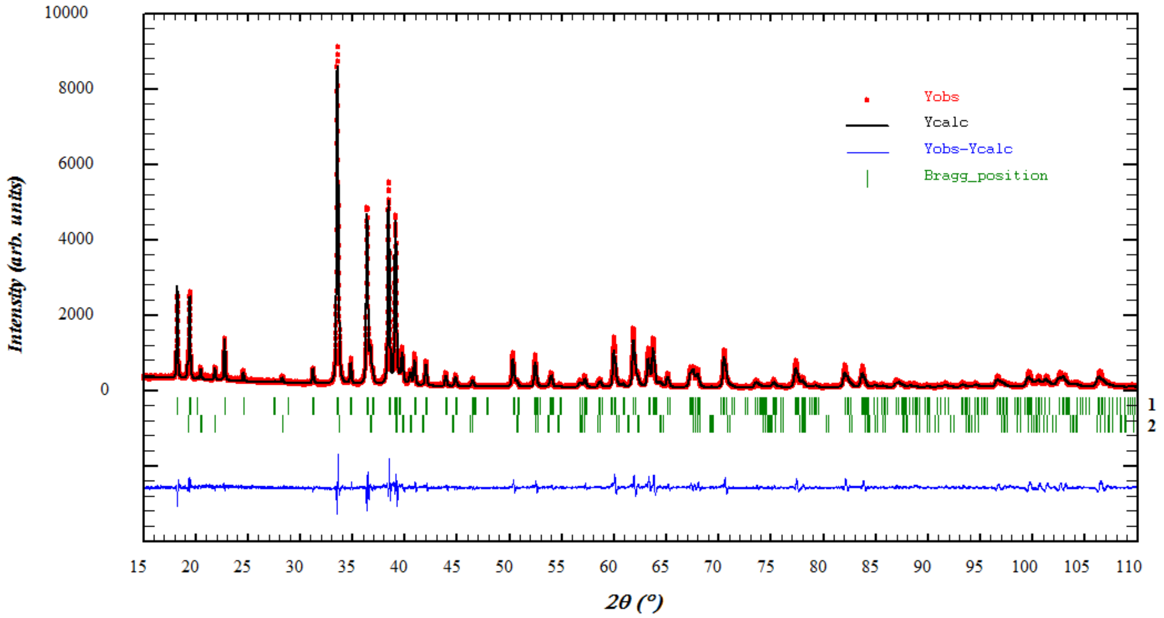

Fig. 3 Rietveld refinement of the sample $Hf_{46}Cu_7Al_{47}$ (1 – Hf_6AgAl_6, R_B = 6.50 %; 2 – $HfAg_{0.3}Al_{1.7}$, R_B = 6.27 %) (Cu $K\alpha$-radiation, R_p = 9.70 %, R_{wp} = 12.7 %, χ = 2.13)

Two other ternary phases, namely, $Zr_6Ag_xAl_{7-x}$ and $Hf_6Ag_xAl_{7-x}$, with the W_6Fe_7 structure type have earlier been identified in systems related to those investigated above [17]. Compared to the present investigation, they formed with smaller amounts of silver (less than 15 at.%) and did not reveal Zr/Al or Hf/Al substitution. Results of the refinement of the Hf_6AgAl_6 compound are shown in Table 3, and its XRD pattern is displayed in Fig. 3. Detailed descriptions of the W_6Fe_7 structure type can be found in [17] and [18].

References

[1] M. Miller, P. Liaw, *Bulk Metallic Glasses: An Overview*, Springer, New York, 2008, 237 p.

[2] C. Suryanarayana, A. Inoue, *Bulk Metallic Glasses*, CRC Press, Taylor and Francis Group, New York, 2011, 523 p.

[3] L. Tretyachenko, *Ternary Alloy Systems: Phase Diagrams, Crystallographic and Thermodynamic Data, Light Metal Systems*, Vol. 11A2, Landolt-Börnstein, Springer, 2005, pp. 206-222.

[4] O.S. Zarechnyuk, A.N Malinkovich, E.A. Lalayan, V.Ya. Markiv, *Izv. Akad. Nauk SSSR, Met.* (6) (1967) 201-204.

[5] V.Ya. Markiv, V.V. Burnashova, *Poroshk. Metall.* 12 (1970) 53-58.

[6] S.A. Syed, D. Swenson, *MRS Proceedings*, 554 (1998) 131.

[7] C.P. Wang, S.B. Tu, Y. Yu, J.J. Han, X.J. Liu, *Intermetallics* 31 (2012) 1-8.

[8] P. Villars (Ed.), *Pearson's Handbook, Crystallographic Data for Intermetallic Phases*, ASM Materials Park, OH, 1997.

[9] A.U. Khan, P. Rogl, G. Giester, *Dalton Trans.* 41 (2012) 2296-2303.

[10] G. Nolze, W. Kraus, *Powder cell for Windows (Version 2.3)*, Federal Institute for Materials Research and Testing, Berlin, 1999.

[11] D. Schwarzenbach, *Program LATCON*, University of Lausanne, Switzerland, 1975.

[12] J. Rodriguez-Carvajal, T. Roisnel, *FullProf.98 and WinPLOTR: New Windows 95/NT Applications for Diffraction Commission For Powder Diffraction*, International Union for Crystallography, Newsletter No.20 (May-August) Summer, 1998.

[13] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *TYPIX, Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*. Berlin: Springer-Verlag, 1994.

[14] G.B. Bokiy, *Crystal Chemistry*, Nauka, Moscow, 1971, 400 p. (in Russian).

[15] H. Oesterreicher, H. Nowotny, R. Kieffer, *Monatsh. Chem.* 96 (1965) 351-359.

[16] H. Nowotny, H. Oesterreicher, *Monatsh. Chem.* 95 (1964) 982-989.

[17] Yu. Verbovytskyy, *Thesis*, Ivan Franko National University of Lviv, 2003.

[18] W.B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, New York, 1972, 806 p.