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Structure peculiarities of the new ternary gallide $Tm_{14}Cu_{46}Ga_5$

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The crystal structure of the new ternary compound $Tm_{14}Cu_{46}Ga_5$ (*hP*74-9, *P*6/*m*, *a* = 11.573(3), *c* = 8.559(2) Å) has been refined based on X-ray single-crystal diffraction data. It displays similarities with the binary structure types $Ce_{14}Cu_{51}$ and $Gd_{14}Ag_{51}$. In one of the monoatomic layers perpendicular to [0 0 1], a disordered atom arrangement, modeled by a half-occupied 6-fold site of Cu atoms and splitting of the Tm site into two half-occupied 6-fold positions, was observed. The structure is characterized by single Cu atoms, [Cu_3] triangles, and [Cu_3] finite chains; the Ga atoms are arranged in isolated [$(Ga,Cu)_6$] hexagons.

Gallide / Thulium / Copper / Single-crystal X-ray diffraction / Crystal structure / Element substructure

Introduction

A ternary phase, characterized by a limited homogeneity range and $Gd_{14}Ag_{51}$-type structure (Pearson symbol *hP*68-3, space group *P*6/*m*, cell parameters *a* = 12.681(3), *c* = 9.289(4) Å [1]), was found during systematic investigations of the phase equilibria in the ternary system Er–Cu–Ga at 600ºC. The crystal structures of two single crystals of the compositions $Er_{14}Cu_{48}Ga_3$ (*hP*74-9, *P*6/*m*, *a* = 11.5720(2), *c* = 8.6243(2) Å) and $Er_{14}Cu_{45}Ga_6$ (*hP*68-3, *P*6/*m*, *a* = 11.519(2), *c* = 8.573(1) Å), within the homogeneity range of the phase, were determined by X-ray diffraction [2,3]. The structure is characterized by partial ordering of the Cu and Ga atoms in the case of $Er_{14}Cu_{48}Ga_3$ and by complete ordering in the case of $Er_{14}Cu_{45}Ga_6$.

The structure type $Gd_{14}Ag_{51}$ and derivatives have been reported in the binary systems {Ca, Ce}–Cu, *R*–Ag (*R* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er), {Th, Pu}–Ag, *R*–Au (*R* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho), {U, Th, Pu}–Au, {Ca, Eu, Yb}–Cd, and {Ca, Sr, Eu, Yb}–Hg, and in the ternary systems *R*–{Cu, Ag}–Ga (*R* = Gd, Tb), U–{Ag, Au}–Ga, and Pr–Ag–Sn [4]. Crystallographic parameters including atomic coordinates have been determined for four ternary gallides: $Sc_{14}(Cu_{0.72}Ga_{0.28})_{51}$ [5], $Sm_{14}(Cu_{0.9}Ga_{0.1})_{51}$ [6], $Gd_{14}Cu_{46.1}Ga_{4.9}$ [7], and $Tb_{14}Ag_{42.3}Ga_{7.8}$ [8], in addition to the two refinements referred to above. For the first three phases, statistical mixtures of copper and gallium atoms in all the small-atom sites were reported. However, a clear tendency toward ordering of Cu and Ga atoms was observed in the structures of $Er_{14}Cu_{48}Ga_3$, $Er_{14}Cu_{45}Ga_6$, and $Tb_{14}Ag_{42.3}Ga_{7.8}$. In the case of the compound $Tb_{14}Ag_{42.3}Ga_{7.8}$, four of the seven crystallographic sites are occupied by statistical mixtures of Ag and Ga atoms, whereas the remaining three sites are occupied exclusively by Ag atoms. Three split positions: Er 6*j*, Cu 6*j* and Cu 2*e*, were refined for $Er_{14}Cu_{48}Ga_3$ and only one position 6*k* was found to be occupied by a statistical mixture of Cu/Ga. The compound $Er_{14}Cu_{45}Ga_6$ is fully ordered and has one split position Cu 6*j*.

In this work a detailed study of the crystal structure of a new ternary thulium copper gallide belonging to the $Gd_{14}Ag_{51}$ structure family is reported.

Experimental

An alloy of nominal composition $Tm_{21.5}Cu_{71}Ga_{7.5}$ (in at.%) was synthesized from the elements (Tm ≥ 99.82 wt.%, Cu and Ga ≥ 99.99 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. The ingot was annealed (furnace VULCAN A-550) at 600±5ºC in a quartz ampoule under vacuum for 1000 h and subsequently quenched in cold water. The weight loss during the preparation of the sample was less than 0.5 % of the total mass, which was 1 g.

According to the X-ray phase analysis the alloy contained one phase. An X-ray diffraction pattern of the powdered sample was obtained on a diffractometer DRON-2M (Fe *Kα*-radiation, λ = 1.936042 Å, manganese *β*-filter, angular range $20 \le 2\theta \le 120^\circ$, Bragg-Brentano geometry). The crystal structure of

the ternary phase $Tm_{14}Cu_{46}Ga_5$ (a = 11.584(6), c = 8.565(9) Å) was first refined by the Rietveld method, starting from the coordinates reported in [2]. Profile and structural parameters were obtained using the program package FullProf Suite [9]. Experimental, calculated and difference X-ray powder diffraction patterns of the sample of composition $Tm_{21.5}Cu_{71}Ga_{7.5}$ are shown in Fig. 1.

A single crystal was extracted from the same alloy. It was mounted on a glass fiber and X-ray diffraction data were collected in the ω-2θ scan mode at room temperature on a CAD-4T diffractometer (Mo $K\alpha$-radiation, λ = 0.71073 Å). The unit-cell parameters were obtained from a least-squares refinement based on the angles of 25 reflections. The structure of $Tm_{14}Cu_{46}Ga_5$ was solved by direct methods in the space group $P6/m$. A full-matrix least-squares refinement of the positional and anisotropic displacement parameters was performed on F^2 using the WinCSD program package [10]. Details of the data collection and structure refinement for $Tm_{14}Cu_{46}Ga_5$ are given in Table 1.

Results and discussion

The refined atomic coordinates, site occupancies, and displacement parameters for the structure of $Tm_{14}Cu_{46}Ga_5$ are listed in Table 2. The arrangement of the thulium atoms in the layer at z = 0 is described by two half-occupied 6j Wyckoff positions (sites Tm2.1 and Tm2.2). The distance between the split-atom sites is 0.429(6) Å. The arrangement of Cu atoms around the origin is modeled by one half-occupied 6j Wyckoff position (site Cu4). The effective occupancy of this site cannot exceed 1/2 because higher occupancy would lead to the appearance of impossibly short Cu-Cu distances (1.429(2) Å) in the structure.

The structures of the binary compounds of composition $R_{14}T_{51}$ formed in the systems R–{Ag, Au} (R = La-Sm, Gd-Er) [4] belong to the structure type $Gd_{14}Ag_{51}$. A binary compound with rare-earth metal and copper having the stoichiometry $R_{14}Cu_{51}$ is known only for cerium. However, it crystallizes in an own-type structure ($hP78$-13, $P6/m$, a = 11.858(4), c = 9.107(3) Å) [11], which is derived from the $Gd_{14}Ag_{51}$ type. The two structure types differ by the partly disordered arrangement of the atoms in the layer at z = 0, which is modeled by split atom positions. In the structure of $Gd_{14}Ag_{51}$ the 6j position of one of the Ag sites is half-occupied, indicating that [Ag_3] atom triangles with two possible orientations are formed. Similar, disordered [Cu_3] triangles are formed around the origin of the unit cell in the structure of $Ce_{14}Cu_{51}$. However, one of the 6j positions occupied by Gd atoms in the structure of $Gd_{14}Ag_{51}$ is split into two positions 6j occupied by Ce atoms in the structure of $Ce_{14}Cu_{51}$ with the occupancy 1/2. The Wyckoff position 2c, which is fully occupied by Ag atoms in the structure of $Gd_{14}Ag_{51}$, is split into a position 6j with 1/3 occupancy by Cu atoms in the structure of $Ce_{14}Cu_{51}$.

Table 1 Experimental details and crystallographic data for $Tm_{14}Cu_{46}Ga_5$.

Refined composition		$Tm_{14}Cu_{46}Ga_5$
Formula weight M_r		5636.291
Structure type		$Gd_{14}Ag_{51}$
Pearson symbol		$hP74$-9
Space group		$P6/m$
Unit-cell parameters:	a, Å	11.573(3)
	c, Å	8.559(2)
Cell volume V, Å^3		992.8(8)
Formula units per cell Z		1
F(000)		2457.6
Density D_X, g cm^{-3}		9.437(7)
Absorption coefficeint μ (Mo $K\alpha$), mm^{-1}		60.42
Crystal shape		prism
Crystal size, mm		0.03 × 0.03 × 0.10
$2\theta_{max}$, °		80
No. of reflections:	measured	3729
	independent	1152
	with $F > 10\sigma(F)$	577
Reliability factor R_{int}		0.0919
Range of h, k, l		$-15 \le h \le 15$, $0 \le k \le 15$, $-15 \le l \le 15$
No. of refined parameters		33
Weighting scheme (w)		Var
Reliability factors:	R_F	0.0423
	R_w	0.0433

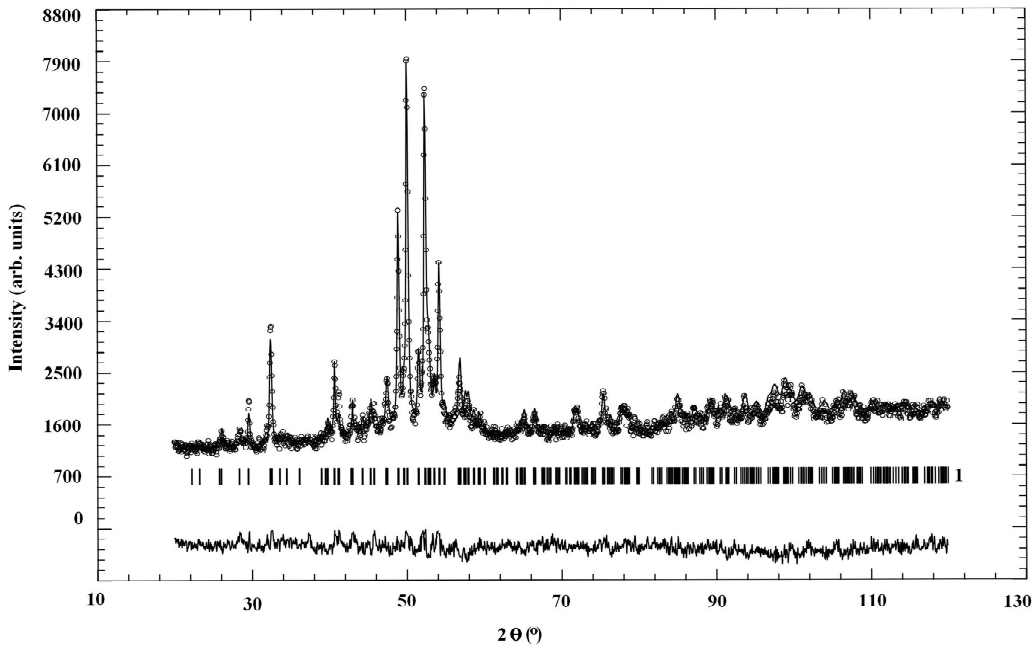


Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the $Tm_{21.5}Cu_{71}Ga_{7.5}$ sample (Fe *Kα*-radiation). Vertical bars indicate the positions of reflections from the $Tm_{14}Cu_{46}Ga_5$ compound.

Table 2 Atomic coordinates, site occupancies, and displacement parameters (Å^2) for $Tm_{14}Cu_{46}Ga_5$ (*hP*74-9, *P*6/*m*, *a* = 11.573(3), *c* = 8.559(2) Å).

Site	Wyckoff position	*x*	*y*	*z*	$B_{(iso/eq)}$ [a]	Occupancy
Tm1	6*k*	0.4721(2)	0.1386(2)	1/2	0.58(5)	1
Tm2.1	6*j*	0.1114(6)	0.3653(5)	0	0.63(15)	0.501(8)
Tm2.2	6*j*	0.1286(5)	0.4082(5)	0	0.50(14)	0.503(8)
Tm3	2*e*	0	0	0.3047(4)	0.49(5)	1
Cu1	12*l*	0.1104(4)	0.4377(4)	0.3273(4)	0.95(11)	1
Cu2	12*l*	0.2671(4)	0.0678(4)	0.2426(4)	0.81(10)	1
Cu3	12*l*	0.4938(4)	0.1098(4)	0.1537(4)	0.90(10)	1
Cu4	6*j*	0.0397(11)	0.1383(10)	0	0.9(3)	0.51(2)
Cu5	4*h*	1/3	2/3	0.2784(8)	0.77(11)	1
Cu6	2*c*	1/3	2/3	0	2.7(3)	1
M [b]	6*k*	0.0630(5)	0.2418(5)	1/2	0.85(13)	1

Site	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tm1	0.47(6)	0.65(7)	0.65(5)	0.29(5)	0	0
Tm2.1	0.4(2)	1.0(2)	0.55(12)	0.4(2)	0	0
Tm2.2	0.2(2)	0.6(2)	0.58(12)	0.17(14)	0	0
Tm3	0.53(6)	0.53(6)	0.28(8)	0.26(3)	0	0
Cu1	1.03(14)	0.84(14)	0.99(11)	0.47(12)	0.30(11)	0.12(10)
Cu2	0.86(12)	1.29(13)	0.53(9)	0.73(11)	-0.31(10)	-0.33(11)
Cu3	0.67(13)	0.72(13)	1.04(11)	0.16(10)	-0.01(11)	-0.10(10)
Cu4	0.2(3)	0.8(4)	1.4(4)	-0.1(3)	0	0
Cu5	0.31(12)	0.31(12)	1.4(3)	0.16(6)	0	0
Cu6	3.1(4)	3.1(4)	1.0(4)	1.6(2)	0	0
M [b]	0.7(2)	0.5(2)	1.3(2)	0.24(14)	0	0

[a] $B_{eq} = \frac{1}{3}\sum_{ij} B_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$

[b] M = 0.833Ga + 0.167Cu

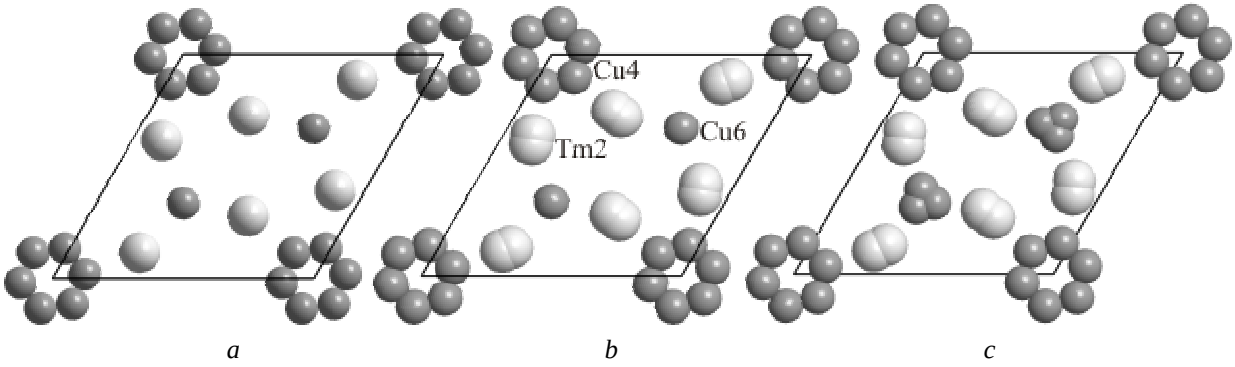


Fig. 2 Monoatomic layers at $z = 0$ in the structures of $Gg_{14}Ag_{51}$ (*a*), $Tm_{14}Cu_{46}Ga_5$ (*b*) and $Ce_{14}Cu_{51}$ (*c*).

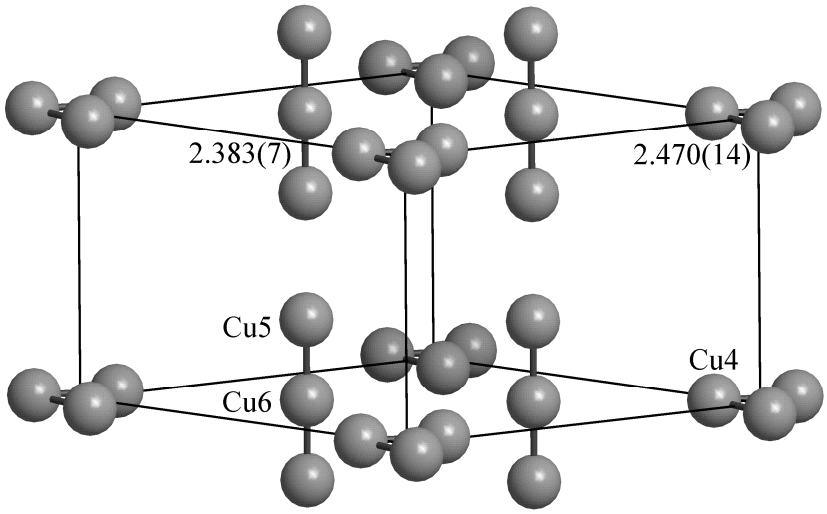


Fig. 3 Cu-atom segments in the structure of $Tm_{14}Cu_{46}Ga_5$. One of the two possible orientations of the $[Cu_3]$ triangle is shown at each vertex of the unit cell.

The structure of the compound $Tm_{14}Cu_{46}Ga_5$ studied here is intermediate between the structure types $Gd_{14}Ag_{51}$ and $Ce_{14}Cu_{51}$ (Fig. 2). Similarly to the two binary structure types, the copper atoms in Wyckoff position 6*j* form disordered triangles around the origin of the unit cell. Like the corresponding Ce site in the structure of $Ce_{14}Cu_{51}$, the 6*j* position occupied by Tm atoms is split (occupancy = 1/2). However, as in the structure of $Gd_{14}Ag_{51}$, the 2*c* position occupied by copper atoms is not split in $Tm_{14}Cu_{46}Ga_5$, even if a tendency towards atomic disorder is reflected in the large displacement parameters refined for this site.

The close values of the X-ray radiation scattering factors for Cu and Ga make an accurate refinement of the site occupancies difficult. The refined site occupancies were supported by the crystal chemical analysis of the structure. Two types of cluster of composition $[Cu_3]$ are observed in the structure of $Tm_{14}Cu_{46}Ga_5$ (Fig. 3): triangles composed by atoms of the site Cu4 ($\delta_{Cu–Cu}$ = 2.470(14) Å) and linear finite chains Cu5–Cu6–Cu5 ($\delta_{Cu–Cu}$ = 2.383(9) Å). The major part of the copper atoms (Cu1, Cu2, Cu3, and Cu5) form corrugated graphite-like nets. We exclude the possibility of replacement of Cu1 and Cu3 atoms (Wyckoff position 2*c* and 6*j*, respectively) by Ga atoms. The Ga atoms are arranged in isolated $[(Ga,Cu)_6]$ hexagons. No ternary compound of the $Gd_{14}Ag_{51}$ structure family has been studied by neutron diffraction so far.

The interatomic distances (Table 3) in the structure of $Tm_{14}Cu_{46}Ga_5$ agree well with the sums of the atomic radii of the elements (r_{Tm} = 1.746, r_{Cu} = 1.278, r_{Ga} = 1.221 Å [12]). Insignificant contractions are observed only for the copper atoms composing clusters.

Conclusions

The structure of the new ternary gallide $Tm_{14}Cu_{46}Ga_5$ is intermediate between the structure types $Gd_{14}Ag_{51}$ and $Ce_{14}Cu_{51}$. It is characterized by a half-occupied 6*j* position for the Cu4 site, forming Cu_3 triangles around the origin of the unit cell as in the binary structure

Table 3 Interatomic distances and coordination polyhedra for $Tm_{14}Cu_{46}Ga_5$.

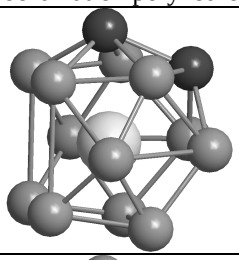
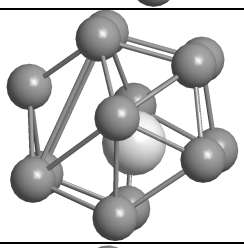
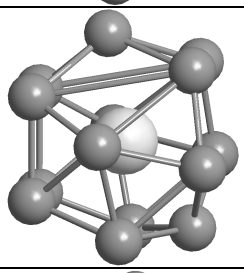
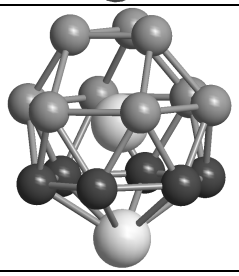
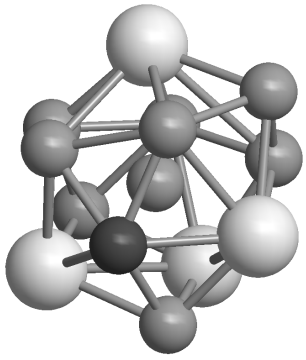
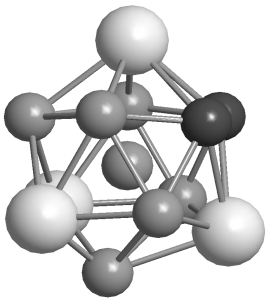
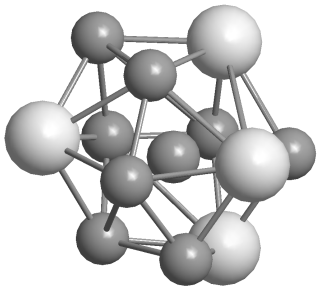
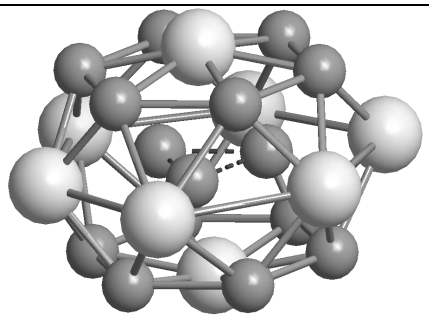
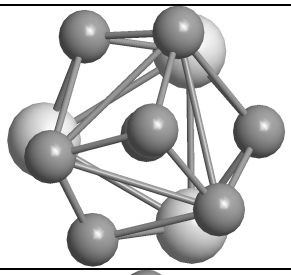
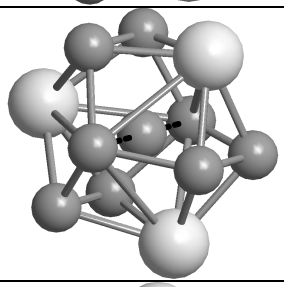
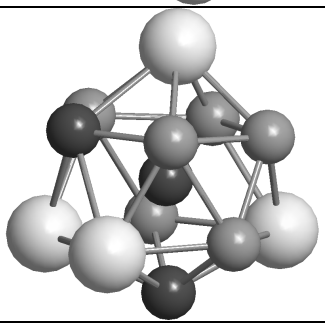
Atoms		δ, Å	Coordination polyhedron
Tm1	– 1 *M* [a] – 2 Cu1 – 2 Cu1 – 1 *M* [a] – 2 Cu3 – 2 Cu3 – 2 Cu1 – 2 Cu2	2.926(6) 2.825(4) 2.905(4) 3.007(6) 2.945(5) 3.007(4) 2.910(4) 3.035(4)	
Tm2.1	– 2 Cu2 – 2 Cu2 – 2 Cu1 – 2 Cu3 – 2 Cu3 – 1 Cu6 – 2 Cu3	2.792(6) 2.884(6) 2.926(4) 2.981(7) 3.033(7) 3.131(6) 3.195(7)	
Tm2.2	– 1 Cu6 – 2 Cu1 – 2 Cu3 – 2 Cu3 – 2 Cu3 – 2 Cu2 – 2 Cu4 – 1 Cu2	2.733(6) 2.843(4) 2.844(7) 2.919(7) 2.941(7) 2.988(6) 2.757(13) 2.998(6)	
Tm3	– 6 Cu2 – 3 Cu4 – 6 *M* [a] – 1 Tm3	2.833(4) 2.973(6) 3.019(5) 3.344(4)	
Cu1	– 1 *M* [a] – 1 Cu3 – 1 Cu2 – 1 Cu5 – 1 Cu2 – 1 Cu3 – 1 Tm1 – 1 Tm2.2 – 1 Tm1 – 1 Tm1 – 1 Cu1 – 1 Cu3 – 1 Cu1	2.526(6) 2.546(6) 2.588(6) 2.649(4) 2.741(6) 2.739(6) 2.825(4) 2.843(4) 2.905(4) 2.910(3) 2.956(5) 3.255(6) 3.507(6)	
Cu2	– 1 Cu3 – 1 *M* [a] – 1 Cu1 – 1 *M* [a] – 1 Cu4 – 1 Cu1 – 2 Cu2 – 1 Tm2.1 – 1 Tm3 – 1 Tm2.1 – 1 Tm1	2.534(6) 2.577(5) 2.588(6) 2.639(5) 2.681(9) 2.741(6) 2.283(6) 2.792(6) 2.833(4) 2.884(6) 2.998(6)	

Table 3 Interatomic distances and coordination polyhedra for $Tm_{14}Cu_{46}Ga_5$ (continued).

Cu3	– 1 Cu4 – 1 Cu1 – 1 Cu5 – 1 Cu3 – 1 Cu3 – 1 Cu6 – 1 Cu1 – 1 Tm2.2 – 1 Tm2.2 – 1 Tm2.2 – 1 Tm1 – 1 Cu1	2.534(6) 2.546(6) 2.580(5) 2.616(6) 2.632(5) 2.693(4) 2.739(6) 2.844(7) 2.919(7) 2.941(7) 3.007(4) 3.255(6)	
$[Cu4_3]$ [b]	– 12 Cu2 – 3 Tm2.1 – 3 Tm2.2 – 2 Tm3	3.467(7) 3.756(7) 4.184(2) 2.611(4)	
Cu5	– 1 Cu6 – 3 Cu3 – 3 Cu1 – 3 Tm1	2.383(7) 2.580(5) 2.649(4) 2.945(5)	
Cu6	– 2 Cu4 – 6 Cu3 – 3 Tm2.2	2.383(7) 2.693(4) 2.733(6)	
M [a]	– 2 *M* [a] – 2 Cu1 – 2 Cu2 – 2 Cu2 – 1 Tm1 – 1 Tm1 – 2 Tm3	2.514(8) 2.526(6) 2.577(6) 2.639(5) 2.926(6) 3.007(6) 3.019(5)	

[a] $M = 0.833Ga + 0.167Cu$

[b] The distances in polyhedron determined from the center of cluster $[Cu_3]$

types. The position of Tm2 is split into two half-occupied 6*j* positions, like the corresponding site in the $Gd_{14}Ag_{51}$ type. The Cu atoms form [Cu_3] clusters of two types: triangles and linear finite fragments.

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