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CRYSTAL STRUCTURE OF THE $TmNi_5$

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Crystal structure of the $TmNi_5$ compound has been investigated by means of X-ray single crystal method (Oxford Diffraction X'calibur four-circle diffractometer, MoK_α radiation) for the first time: $CaCu_5$-type structure, Pearson symbol *hP*6, space group *P*6/*mmm*, a = 4.8684(12), c = 3.9541(7) Å, $R1$ = 0.0529, $wR2$ = 0.1835 for 80 reflections. Similarly to intermetallic compounds with high transition metal content, atoms in the title structure have rather high coordination numbers: 20 for thulium and 12 for nickel.

Key words: thulium, nickel, crystal structure, single crystal method.

INTRODUCTION. The most efficient method of new compound discovering is the complex investigation of component interaction in ternary system and construction the isothermal section. Such investigations always start from the study the binary systems bounding the investigated ternary system. So far as, the character of component interactions in bounding binary systems have a great influence on interaction in ternary system. As it is shown by our research group systematic research of the phase relations and the crystal chemistry in the ternary systems with rare earth, transition metal and silicon the great influence have the binary *RE-T* system (*RE* – rare earth metals, *T* – transition metal). Unfortunately, these binary systems have not yet been fully investigated and crystal structure not of all binary compounds have been determined. Good example of this is the Tm-Ni system, where compound $TmNi_5$ with the $CaCu_5$-type structure exist [1–5]. However, according to the literature data, a detailed study of the crystal structure of this compound has not previously been performed. Therefore, we present the results of the complete crystal structure investigation of the $TmNi_5$ compound.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Starting materials for the preparation of the alloys were ingots of the thulium and nickel with nominal purities Tm ≥ 99.88 wt.%, and Ni ≥ 99.99 wt.%. The samples

were synthesized by arc-melting under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components, the sample was melted twice. The ingot was annealed at 600°C in an evacuated quartz ampoule for 720 h and subsequently quenched in cold water. The weight loss during the preparation of the sample was less than 1 % of the total mass, which was 2 g. After annealing no reaction with quartz was observed and the irregularly shaped single crystals were grown on the surface of the specimen. Single crystals exhibit metallic lustre while ground powders are grey.

The crystal structures of the $TmNi_5$ compound were investigated by X-ray single-crystal diffraction. X-ray diffraction was performed at room temperature on an Oxford Diffraction X'calibur four-circle diffractometer (Mo*K*α radiation). The structures were solved by direct methods and refined by the SHELX-2018/3 program package [6] with anisotropic atomic displacement parameters. The crystallographic data and details on the data collection for $TmNi_5$ are listed in Table 1. The final atomic positional and displacement parameters of the compounds are listed in the Table 2. All the crystallographic positions are fully occupied.

Table 1

Crystal data and structure refinement details for $TmNi_5$.

Empirical formula	$TmNi_5$
Formula weight	462
T, K	295(2)
Space group	$P6/mmm$
Pearson code	$hP6$
Unit cell dimensions, Å	a = 4.8684(12), c = 3.9541(7)
Volume, Å^3	81.16(4)
No. formula units per unit cell	1
Calculated density, g·cm^{-3}	9.46
Absorption coefficient, mm^{-1}	55.137
F(000), e	209
Crystal color	metallic
Crystal size, mm	0.027×0.023×0.018
θ range for data collection	4.795–31.996
Index ranges	$-6 \le h \le 7$, ±7, ±5
Measured reflections	2395
Independent reflections / R_{int}	81 / 0.0858
Reflections with $I > 2\,\sigma(I)$ / R_σ	80 / 0.0220
Data / restraints / parameters	81 / 0 / 9
Goodness-of-fit on F^2	1.386
Final $R1$ / $wR2$ [$I > 2\,\sigma(I)$]	0.0529 / 0.1835
Final $R1$ / $wR2$ (all data)	0.0514 / 0.1827
Largest diff. peak / hole, e Å^{-3}	2.772 / −4.079

Table 2

Atomic coordinates and thermal displacement parameters for $TmNi_5$.

Atom	Wyckoff Site	x	y	z	U_{eq}, Å^2
Tm	1*a*	0	0	0	0.0194(12)
Ni1	2*c*	2/3	1/3	0	0.0168(14)
Ni2	3*g*	1/2	0	1/2	0.0265(15)
Atom	U_{11}	U_{22}	U_{33}	U_{12}	$U_{13} = U_{23}$
Tm	0.0253(13)	0.0253(13)	0.0076(14)	0.0126(7)	0
Ni1	0.0239(19)	0.0239(19)	0.003(2)	0.0119(9)	0
Ni2	0.038(2)	0.026(3)	0.012(2)	0.0132(13)	0

Interatomic distances (δ), reduced values of interatomic distances ($\Delta = 100(d - \sum r)/\sum r$, where $\sum r$ is the sum of the respective atomic radii) and coordination numbers of atoms for $TmNi_5$ are listed in Table 3. Most of interatomic distances in the structure of our compound are in good agreement with the atomic sizes. The Tm-Ni1 and Ni1-Ni2 interatomic distances are rather short in comparison with the sum of the respective atomic radii.

Table 3

Interatomic distances (*d*, Å), Δ values and coordination numbers of the atoms for $TmNi_5$ (r_{Tm} = 1.746 Å, r_{Ni} = 1.246 Å [8]).

Atom		*d* (Å)	Δ (%)	CN	Atom		*d* (Å)	Δ (%)	CN
Tm	6 Ni1	2.8107(7)	-6.0	18	Ni2	4 Ni1	2.4257(4)	-2.7	12
	12 Ni2	3.1359(5)	4.8			4 Ni2	2.4342(6)	-2.3	
						4 Tm	3.1359(5)	4.8	
Ni1	6 Ni2	2.4257(4)	-2.7	12					
	3 Ni1	2.8107(7)	12.8						
	3 Tm	2.8107(7)	-6.0						

The projection of the crystal structure of $TmNi_5$ on the *ab* plane and the coordination polyhedra (CP) of the atoms are shown in Fig. 1. All CP are typical for the structure of compounds with $CaCu_5$-type structure. The coordination polyhedron of the thulium atoms [$Tm(Ni1_6Ni2_{12})$] is hexagonal prism with Ni-capped lateral sides. The Ni1 atom is surrounded by 12-vertices polyhedron [$Ni1(Ni2_6Ni1_3Tm_3)$]. The Ni2 atoms are located inside the icosahedra [$Ni2(Ni1_4Ni2_4Tm_4)$].

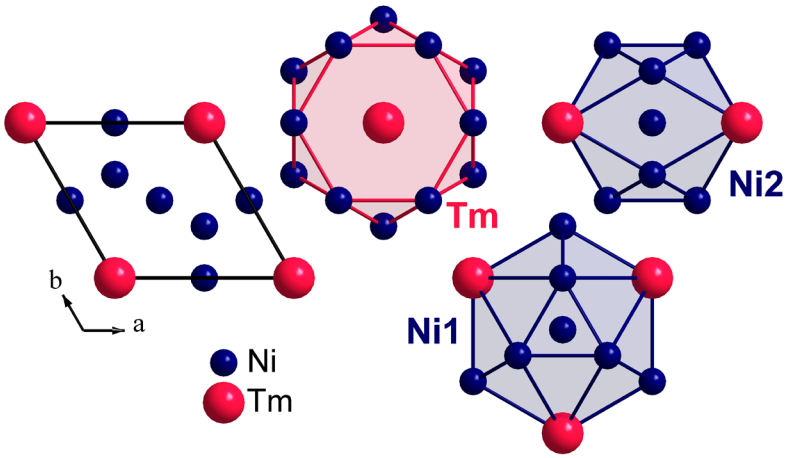

Fig. 1. A projection of the $TmNi_5$ unit cell on the *ab* plane and a view of the coordination polyhedra of the atoms.

The structure of $TmNi_5$ compound (Fig. 2) can be considered as a packing of trigonal bypiramids from nickel atoms which are connected by common apexes along the *c* direction and in the *bc* plane. Six such bypiramids build up ring units, which in turn form a hexagonal atomic network. Tm atoms fill holes in the hexagonal rings.

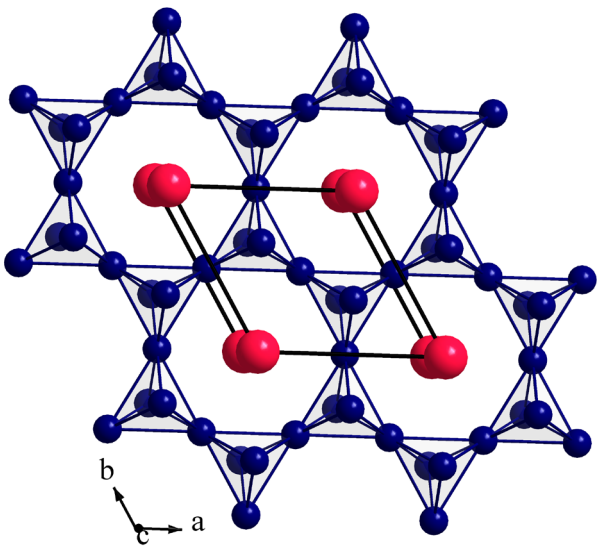

Fig. 2. The hexagonal rings of trigonal bypiramids in the $TmNi_5$ structure.

Binary $RENi_5$ compounds with $CaCu_5$-type exist in all the systems with rare-earth metals and nickel [7]. Fig.3 displays variations of the linear parameter (*V*/*N*) (where *V* is a volume of the unit cell, *N* is a number of atoms per unit cell) depending on the size of the RE^{3+} ion (according to Shannon [9]) for the series of the isostructural compounds. The trend observed confirms the effect of the lanthanide contraction.

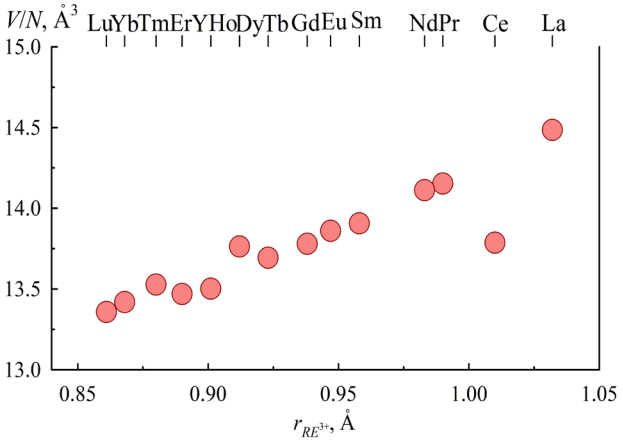

Fig. 3. Dependence of the parameter (V/N) on RE^{3+} radii in the $RENi_5$ compounds.

CONCLUSIONS. The crystal structure of binary $TmNi_5$ have been investigated in detail using single crystal X-ray data for the first time. This compound is isotypical to $CaCu_5$-type structure. All three crystallographic positions (1*a*, 2*c* and 3*g*) are fully occupied by Tm and Ni respectively. The coordination polyhedral are typical for rare earth binary compounds with high content of nickel.

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КРИСТАЛІЧНА СТРУКТУРА СПОЛУКИ $TmNi_5$

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Із літератури відомо про існування сполуки складу $TmNi_5$ у подвійній системі Tm-Ni. Однак детального дослідження кристалічної структури цієї сполуки досі не проводили. Оскільки нам вдалося отримати монокристал, ми вперше провели повне дослідження кристалічної структури сполуки $TmNi_5$. Зразок синтезовано методом електродугового плавлення. Монокристал відібрано зі зразка, відпаленого за температури 600 °C упродовж 720 год. Масив експериментальних інтенсивностей відбить отримано на автоматичному монокристальному дифрактометрі X'calibur four-circle Oxford Diffraction (MoKα промінння). Структуру визначено прямими методами за допомогою комплексу програм SHELX-2018/3. Параметри теплового зміщення всіх атомів уточнено в анізотропному наближенні. Сполука кристалізується в структурному типу $CaCu_5$, символ Пірсона символ *hP*6, просторова група *P*6/*mmm* (№ 191), a = 4,8684(12), c = 3,9541(7) Å, R = 0,0529, wR = 0,1835 для 80 рефлексів. Усі кристалографічні позиції в структурі досліджуваної сполуки зайнято повністю.

Міжатомні віддалі у структурі сполуки $TmNi_5$ добре узгоджуються із сумами атомних радіусів компонентів. Атоми тулію характеризуються координаційним числом 20, а менші за розміром атоми нікелю – 12. Координаційні поліедри атомів у структурі сполуки $TmNi_5$ є типовими для представників структурного типу $CaCu_5$. Координаційними багатогранниками атомів тулію [$Tm(Ni1_6Ni2_{12})$] є гексагональні призми з бічними сторонами, центрованими атомами нікелю. Координаційними багатогранниками для атомів Нікелю є: 12-вершинники [$Ni1(Ni2_6Ni1_3Tm_3)$] для атомів Ni1 та ікосаедри [$Ni2(Ni1_4Ni2_4Tm_4)$] для атомів Ni2.

Структуру сполуки $TmNi_5$ можна представити як укладку тригональних біпірамід з атомів нікелю, які з'єднані по-шість спільними гранями вздовж напрямку *c* та в

площині *bc*. Простір між біпірамідами заповнений атомами тулію.

Бінарні сполуки складу *RE*Ni_5 з типом структури $CaCu_5$ існують у подвійних системах *RE*-Ni з усіма рідкісноземельними металами.

Ключові слова: тулій, нікель, кристалічна структура, метод монокристалу.

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