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Synthesis and Crystal Structure Determination of the New Ternary Intermetallic Phase $Na_{17}Cu_6Ga_{46.5}$ ($Na_{102}Cu_{36}Ga_{279}$)

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$Na_{17}Cu_6Ga_{46.5}$ crystallizes in the trigonal system, space group $R\bar{3}m$ with $a = b = 16.183(6)$, $c = 35.190(9)$ Å; $Z = 6$. Diffraction data were collected on a Nonius CAD 3 diffractometer within the octants hkl and $hk\bar{l}$ of the corresponding A-centered monoclinic cell ($a = 14.993(6)$, $b = 16.184(7)$, $c = 25.254(8)$ Å; $\beta = 119.75(5)°$). The 5091 reflections were transformed and averaged into 1216 observed ($I > 3\sigma(I)$) in the $R\bar{3}m$ space group. The structure was solved by direct methods and refined by full-matrix least-squares to a final $R(F) = 0.056$. The structure of $Na_{102}Cu_{36}Ga_{279}$ contains icosahedra displaying two types of symmetry and a triply fused icosahedron which forms a very unusual polyhedral complex with a copper atom ($M_{28}CuM_{28}$). Clusters are linked to each other to form an intricated three-dimensional anionic lattice. Sodium cations lie inside 12-vertex (Friauf), 15-vertex, and 16-vertex polyhedral cavities. This stoichiometric phase has been interpreted in terms of electron-deficient bonding within clusters and localized (2*c*–2*e*) bonding between clusters. In association with the extended Hückel molecular orbital (EHMO) calculation, the Wade–Mingos electron counting procedure applies successfully.

Introduction

During the last decade, numerous and interesting phases have been discovered in binary or ternary intermetallic systems involving gallium and alkali metals. Generally the binary phases are stoichiometric and simply constituted of classical deltahedral units: dodecahedra in MGa_3 (M = K, Rb, Cs) (*1–4*), icosahedra in Li_2Ga_7 (*5–7*), MGa_7 (M = Rb, Cs) (*8*), K_3Ga_{13} (*9*), and $Na_{22}Ga_{39}$ (*10*) or Na_7Ga_{13} (*11, 12*), and octadecahedra in K_3Ga_{13}. In these phases, polyhedra are linked to each other to form a three-dimensional anionic lattice and their linking mode depends upon the degree of reduction of gallium atoms by alkali metals. Polyhedra are linked either directly or by means of spacers: tri- or tetra-coordinated isolated gallium atoms or junction polyhedra, generally through 2*c*–2*e* bonds. Almost all structures are interpreted in terms of delocalized electron-deficient bonds on clusters and classical localized 2*c*–2*e* bonds between

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them. Combination of these bonding modes are found in $Na_{22}Ga_{39}$, whereas a $3c$–$2e$ interpolyhedral bond has been found in MGa_7. All gallium ternary phases involving two kinds of alkali metal have been found nonstoichiometric. Face-sharing twinned icosahedra are observed in $Li_3Na_5Ga_{19.56}$ (*13*), $Li_9K_3Ga_{28.83}$ (*14*), and $Rb_{0.6}Na_{6.25}Ga_{20.02}$ (*15*), while $K_4Na_{13}Ga_{49.57}$ (*16*) contains a triply fused icosahedron. Nonstoichiometry, i.e., defection of gallium on some cluster vertices, makes the electron counting very difficult in these phases.

As shown recently, ternary phases $Li_{13}Cu_6Ga_{21}$ (*17*) and $Li_{38}(Ga_{0.663}Zn_{0.337})_{101}$ (*18*) incorporating an electron poorer late transition metal still contain metallic clusters. Inclusion of atoms which are different in size yields some beautiful superstructures and allows extended icosahedral arrangements that prefigure quasicrystals.

Experimental

The metals used for the synthesis were sodium and copper from Merck laboratories and gallium (6 *N*) from Rhône–Poulenc Industry. Alloys were prepared by melting together the elements in a niobium reactor which had been weld-sealed in an argon atmosphere. A mixture of composition near to $NaCuGa_3$ was prepared and heated up to 800°C for 36 hr and then allowed to cool slowly at the rate of 6°/hr for crystal growing.

In addition to a small amount of some metallic material which was identified as a binary CuGa compound, the remaining product of the reaction appeared homogeneous, with metallic luster and relatively brittle. It was examined under a stereoscopic microscope inside a glove box filled with purified argon and broken into small pieces to be inserted inside Lindemann glass capillaries and checked by preliminary oscillation and Weissenberg photographs; any contact with oxygen, nitrogen, and moisture was avoided. Several single crystals that displayed the same symmetry and cell parameters were analyzed by conventional atomic absorption spectroscopy giving an Na/Cu/Ga ratio of 1/0.35(1)/2.71(3).

The preliminary photographs indicated the crystal to have monoclinic symmetry with parameters a = 14.99, b = 16.18, and c = 25.25 Å, with β = 119.8°. The centering of the cell (*A*) and relationships between parameters readily indicated that an orthorhombic cell could be deduced. Finally, a trigonal unit was constructed with parameters $a = b = 16.18$, $c = 35.19$ Å, $\gamma = 120°$, the corresponding possible space groups being $R\bar{3}m$, $R3m$, or $R32$.

The best-diffracting crystal of dimensions 0.31 × 0.14 × 0.06 mm was selected and mounted on an Enraf–Nonius CAD 3 diffractometer. Accurate lattice parameters of the monoclinic cell were determined by least-squares refinement of the angular positions of 20 reflections collected and automatically centered on the diffractometer a = 14.993(4), b = 16.184(5), c = 25.254(6) Å, β = 119.75(2)°.

Integrated diffraction intensities were collected at room temperature in the range $50 \geq 2\theta \geq 6°$ within the two octants hkl and $hk\bar{l}$ using graphite monochromated MoK_α radiation. Data were collected in the θ-2θ mode, scan ranges were calculated from the formula $Sr = A + B \tan \theta$, were A depends upon the mosaïc spread of the crystal and B allows for increasing peak width due to $K_{\alpha 1}$ and $K_{\alpha 2}$ splitting; A and B were taken as 1.2° and 0.35° respectively. During data collection, the intensity of one standard reflection was checked after every 60 reflections, and no significant loss in intensity was observed. The data were corrected for background and Lorentz-polarization effects. Once the composition of the crystal was determined, the data were corrected for the absorption effect (μ = 399 cm^{-1}), equivalent data in the trigonal cell ($a_H = (2a + b + c)/2$, b_H =

$(-2a + b - c)/2$, $c_H = -a + c$) were averaged using SHELX facilities (*19*).

A good average ($R_{\text{intensities}} = [\Sigma(F^2 - \bar{F}^2)^2/\Sigma F^4]^{1/2} = 5.1\%$) was obtained for the $\bar{3}m$ Laüe symmetry. The condition $(-h + k + l) = 3n$ limiting possible reflections indicated only the possible $R\bar{3}m$, $R3m$, or $R32$ space groups. The final data set consisted of 1216 unique reflections corresponding to the criterion $I > 3\sigma(I)$.

Structure Solution and Refinement

The structure was solved using the direct methods provided by SHELXS 86 (*20*), the statistical test of the program clearly indicated the structure to be centrosymmetric, hence the $R\bar{3}m$ space group was chosen and used successfully in structure refinement. The output of the Fourier step contained all the peaks corresponding to the heavy atoms. After a few cycles of positional and isotropic thermal parameters refinement, a Fourier synthesis revealed the presence of the remaining sodium atoms. Finally the structure was refined, using anisotropic thermal parameters for all heavy atoms and isotropic temperature factors for sodium atoms, minimizing the function $w(|F_o| - |F_c|)^2$ with $w = 3.761/\sigma^2(F) + 0.001F^2$ to a final reliability factor $R(F) = \Sigma\, ||F_o|| - |F_c||/\Sigma|F_o|$ of 0.056 ($Rw(F) = 0.055$). The last difference Fourier map was flat except for residuals in the very close neighborhood of heavy atoms less than 2.0 e$^-$/Å^3. Except for one heavy atom position that might be assigned to a copper atom, gallium cannot be distinguished from copper.

Results and Discussion

The final positional and thermal parameters are listed in Table I and main bond distances are given in Table II. The unit cell contains six formula units of $Na_{17}Cu_6Ga_{46.5}$ ($Na_{102}Cu_{36}Ga_{279}$) and two cluster types: atoms $M(5)$ and $M(11)$ compose the icosahedron (A) located at the $3(a)$ position with symmetry $\bar{3}m$, and atoms $M(2, 3, 7, 8)$ are arranged on icosahedron (B) centered at the $9(d)$ position and displaying $2/m$ symmetry. The remaining atoms $M(1, 4, 6, 9, 10, 12, 13$, and $14)$ form a triply fused polyhedron which results from the condensation of three icosahedral units, each of them sharing two triangular faces with its two neighbors; this polyhedron (C) displays $3m$ symmetry. Such polyhedral complex has already been found in β-rhombohedral boron as well as in the very similar (to $Na_{102}Cu_{36}Ga_{279}$) phase $K_4Na_{13}Ga_{49.57}$ (*16*). The polyhedral stacking in the unit cell is represented in Fig. 1. Each icosahedron is directly linked to neighboring polyhedra through $2c$–$2e$ bonds; worth noting is the fact that in this structure, interpolyhedral bonding does not involve isolated gallium atoms as generally observed in binary phases. Icosahedron (A) is linked to six icosahedra (B) and six triply fused icosahedra (C); icosahedron (B) to two icosahedra (A), four icosahedra (B) and six triply fused icosahedra (c). Each triply fused icosahedron (C) is linked to three icosahedra (A), nine icosahedra (B), and linked to three homologous units (3×2 $M(1)$–$M(1)$ $2c$–$2e$ bonds). As represented in Fig. 2, with its $\bar{3}m$ inverted unit, the triply fused icosahedron (C) forms a complex incorporating a six-coordinated central atom. The related interatomic distance of 2.540 Å is too short for a bond involving a six-coordinated gallium, but agrees with copper as central atom.

The metallic radii of 1.245 and 1.173 Å (single bond) and 1.408 and 1.276 Å (CN12) given by Pauling (*21*) for Ga and Cu, respectively, can be used to estimate bond lengths for six-coordinated atoms. The values are 2.550 and 2.652 Å for Cu–Ga and Ga–Ga. The latter is in the order of the mean interatomic distance found in α-orthorhombic gallium (2.700 Å) where gallium is seven-coordinated (*22*). It is also very close to the mean distances observed in icosahedral

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Na_{102}Cu_{36}Ga_{279}$

Atom[a]	Position	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	36(*i*)	.3019(1)	−.1185(1)	.3202(1)	.012(1)	.011(1)	.014(1)	.000(1)	.001(1)	.006(2)
M(2)	36(*i*)	.3447(1)	.0355(1)	.2029(1)	.016(1)	.012(1)	.009(1)	−.002(1)	−.003(1)	.008(1)
M(3)	36(*i*)	.4972(1)	.1606(1)	.1544(1)	.008(1)	.010(1)	.007(1)	−.001(1)	−.003(1)	.004(1)
M(4)	36(*i*)	.3693(1)	−.0808(1)	.2456(1)	.013(1)	.009(1)	.014(1)	−.001(1)	−.003(1)	.004(1)
M(5)	18(*h*)	.1083(2)	$x/2$	.0581(1)	.009(1)	.009(1)	.010(1)	.002(1)	−.002(1)	.005(2)
M(6)	18(*h*)	$y/2$	.4903(2)	.2664(1)	.015(1)	.015(1)	.015(1)	.001(1)	−.001(1)	.009(2)
M(7)	18(*h*)	.2192(2)	$x/2$	.1174(1)	.009(1)	.009(1)	.012(1)	.001(1)	−.001(1)	.004(2)
M(8)	18(*h*)	.4143(2)	$x/2$	.1015(1)	.012(1)	.012(1)	.009(1)	.001(1)	−.001(1)	.004(2)
M(9)	18(*h*)	$y/2$	.9839(2)	.3050(1)	.008(1)	.008(1)	.009(1)	−.003(1)	.003(1)	.002(2)
M(10)	18(*h*)	.4730(2)	$x/2$	.0320(1)	.011(1)	.011(1)	.010(1)	−.002(1)	.002(1)	.005(2)
M(11)	18(*h*)	.1728(2)	$x/2$	−.0138(1)	.007(1)	.007(1)	.011(1)	−.000(1)	.000(1)	.003(2)
M(12)	18(*h*)	$y/2$	.7803(2)	.2229(1)	.014(1)	.014(1)	.018(2)	−.002(1)	.002(1)	.003(2)
M(13)	18(*h*)	$y/2$	.5596(2)	.3408(1)	.016(1)	.016(1)	.018(2)	.002(1)	−.002(1)	.011(2)
M(14)	6(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	.2827(1)	.016(1)	.016(1)	.006(3)	0	0	.008(1)
Cu	3(*b*)	0	0	$\frac{1}{2}$	.015(2)	.015(2)	.004(4)	0	0	.007(1)
Na(1)	36(*i*)	.3732(5)	.2887(5)	.2879(2)	.015(1)					
Na(2)	18(*h*)	.8906(6)	$x/2$	.2301(3)	.013(2)					
Na(3)	18(*h*)	$y/2$	.4085(6)	.4072(3)	.023(2)					
Na(4)	18(*h*)	$y/2$	.9227(9)	.1542(4)	.032(3)					
Na(5)	6(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	.4260(6)	.034(5)					
Na(6)	6(*c*)	$\frac{2}{3}$	$\frac{1}{3}$	.1942(5)	.018(4)					

Note. The thermal parameter expression is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*$.

[a] M = Ga or Cu.

units of intermetallic phases of gallium where six-coordination is achieved by exobonding. In $Li_{13}Cu_6Ga_{21}$ phase, the copper atom found inside Samson's polyhedron is bonded to six gallium atoms (one at 2.416 Å, two at 2.481 Å, two at 2.570 Å, and one at 2.767 Å) and the mean bond length is 2.547 Å.

$Na_{102}Cu_{36}Ga_{279}$ displays a structure ($R\bar{3}m$ symmetry) which is very close to that of $K_4Na_{13}Ga_{49.56}$ and Na_7Ga_{13}(I) phases, which are respectively nonstoichiometric and stoichiometric. In these phases, icosahedra sit on 3(*a*) ($\bar{3}m$) and 9(*d*) (2/*m*) positions, the difference in the structures stems from the way the icosahedra are interconnected. A 15-vertex spacer with tetra- and penta-coordinated gallium atoms is encountered in Na_7Ga_{13} (I), while a triply fused icosahedron has been found as a defective unit in $K_4Na_{13}Ga_{49.57}$. Actually gallium defection from the apical triangle (*A*, *B*, *C* in Fig. 2) of the triply fused icosahedron leads to "twice-*nido*" and "triply-*nido*" units (Fig. 3). The defection is not observed in the triply fused icosahedron of $Na_{102}Cu_{36}Ga_{279}$, instead, the apical atoms are coordinated to the central copper atom to form a double (triply fused icosahedron) complex with $\bar{3}m$ symmetry (Fig. 2).

In this structure the alkali metal atoms Na(1), Na(2), and Na(6) sit inside Friauf polyhedra (12-vertex truncated tetrahedron cavities), Na(3) lie inside a 16-vertex cavity,

TABLE II

PRINCIPAL INTERATOMIC DISTANCES IN $Na_{102}Cu_{36}Ga_{279}$

M(1)–	*M*(13)	2.556(3)
	– *M*(6)	2.597(4)
	– *M*(1)	2.610(4)
	– *M*(9)	2.719(2)
	– *M*(10)	2.768(3)
	– *M*(4)	2.791(5)
	– *M*(1)	2.968(3)
M(2)–	*M*(2)	2.570(7)
	– *M*(4)	2.591(3)
	– *M*(7)	2.681(2)
	– *M*(3)	2.714(2)
	– *M*(8)	2.760(3)
	– *M*(3)	2.847(3)
M(3)–	*M*(8)	2.616(4)
	– *M*(3)	2.690(3)
	– *M*(7)	2.684(4)
	– *M*(2)	2.714(2)
	– *M*(3)	2.848(3)
	– *M*(2)	2.847(3)
M(4)–	*M*(6)	2.511(2)
	– *M*(12)	2.561(3)
	– *M*(2)	2.591(3)
	– *M*(9)	2.706(4)
	– *M*(1)	2.791(5)
	– *M*(4)	2.919(3)
M(5)–	*M*(7)	2.599(5)
	–2 *M*(5)	2.629(4)
	–2 *M*(11)	2.633(3)
	– *M*(11)	2.690(5)
M(6)–	2 *M*(4)	2.511(2)
	– *M*(14)	2.537(3)
	–2 *M*(1)	2.597(4)
	–2 *M*(12)	2.656(3)
	– *M*(13)	2.792(5)
Cu–	6 *M*(12)	2.540(3)
Na(1)–	*M*(4)	3.036(7)
	– *M*(10)	3.048(7)
	– *M*(2)	3.070(8)
	– *M*(8)	3.081(8)
	– *M*(1)	3.088(7)
	– *M*(1)	3.104(7)
	– *M*(5)	3.107(7)
	– *M*(9)	3.136(7)
	– *M*(11)	3.139(7)
	– *M*(11)	3.151(8)
	– *M*(9)	3.175(8)
M(7) –	*M*(5)	2.599(5)
	–2 *M*(2)	2.681(2)
	–2 *M*(3)	2.684(4)
	– *M*(8)	2.791(4)
M(8) –	*M*(10)	2.580(5)
	–2 *M*(3)	2.616(4)
	–2 *M*(2)	2.760(3)
	– *M*(7)	2.791(4)
M(9) –	*M*(11)	2.528(4)
	–2 *M*(4)	2.706(4)
	–2 *M*(1)	2.719(2)
	– *M*(10)	2.740(5)
M(10)–	2 *M*(13)	2.508(3)
	– *M*(8)	2.580(5)
	– *M*(9)	2.740(5)
	–2 *M*(1)	2.768(3)
M(11)–	*M*(9)	2.528(4)
	–2 *M*(11)	2.609(3)
	–2 *M*(5)	2.633(3)
	–2 *M*(5)	2.690(5)
M(12)–	Cu	2.540(3)
	–2 *M*(4)	2.561(3)
	– *M*(14)	2.638(4)
	–2 *M*(6)	2.656(3)
	–2 *M*(12)	2.758(4)
M(13)–	2 *M*(10)	2.508(3)
	– *M*(14)	2.537(4)
	–2 *M*(1)	2.556(3)
	–2 *M*(13)	2.599(4)
	– *M*(6)	2.792(5)
M(14)–	3 *M*(6)	2.537(3)
	–3 *M*(13)	2.537(4)
	–3 *M*(12)	2.638(4)
Na(2)–	2 *M*(3)	3.069(10)
	–2 *M*(4)	3.088(9)
	–2 *M*(2)	3.136(5)
	–2 *M*(7)	3.146(5)
	–2 *M*(5)	3.147(9)
	– *M*(9)	3.169(11)
	– *M*(11)	3.228(11)
Na(3)–	*M*(13)	3.153(11)
	– *M*(6)	3.262(12)
	–2 *M*(3)	3.358(10)
	– *M*(7)	3.197(8)
	–2 *M*(1)	3.406(10)
	–2 *M*(1)	3.455(10)
	–2 *M*(10)	3.579(8)
	–2 *M*(4)	3.596(9)
	–2 *M*(8)	3.708(6)
	–2 *M*(2)	3.733(6)
Na(4)–	*M*(12)	3.135(13)
	– *M*(6)	3.268(14)
	–2 *M*(4)	3.351(10)
	–2 *M*(12)	3.474(11)
	–2 *M*(2)	3.491(6)
	–2 *M*(4)	3.532(13)
	–2 *M*(3)	3.595(10)
	– Cu	3.615(11)
	–2 *M*(2)	3.644(9)
Na(5)–	3 *M*(13)	3.350(22)
	–3 *M*(10)	3.451(16)
	–6 *M*(3)	3.522(16)
	–3 *M*(8)	3.551(4)
Na(6)–	6 *M*(3)	3.102(8)
	–3 *M*(7)	3.167(5)
	–3 *M*(5)	3.230(16)

and finally Na(4) and Na(5) are located inside 15-vertex cavities; the environment of sodium atoms is represented in Fig. 4.

As it has been clearly demonstrated in recent works on gallium cluster intermetallic phases (*13–18*), the electron content largely governs the formation of cluster varieties as well as their linking within the macroanionic lattice. The electronic contribu-

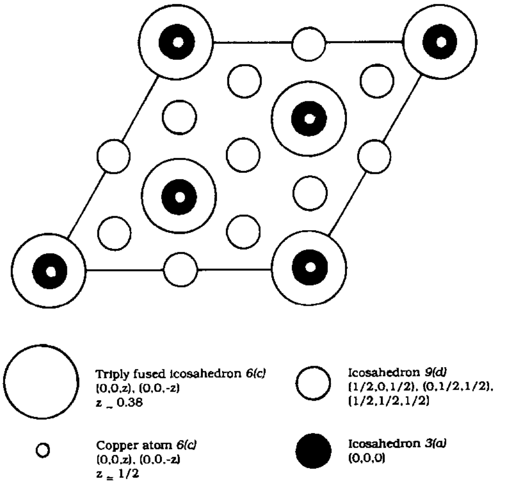

FIG. 1. Schematic representation of polyhedra stacking in the unit cell (projection along *z*-axis) of $Na_{102}Cu_{36}Ga_{279}$.

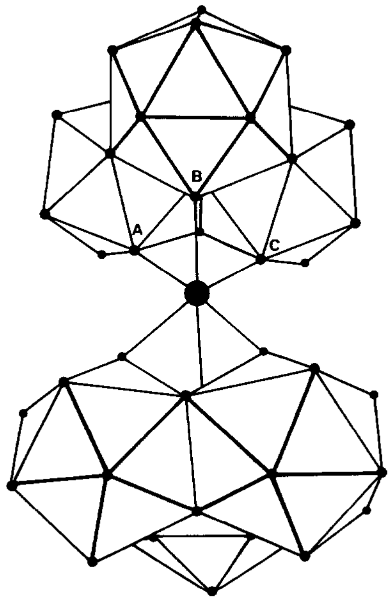

FIG. 2. The triply fused icosahedron $M_{28}CuM_{28}$ complex (symmetry $\bar{3}m$) in $Na_{102}Cu_{36}Ga_{279}$.

tion of alkali atoms to the electron-deficient lattice of gallium has been generally assumed and experimentally verified for some phases: NMR measurements have shown that lithium is completely ionized in Li_2Ga_7 (*23*). The majority of intermetallic gallium phases has been successfully interpreted using the Wade–Mingos rules (*24, 25*) for electron-deficient delocalized-orbital systems. In the case of intricated clusters, particularly those in which nonstoichiometry occurs, the skeletal bonding electron count is obtained by extended Hückel molecular orbital (EHMO) calculations (*26*).

Let us consider the phase $Na_{102}Cu_{36}Ga_{279}$: the stabilization of the icosahedron requires 26 skeletal bonding electrons while 12 electrons participate to exo-bonding. EHMO calculation clearly indicates that the capped triply fused icosahedron (29 atom–28 vertex) is stabilized with 68 skeletal bonding electrons. The ($M_{28}CuM_{28}$) complex may be regarded as resulting from the fusion, by vertex sharing, of two $M_{28}Cu$ (68 skeletal bonding electrons) parent units.

The total electron count may be estimated using the Mingos approach for cluster condensation, the initial Mingos rule (*31*) is: "the total electron count in the condensed polyhedron is equal to the sum of the electron counts for the parent polyhedra *A* and *B* minus the electron count characteristic of the atom, pair of atoms, or face of atoms common to both polyhedra." It has been reported elsewhere (*27, 28*) that the rules developed by Mingos (*29*), as well as by Teo (*30*) for polyhedral condensations, work relatively well for fusion of transition metal clusters but often give unsatisfactory results with main group elements; however, some success has been reported in the case of face fusion of two gallium icosahedra (*27*).

In this work, the very complicated poly-

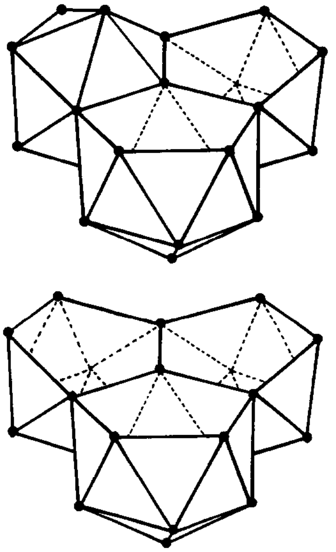

FIG. 3. The triply fused icosahedron (symmetry $\bar{3}m$) in $K_4Na_{13}Ga_{49.57}$. Owing to atom defection on the apical sites, the polyhedron is assumed to be "twice-*nido*" or "triply-*nido*" (in 1 : 1 proportion).

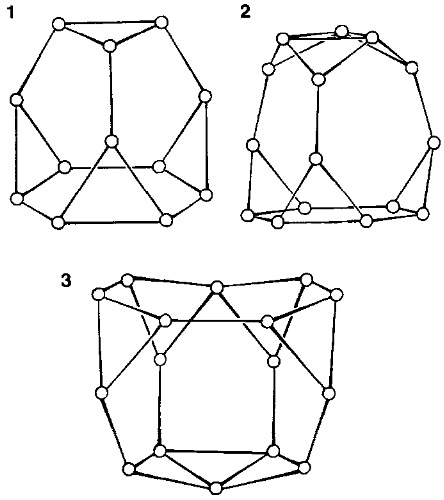

FIG. 4. Representation of polyhedral cavities (Ga and Cu) surrounding sodium atoms in $Na_{102}Cu_{36}Ga_{279}$, deltahedral faces are shared with icosahedra (*A*, *B*) and $M_{28}CuM_{28}$ complex (*T*). (1) Friauf polyhedron in which Na(1) is between (*A*), (*B*) and 2 × (*T*), Na(2) is between (*A*), 2 × (*B*) and (*T*), and Na(6) (*A*) and 3 × (*B*); (2) 15-vertex polyhedron containing Na(4) is formed between 2× (*B*) and 2 × (*T*) and Na(5) 3 × (*B*) and (*T*); (3) 16-vertex polyhedron containing Na(3) is formed between 2 × (*B*) and 2 × (*T*).

hedral complex is not spherical, even not convex, and moreover each parent unit might be considered as containing an encapsulated metal atom ($M(14)$) which should be treated rather as an electron contributor than as a part of the outer shell framework. In these conditions it is really difficult to apply Teo's rules for polyhedral condensation, which need to deal with proper numbers of vertices and faces.

According to Mingos' rules the ($M_{28}CuM_{28}$) complex has a total electron count of $2 \times A - X$, where A is the total electron count (skeletal electrons plus outer electrons on interpolyhedral bonds or lone pairs) for the single parent unit $M_{28}Cu$, and X is the electron count relative to the shared atom; 106 electrons have been found for A (53 filled bonding molecular orbitals) so the total electron count is $2 \times 106 - 4 = 208$, while the skeletal electron count is $2 \times 68 - 0 = 136$. The difference between total and skeletal electron counts stems from the number of outward electron pairs (2 × 18).

Recent MO calculations by Burdett and Canadell (*27*) for condensed boride or gallide octahedral units have shown that such skeletal electron counts may be lowered by Δ, owing to molecular orbital interactions between the two bases of parent *nido* fragments; this happens when the shared atom is small, for example, the double boron octahedron fused by vertex-sharing has skeletal counts of 24 ($2 \times 14 - 4$) and 28 ($2 \times 14 - 0$) when the shared atom is boron or gallium. In former case, two levels which are filled in the *nido* fragments have been raised above the non bonding limit. Since EHMO calculation for the $M_{28}CuM_{28}$ unit exceeded our program capacity such decrease (Δ) in the skeletal electron count could not be checked.

In Table III are reported the electron counts for $Na_{102}Cu_{36}Ga_{279}$ and $K_4Na_{13}Ga_{49.57}$ in a single unit cell. For $Na_{102}Cu_{36}Ga_{279}$, the two alternative counts $2 \times 68 - 0 = 136$ and $2 \times 68 - 4 = 132$ for the triply fused icosahedron complex ($M_{28}CuM_{28}$) are reported. The total of electrons required in the first case is perfectly balanced by the sum of valence electrons provided by Cu, Ga and Na.

It is interesting to compare this structure to that of $K_4Na_{13}Ga_{49.57}$, which contains defective triply fused icosahedra with no intercalated gallium between the inverted units. For this polyhedron, a skeletal electron count of 62 has been obtained by EHMO calculation, the total of available valence electrons (994 e) is largely exceeding the count required for stabilization of the anionic lattice (934 e), hence some electrons remain in the valence band of the alkali metals and the material should behave as a (poor?) metallic conductor, while Na_{102}

TABLE III

ELECTRON COUNTS FOR $Na_{102}Cu_{36}Ga_{279}$ IN THE TWO ALTERNATIVES ($\Delta = 0$ OR 4) AND FOR $K_4Na_{13}Ga_{49.57}$

	$Na_{102}Cu_{36}Ga_{279}$		
	$\Delta = 0$	$\Delta = 4$	$K_4Na_{13}Ga_{49.57}$
Icosahedron (A) skeleton bonding electrons	$3 \times 26 = 78$	$3 \times 26 = 78$	$3 \times 26 = 78$
Icosahedron (A) exobond electron participation	$3 \times 12 = 36$	$3 \times 12 = 36$	$3 \times 12 = 36$
Icosahedron (B) skeleton bonding electrons	$9 \times 26 = 234$	$9 \times 26 = 234$	$9 \times 26 = 234$
Icosahedron (B) exobond electron participation	$9 \times 12 = 108$	$9 \times 12 = 108$	$9 \times 12 = 108$
Triply fused icosahedra complex $M_{28}CuM_{28}$ skeleton bonding electrons	$3 \times 136 = 408$	$3 \times 132 = 396$	
Triply fused icosahedra complex $M_{28}CuM_{28}$ Exobond electron participation	$6 \times 18 = 108$	$6 \times 18 = 108$	
Triply fused icosahedron skeleton bonding electrons			$6 \times 62 = 372$
Triply fused icosahedron exobond electron participation			$6 \times 18 = 108$
Lone pair electrons on triply fused (twice or triply-*nido*) icosahedron			$3.43^{(a)} \times 2 = 7$
Total of electrons required for stabilization of anionic lattice	972	960	943
Total of valence electrons from Na,Cu,Ga	975	975	
from Na,K,Ga			994

[a] A partial occupancy of 19.08% (3.43 atom per unit cell) has been taken into account in calculation.

$Cu_{36}Ga_{279}$ should be considered as a Zintl phase with semi-conducting properties.

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