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# Cluster Self-Organization of Intermetallic Systems: Three-Layer Icosahedral Nanoclusters K132 = $0@12(In_6Tl_6)@30(In_6Na_6K_{18})@90(In_{72}Na_{12}K_6)$ and K116 = $0@12(In_6Tl_6)@26(In_{12}K_{14})@78(In_{36}Tl_{20}K_{12})$ for the Self-Assembly of the $K_{52}Na_{12}Tl_{36}In_{122}$-*hP*224 Crystalline Structure

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**Abstract**—The TOPOS software package is used for the combinatorial topological analysis and simulation of the self-assembly of the $K_{52}Na_{12}Tl_{36}In_{122}$-*hP*224 (spatial group *P*-3*m*1, $a = b = 16.909$, $c = 28.483$ Å, $V = 7\,052$ Å$^3$) crystalline structure. A total of 1649 variants of the cluster representation of a 3*D* atomic lattice with the number of structural units ranging from 4 to 10 are found. Two frame-forming three-layer icosahedral nanoclusters are detected: K132 and K116 with symmetry $g = -3m$ and a diameter of 17 Å. The chemical composition of the shells of the three-layer 132-atom nanocluster K132 is $0@12(In_6Tl_6)@30(In_6Na_6K_{18})@90(In_{72}Na_{12}K_6)$ and that of the 116-atom nanocluster K116 is $(0@12(In_6Tl_6)@26(In_{12}K_{14})@78(In_{36}Tl_{20}K_{12})$. The symmetrical and topological code of the self-assembly of the 3D $Na_{12}K_{52}Tl_{36}In_{122}$ structure from the precursor K132 and K116 nanoclusters is reconstructed in the following form: primary chain → layer → frame. The framework's voids are occupied by spacer atoms K and Tl.

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## INTRODUCTION

Crystallization of potassium intermetallic compounds was detected in binary systems K–*M* (with the participation of 15 chemical elements *M*), in 63 ternary systems K–*M*1–*M*2 (with the participation of 27 elements) and in 30 quaternary systems K–*M*1–*M*2–*M*3 (with the participation of 29 elements) [1, 2].

Twelve quaternary intermetallic compounds are formed in 11 systems K–Na–*M*1–*M*2 with the participation of atoms *M*1 and *M*2 = Au, Mg, Zn, Cd, Al, Ga, In, Sn, Sb, Bi) (Table 1, [3–14]). In the K–Na–Cd–Tl system, the formation of two compounds is detected; and in the other systems, of one compound (Table 1). With the participation of the large atoms K and Rb, and K and Cs in quaternary systems only 3 and 2 intermetallic compounds are formed [1, 2].

In [15] for the quaternary intermetallic compound $K_{23}Na_8Cd_{12}In_{48}$-*hP*91 ($a = b = 17.114$, $c = 10.442$ Å, spatial group *P*6/*mmm*), a new type of polyhedral precursor cluster was detected: K8 = $0@8(Na_2In_6)$ and K8 = $0@K_2In_6$ in the form of a hexagonal bipyramid. The $Na_2In_6$ clusters were templates on the surfaces of which atomic shells of 36 atoms were formed. The composition of the two-layer templated cluster is K44 = $0@8(Na_2In_6)@36(In_6Cd_6K_6)_2$.

The crystalline structure of the most complex quaternary intermetallic compound $K_{52}Na_{12}Tl_{36}In_{122}$-*hP*224 in terms of crystalline chemistry [13] is characterized by the high values of the parameters of the hexagonal cell: $a = b = 16.909$ Å, $c = 28.483$ Å, $V = 7\,052$ Å$^3$, spatial group *P*-3*m*1(164), and 32 crystallographic independent atoms with unique Wyckoff positions $j^8i^{20}d^3c$. Two Na atoms have coordination numbers (CN) = 13 and 15; eight K atoms have CN = 12, 14, 15, and 16; sixteen In atoms have CN = 9, 10, 11, 12, and 16; and six Tl atoms have CN = 10, 11, 13, and 14.

This work using the ToposPro software package [16] performs geometrical and topological analysis of the crystalline structure of the intermetallic compound $K_{52}Na_{12}Tl_{36}In_{122}$-*hP*224. The symmetrical and topological code of the self-assembly of the crystalline structure of the intermetallic compound made of nanoclusters K132 and K116 is reconstructed in the following form: primary chain → microlayer → microframe.

**Table 1.** Crystallographic data of intermetallic compounds formed in the systems K–Na–*M*1–*M*2, where *M*1, *M*2 = Au, Mg, Zn, Cd, Al, Ga, In, Sn, Sb, Bi

| Compound | Spatial group | Pearson class | Parameters of unit cell in Å and angles in degrees | *V*, Å$^3$ |
|---|---|---|---|---|
| $K_6Na_3AlSb_4$ [3] | *P*6$_3$/*mmc* (194) | *hP*28 | 10.168, 10.168, 10.527 | 942.6 |
| $K_6Na_3GaSb_4$ [4] | *P*6$_3$/*mmc* (194) | *hP*28 | 10.218, 10.218, 10.590 | 957.5 |
| $K_2Na_4Sn_2Zn$ [5] | *P*12$_1$/*c*1 (14) | *mP*36 | 11.572, 9.862, 11.382,<br>90.00, 119.33, 90.00 | 1132.3 |
| $KNa_4SnSb_3$ [6] | *P*12$_1$/*c*1 (14) | *mP*36 | 9.091, 8.375, 17.463,<br>90.00, 121.37, 90.00 | 1135.2 |
| $K_6Na_2Cd_3Tl_{12}$ [7] | *Im*-(204) | *c*I46 | 11.321, 11.321, 11.321 | 1451.0 |
| $K_6Na_{14}MgTl_{18}$ [8] | *Pm*-3 (200) | *c*P39 | 11.591, 11.591, 11.591 | 1557.4 |
| $K_3\ Na_2\ Sn\ Bi_3$ [9] | *Ibca* (73) | *o*I72 | 7.182, 16.926, 21.595 | 2625.1 |
| $Na_8K_{23}Cd_{12}In_{48}$ [10] | *P*6/*mmm* (191) | *h*P91 | 17.114, 17.114, 10.442 | 2648.6 |
| $K_{16}Na_9\ Cd_3Tl_{18}$ [11] | *P*6$_3$/*mmc* (194) | *hP*98 | 11.136, 11.136, 29.352 | 3152.3 |
| $K_{38}Na_{12}Au_2Tl_{48}$ [12] | *P*-62*m* (189) | *hP*100 | 19.343, 19.343, 11.498 | 3725.6 |
| **$K_{26}Na_6In_{61}Tl_{18}$ [13]** | ***P*-3*m*1 (164)** | ***hP*224** | **16.909, 16.909, 28.483** | **7052.6** |
| $K_{14}Na_{21}Cd_{17}Ga_{84}$ [14] | *R*-3*m* (166) | *hR*139 | 16.669, 16.669, 36.472 | 8776.3 |

This work is a continuation of the studies [15, 17–23] in the field of simulation of the self-organization of systems at the supra-polyhedral level and the geometrical and topological analysis of crystalline structures by advanced computer methods.

## METHODS OF COMPUTER ANALYSIS

The geometrical and topological analysis was performed using the ToposPro software package [16], which allows us to perform a multipurpose automatic study of the crystalline structure based on the representation of structures in the form of convoluted graphs (factor graphs). The data on the functional role of atoms upon the formation of a crystalline structure were obtained by computing the coordination sequences, that is, the sets of numbers $\{N_k\}$, where $N_k$ is the number of atoms in the *k*th coordination sphere of the given atom.

The obtained values of the coordination sequence of atoms in 3*D* lattices are summarized in Table 2, where the number of neighboring atoms in the nearest surrounding area is highlighted in bold, that is, in the first coordination sphere of the atom. All atoms are characterized by various sets of coordination sequences $\{N_k\}$.

The automatic decomposition algorithm of the structure of any intermetallic compound was described elsewhere and implemented using the ToposPro software package [16].

## SELF-ASSEMBLY OF THE $K_{52}Na_{12}Tl_{36}In_{122}$-*hP*224 CRYSTALLINE STRUCTURE

The applied simulation method of the crystalline structure is based on the determination of the hierarchical sequence of its self-assembly in crystallographic space [15, 17]. At the first level of the system's self-organization, the mechanism of the primary chain formation of nanoclusters of the zero level formed at the template stage of the system's chemical evolution is determined, then the mechanism of self-assembly of the layer chain (the 2nd level), and then of the layer of the structure's 3D frame (the 3rd level).

**Crystallographic data.** The spatial group *P*-3*m*1 (no. 164) is characterized by the elements with point symmetry: *g* = –3*m* (1*a*, 1*b*), 3*m* (2*c*, 2*d*), 2/*m* (3*e*, 3*f*), 2 (6*g*, 6*h*), and *m* (6*i*). The group's order is 12.

Table 2 shows the local surrounding of K, Na, Tl, and In atoms and their coordination sequences in a 3*D* atomic lattice.

The number of variants of representing a 3*D* atomic lattice with the number of structural units ranging from 4 to 10 was 1649 (Table 3).

Two variants of different crystallographic icosahedral clusters *ico*-$In_6Tl_6$(0@12) were detected with the symmetry –3*m*, occupying the highly symmetric positions 4*a* and 4*b*.

Icosahedrons *ico*-$In_6Tl_6$(0@12) are templates on which three-layer clusters K132 and K116 are formed with the size of 17 Å (Figs. 1, 2).

The chemical composition of the shells of the nanocluster K132 is 0@12($In_6Tl_6$)@30($In_6Na_6$-$K_{18}$)@-90($In_{72}Na_{12}K_6$). The chemical composition of the

**Table 2.** $K_{52}Na_{12}Tl_{36}In_{122}$-$hP224$. Local surrounding of Na, K, Tl, and In atoms and coordination sequences. Coordination number of atoms is highlighted in bold

| Atom | Local surrounding | Coordination sequences |
|---|---|---|
| | | **N1** N2 N3 N4 N5 |
| Na1 | 3 K + 12 In | **15** 44 103 192 315 |
| Na2 | 5 K + 7 In + 1 Tl | **13** 48 110 196 311 |
| K1 | 4 K + 6In + 6 Tl | **16** 49 103 204 336 |
| K2 | 3 Na + 3 K + 3 In + 2 Tl | **16** 49 105 205 331 |
| K3 | 3 K + 6 In + 6 Tl | **15** 48 105 209 336 |
| K4 | 1 Na + 3 K + 8 In + 3 Tl | **15** 47 106 198 326 |
| K5 | 3 K + 8 In + 3 Tl | **14** 46 102 200 308 |
| K6 | 1 Na + 3 K +10 In + 1 Tl | **15** 45 101 202 330 |
| K7 | 12 In | **12** 36 90 193 297 |
| K8 | 3 K + 9 In + 3 Tl | **15** 46 97 189 321 |
| In1 | 3 K + 3 In + 3 Tl | **9** 36 96 187 298 |
| In2 | 4 K + 4 In + 3 Tl | **10** 42 100 188 317 |
| In3 | 3 K + 3 In + 3 Tl | **9** 37 97 185 303 |
| In4 | 1 Na + 3 K + 4 In + 2 Tl | **10** 40 97 187 301 |
| In5 | 2 Na + 2 K + 6 In | **10** 41 99 193 298 |
| In6 | 4 K + 6 In | **10** 39 92 178 296 |
| In7 | 3 K + 5 In + 1 Tl | **9** 36 94 181 300 |
| In8 | 3 Na + 2 K + 4 In | **9** 42 104 184 301 |
| In9 | 3Na + 2 K + 5 In | **10** 42 102 191 306 |
| In10 | 3 Na + 2 K + 4 In | **9** 41 103 186 299 |
| In11 | 4 K + 4 In + 3 Tl | **11** 47 106 193 318 |
| In12 | 5 K + 4 In + 3 Tl | **12** 48 102 188 319 |
| In17 | 1 Na + 4 K + 5 In + 1 Tl | **11** 41 106 183 292 |
| In18 | 2 Na + 4 K + 4 In | **10** 42 99 182 299 |
| In19 | 4 K + 4 In + 3 Tl | **11** 47 109 189 302 |
| In21 | 12 In + 4 Tl | **16** 40 105 177 282 |
| Tl1 | 4 K + 4 In + 2 Tl | **10** 39 100 173 294 |
| Tl2 | 1 Na + 5 K + 3 In + 2 Tl | **11** 47 101 182 307 |
| Tl3 | 4 K + 5 In + 1 Tl | **10** 39 95 173 286 |
| Tl4 | 5 K + 4 In + 2 Tl | **11** 43 105 179 300 |
| Tl8 | 6 K + 7 In + 1 Tl | **14** 54 115 200 318 |
| Tl10 | 6 K + 7 In | **13** 54 121 198 303 |

**Table 3.** $K_{52}Na_{12}Tl_{36}In_{122}$-*hP*224. Variants of cluster representation of crystalline structure with 4 and 10 structural units. Central atom or void center of polyhedral cluster is shown together with the number of its shells (the first brackets) and number of atoms in each shell (the second and the third brackets). Crystallographic positions corresponding to void centers of polyhedral clusters are denoted as ZA1 and ZA2

| **4 structural units** |
|---|
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(3)(0@12@26@78) K8(1)(1@15) Tl10(1)(1@13) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(3)(0@12@26@78) K8(0)(1) K4(1)(1@15) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(3)(0@12@26@78) K8(1)(1@15) K4(1)(1@15) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(2)(0@12@26) K8(2)(1@15@46) Tl10(0)(1) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(2)(0@12@26) K8(2)(1@15@46) Tl10(1)(1@13) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(2)(0@12@26) In21(1)(1@16) K1(1)(1@16) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(2)(0@12@26) Tl10(1)(1@13) K1(1)(1@16) |
| ZA2(1b)(3)(0@12@30@90) ZA1(1a)(3)(0@12@26@78) K8(1)(1@15) Tl10(1)(1@13) |
| **10 structural units** |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(1)(1@13) Na1(1)(1@15) Na2(1)(1@13) In6(1)(1@10) In11(1)(1@11) Tl3(0)(1) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(1)(1@13) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(0)(1) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(1)(1@13) Na1(1)(1@15) Na2(0)(1) In6(1)(1@10) In11(1)(1@11) Tl3(0)(1) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(1)(1@13) Na1(0)(1) Na2(1)(1@13) In6(1)(1@10) In11(1)(1@11) Tl3(0)(1) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(1)(1@13) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(0)(1) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(0)(1) Tl10(0)(1) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(0)(1) K8(0)(1) Tl10(0)(1) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(0)(1) K8(1)(1@15) Tl10(0)(1) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(0)(1) Tl10(1)(1@13) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(0)(1) K8(0)(1) Tl10(0)(1) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(0)(1) K8(1)(1@15) Tl10(0)(1) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(0)(1) Tl10(1)(1@13) Na1(1)(1@15) Na2(1)(1@13) In6(0)(1) In11(1)(1@11) Tl3(1)(1@10) |
| ZA2(1b)(1)(0@12) ZA1(1a)(1)(0@12) K7(1)(1@12) K8(1)(1@15) Tl10(1)(1@13) Na1(1)(1@15) Na2(1)(1@13) In6(1)(1@10) In11(1)(1@11) Tl3(0)(1) |

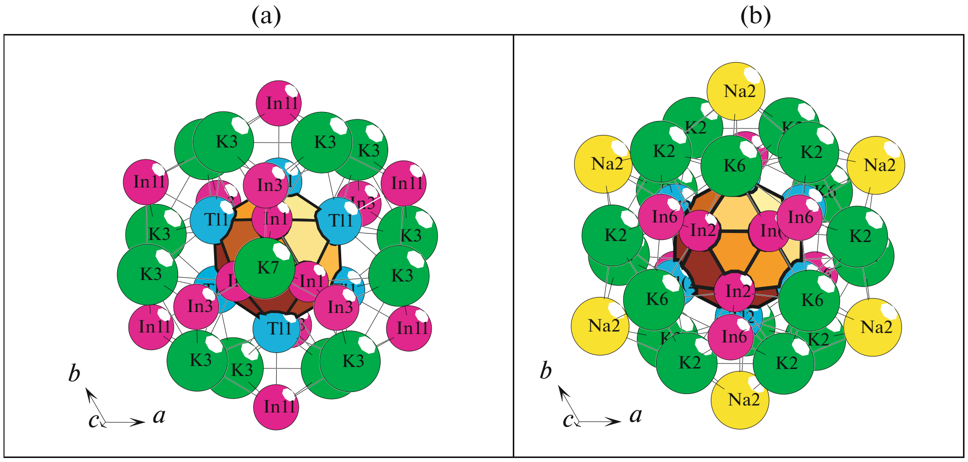

**Fig. 1.** Two-layer clusters 0@12@26 (a) and (0@12@30 (b).

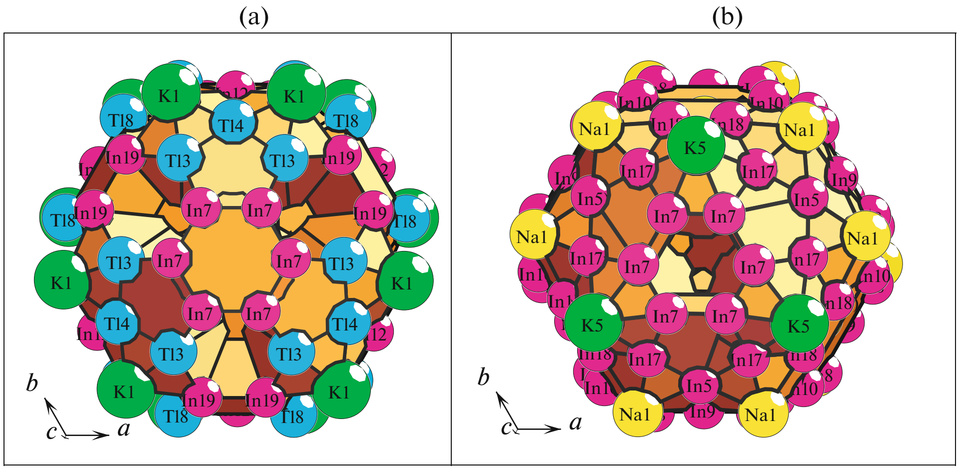

**Fig. 2.** Three-layer clusters K116 (a) and K132 (b).

**Table 4.** Atoms forming 132–atom nanocluster K132. Na and K atoms are highlighted in bold

| Nanocluster K132 | | |
|---|---|---|
| Icosahedral cluster 0@12 | 30-atom shell | 90-atom shell |
| 6 In2 | 6 In6 | 12 In10 |
| 6 Tl2 | **12 K2** | 12 In17 |
| | **6 K6** | 12 In18 |
| | **6 Na2** | 6 In5 |
| | | 12 In7 |
| | | 12 In8 |
| | | 6 In9 |
| | | **6 K5** |
| | | **12 Na1** |

**Table 5.** Atoms forming 116-atom nanocluster K116. K atoms are highlighted in bold

| Cluster K116 | | |
|---|---|---|
| Icosahedral cluster 0@12 | 26-atom shell | 78-atom shell |
| 6 In1 | 6 IN11 | 6 In12 |
| 6 Tl1 | 6 In3 | 12 In19 |
| | **12 K3** | 6 In21 |
| | **2 K7** | 12 In7 |
| | | 6 Tl4 |
| | | 12 Tl3 |
| | | 12 Tl8 |
| | | **12 K1** |

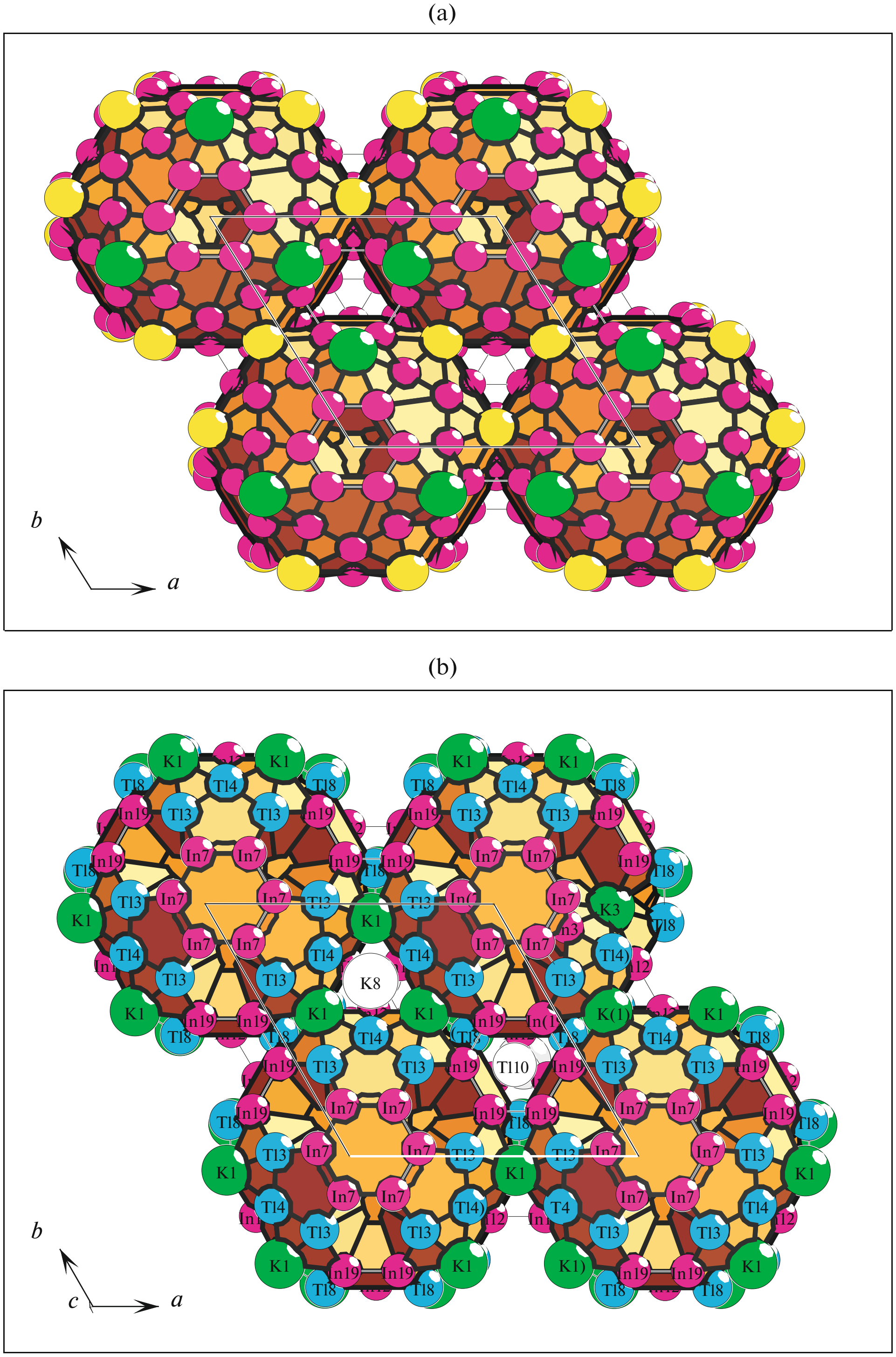

**Fig. 3.** Binding of clusters K132 (a) and K116 (b) upon layer formation.

shells of the nanocluster K116 is $0@12(In_6Tl_6)@26(In_{12}K_{14})@78(In_{36}Tl_{20}K_{12})$.

**Self-assembly of crystalline structure.** The nanoclusters K132 (Table 4) and K116 (Table 5) are the frame-forming clusters.

*Layer*. The $S_3^2$ basic layer is formed of clusters K132 upon the binding of the primary chains with a shift (Fig. 3). The distance between the centers of clusters K132 in the primary chain and in the layer determines the values of the translation vectors $a = b = 16.909$ Å.

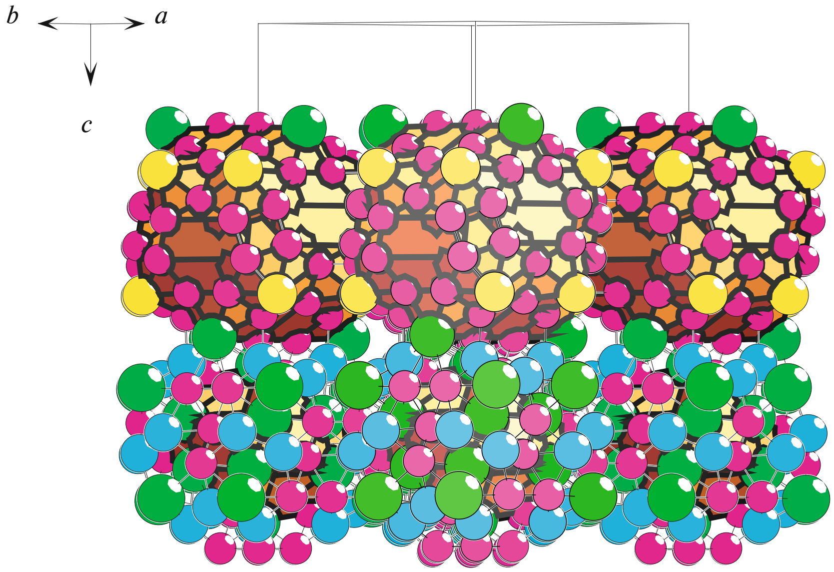

**Fig. 4.** Binding of layers of clusters K116 and K132 upon formation of packet.

*Packet*. The layer of clusters K116 is formed on the surface of the layer of clusters K132 (Fig. 4). In the voids of the layer of clusters K116, spacer atoms K8 and Tl10 occupy positions 2*d* (1/3, 2/3, 0.174) and Tl10 (2/3, 1/3, 0.185) with symmetry 3*m*. The thickness of the two-layer packet corresponds to the absolute value of the translation vector $c = 28.483$ Å.

*Self-assembly of shell*. The 3*D* framework structure $S_3^3$ is formed upon the binding of two-layer packets in the Z direction.

## CONCLUSIONS

Two frame-forming nanoclusters have been detected using the decomposition of the 3*D* atomic lattice: K132 and K116 with symmetry $g = -3m$. The voids of the layer of K116 clusters are occupied by spacer atoms K and Tl.

The chemical composition of shells of the nanocluster K132 is $0@12(In_6Tl_6)@30(In_6Na_6K_{18})$-$@90(In_{72}Na_{12}K_6)$ and that of the nanocluster K116 is $0@12(In_6Tl_6)@26(In_{12}K_{14})@78(In_{36}Tl_{20}K_{12})$.

The symmetrical and topological code of the self-assembly of the 3*D* structure from the precursor nanoclusters K132 and K116 has been reconstructed in the following form: primary chain → layer → frame.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

## REFERENCES

1. Villars, P. and Cenzual, K., *Pearson's Crystal Data-Crystal Structure Database for Inorganic Compounds (PCDIC),* Materials Park, OH: ASM Int., 2018.
2. Inorganic Crystal Structure Database (ICSD), Karlsruhe, Germany: Fachinformationszentrum; USA: Natl. Inst. Standard Technol.
3. Somer, M., Carrillo-Cabrera, W., Peters, E.M., Peters, K., and von Schnering, H.G., Crystal structure of sodium potassium antimonidetriantimonidoaluminate, $Na_3K_6Sb(AlSb_3)$, *Z. Kristallogr.,* 1995, vol. 210, pp. 527–527.
4. Somer, M., Carrillo-Cabrera, W., Peters, E.M., Peters, K., and Vonschnering, H.G., Crystal structure of sodium potassium antimonidetriantimonidogallate, $K_6Na_3Sb(GaSb_3)$, *Z. Kristallogr.,* 1995, vol. 210, pp. 143–143.
5. Kim, S.-J., Kraus, F., and Faessler, T.F., $Na_6ZnSn_2$, $Na_{4.24}K_{1.76}ZnSn_2$, and $Na_{20}Zn_8Sn_{11}$: Three intermetallic structures containing the linear $\{Sn-Zn-Sn\}_6$-unit, *J. Am. Chem. Soc.,* 2009, vol. 131, pp. 1469–1478.
6. Eisenmann, B. and Klein, J.D., Zintl-anionen $[Sn_2As_6]_{10-}$ und $[Sn_2Sb_6]_{10-}$ in alkaliverbindungen, *Z. Kristallogr.,* 1991, vol. 196, pp. 213–229.
7. Tillard-Charbonnel, M.M., Belin, C.H.E., Manteghetti, A.P., and Flot, D.M., Heteroatomic centering of icosahedral clusters. Crystal and electronic structure of the $K_6(NaCd)_2Tl_{12}Cd$ compound containing the not-so-naked $Tl_{12}Cd_{12}$-polyanion, *Inorg. Chem.,* 1996, vol. 35, pp. 2583–2589.
8. Dong, Z-C. and Corbett, J.D., $Na_{14}K_6Tl_{18}M$ (M = Mg, Zn, Cd, Hg) and $Na_{13.5}Sm_{0.5}K_6Tl_{18}Na$: Novel octahedral and centered icosahedral cluster phases related

to the $Mg_2Zn_{11}$-type structure, *Angew. Chem., Int. Ed. Engl.,* 1996, vol. 36, pp. 1006–1008.

9. Asbrand, M., Eisenmann, B., and Engelhardt, H., Dimere und polymere Pnictidostannat(IV)-anionendarstellung und kristallstrukturen von $Na_2K_3[SnP_3]$, $Na_2Cs_3[SnP_3]$ und $Na_2K_3[SnBi_3]$, *Zeitschr. Naturforsch., B,* 1998, vol. 53, pp. 405–410.
10. Flot, D.M., Tillard-Charbonnel, M., and Belin, C., $Na_8K_{23}Cd_{12}In_{48}$: A zintl phase containing icosahedral and triangular indium units and displaying a remarkable condensed metal fullarene stuffed with a tubular cluster. Synthesis, crystal, and electronic structures, *J. Am. Chem. Soc.,* 1996, vol. 118, pp. 5229–5235.
11. Huang, D. and Corbett, J.D., $Na_9K_{16}Tl_{18}Cd_3$: A novel phase containing $(T_{18}Cd_3)(-)$ and $Tl_5(7)$ clusters, *Inorg. Chem.,* 1999, vol. 38, pp. 316–320.
12. Huang, D., Dong, Zh.-ch., and Corbett, J.D., $Na_{12}K_{38}Tl_{48}Au_2$: A metallic zintl phase with naked icosahedral fragments $Tl_7(7-)$ and $Tl_9(9-)$ plus Au(–), *Inorg. Chem.,* 1998, vol. 37, pp. 5881–5886.
13. Flot, D.M., Tillard Charbonnel, M.M., and Belin, C., Crystal structure of sodium potassium thallide indide, $Na_6K_{26}In_{42-x}(In_yTl_{38-y})$ ($x = 1.08$; $y = 20.12$), *Z. Kristallogr. (New Struct.),* 1998, vol. 213, pp. 225–226.
14. Flot, D., Vincent, L., Tillard-Charbonnel, M., and Belin, C., Crystal structure of sodium potassium cadmium gallium, $Na_{21}K_{14}Cd_{17}Ga_{84}$, *Z. Kristallogr. (New Struct.),* 1997, vol. 212, pp. 509–510.
15. Shevchenko, V.Ya., Blatov, V.A., and Ilyushin, G.D., Modeling self-organization processes in crystal-forming systems: New two-layer cluster–precursor K44 = $0@8(Na_2In_6)@36(In_6Cd_6K_6)_2$ for the self-assembly of the $K_{23}Na_8Cd_{12}In_{48}$–hP91 crystal structure, *Glass Phys. Chem.,* 2019, vol. 45, no. 6, pp. 405–411.
16. Blatov, V.A., Shevchenko, A.P., and Proserpio, D.M., Applied topological analysis of crystal structures with the program package ToposPro, *Cryst. Growth Des.,* 2014, vol. 14, pp. 3576–3585.
17. Ilyushin, G.D., *Modelirovanie protsessov samoorganizatsii v kristalloobrazuyushchikh sistemakh* (Modeling of Self-Organization Processes in Crystal-Forming Systems), Moscow: Editorial URSS, 2003.
18. Ilyushin, G.D., Modeling of the self-organization processes in crystal-forming systems. tetrahedral metal clusters and the self-assembly of crystal structures of intermetallic compounds, *Crystallogr. Rep.,* 2017, vol. 62, pp. 670–683.
19. Ilyushin, G.D., Symmetry and topology code of the cluster self-assembly of intermetallic compounds $A_2^{[16]}B_4^{[12]}$ of the friauf families $Mg_2Cu_4$ and $Mg_2Zn_4$, *Crystallogr. Rep.,* 2018, vol. 63, pp. 543–552.
20. Blatov, V.A., Ilyushin, G.D., and Proserpio, D.M., New types of multishell nanoclusters with a Frank-Kasper polyhedral core in intermetallics, *Inorg. Chem.,* 2011, vol. 50, pp. 5714–5724.
21. Ilyushin, G.D., Modeling of self-organization processes in crystal-forming systems: Symmetry and topology code for the cluster self-assembly of crystal structures of intermetallic compounds, *Russ. J. Inorg. Chem.,* 2017, vol. 62, pp. 1730–1769.
22. Pankova, A.A., Akhmetshina, T.G., Blatov, V.A., and Proserpio, D.M., A collection of topological types of nanoclusters and its application to icosahedra-based intermetallics, *Inorg. Chem.,* 2015, vol. 54, no. 13, pp. 6616–6630.
23. Ilyushin, G.D., Crystal chemistry of lithium intermetallic compounds: A survey, *Russ. J. Inorg. Chem.,* 2018, vol. 63, no. 14, pp. 1786–1799.

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