

A New Intermetallic Phase $K_4Na_{13}Ga_{49.57}$: Synthesis and X-ray Crystal Structure

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$K_4Na_{13}Ga_{49.57}$ crystallizes in space group $R\bar{3}m$ with the lattice constants $a = 16.399(4)$, $c = 35.479(9)$ Å, $cla = 2.163$, $Z = 6$. Diffraction data with $4 \leq 2\theta \leq 50^\circ$ (MoK α radiation) were collected on a Nonius CAD4 diffractometer within the two octant hkl and $\bar{h}\bar{k}l$. The structure was solved by trial methods and refined by full-matrix least-squares to a final $R(F) = 0.079$ for 1084 independent reflections with $I > 3\sigma(I)$. The structure of $K_4Na_{13}Ga_{49.57}$ contains gallium icosahedra and a curious novel 27-vertex, 28-atom polyhedral cluster linked to each other through direct interpolyhedral bonds to constitute a three-dimensional anionic lattice whose holes and cavities are filled with the alkaline cations. © 1986 Academic Press, Inc.

Introduction

Recent work on intermetallic systems of gallium with alkali metals has revealed a new class of intermetallic phases containing structural nonisolated clusters of gallium forming a three-dimensional macroanionic lattice. Such compounds can be described in terms of Zintl phases, at least according to the extended concept developed by Schäfer and coworkers (1).

Binary phases Li_3Ga_{14} (2, 3), $RbGa_7$ (4), and $CsGa_7$ (5) contain only gallium icosahedra while KGa_3 (6) and $RbGa_3$ (7) are strictly composed of dodecahedra. In addition to icosahedra, $Na_{22}Ga_{39}$ (8) or Na_7Ga_{13} (9, 10) contain "hypho" 15-vertex polyhedra. In the same way, K_3Ga_{13} (11) contains icosahedra and octadecahedra.

Except for Li_3Ga_{14} which is lithium defi-

cient, all these phases are stoichiometric; the clusters are bound to each other directly or through isolated gallium atoms on a relatively noncompact network containing holes or channels in which the ionized alkaline elements lie.

Some of the phases (particularly K_3Ga_{13}) are suitable for the chemical or electrochemical insertion of large quantities of zero-valent lithium and can be used as very efficient negative electrodes for secondary lithium batteries (12).

Recently, new nonstoichiometric phases have been discovered: $LiGa_{3.42}$ (13) and, in the corresponding ternary systems, $K_3Li_9Ga_{28.83}$ (14), $Li_3Na_5Ga_{19.56}$ (15), and $K_4Na_{13}Ga_{49.57}$. In these phases, owing to the partial occupancy of some gallium atoms, basic clusters are statistically dismantled into opened polyhedra.

This work will describe the synthesis and crystal structure determination of the new phase $K_4Na_{13}Ga_{49.57}$.

Experimental

The metals used were sodium and potassium obtained from Merck laboratories, and Alusuisse gallium. The elements (K:Na:Ga) in the ratio (1:1:5) were inserted in a tantalum tube which was then weld-sealed in an argon atmosphere.

The mixture was heated to 700°C within 1 hr in an induction furnace in order to obtain a good homogenization. In a second step, the mixture was heated again to 700°C in a resistance furnace then allowed to cool slowly to 230°C over 30 hr for crystal growing. The apparently homogeneous and relatively brittle product was examined with a microscope inside a glove box filled with purified argon. No needles of the well-known K_3Ga_{13} or tetragonal crystals of $NaGa_4$ were detected. A well-crystallized chunk of the material was isolated and broken into smaller pieces suitable for X-ray analysis; these were mounted inside Lindemann-glass capillaries and checked by preliminary oscillations and Weissenberg photographs. They showed rhombohedral symmetry (hexagonal axes: $a = 16.40$, $c = 35.48$, space group $R\bar{3}m$, $R3m$, or $R32$).

Since all phases in the Na–Ga and K–Ga systems are well established and their crystal structure determined, these lattice parameters together with the observed symmetry, indicated that this material was probably a novel phase in the ternary K–Na–Ga system.

A few pieces of the material previously checked by X-ray diffraction were analyzed by flame spectrometry giving a K:Na:Ga mole ratio of 0.082(2):0.270(7):1.

A wedge-shaped crystal of dimensions $0.39 \times 0.20 \times 0.15$ mm which gave the best diffraction spots was selected and mounted on an Enraf-Nonius CAD4 automatic dif-

fractometer. Accurate lattice parameters were determined by least-squares refinement of the angular positions of 25 reflections collected and automatically centered on the diffractometer ($a = 16.399(4)$, $c = 35.479(9)$ Å, $\gamma = 120^\circ$). Integrated diffraction intensities were collected at room temperature (22°C) in the range $4 \leq 2\theta \leq 50^\circ$ within the two octants hkl and $h\bar{k}l$, using graphite monochromated $MoK\alpha$ radiation.

The profile analysis of a few angle reflections indicated that an $\omega - \theta$ scan method was the most appropriate for data collection.

During data collection, the intensities of three standard reflections were checked after every 50 reflections and no significant loss in intensities was observed. The data were corrected for background and Lorentz polarization effects.

Once the composition of the compound was exactly determined, the data were corrected for the effect of absorption using a psi-scan method (16) ($\mu = 378.75 \text{ cm}^{-1}$) and equivalent data were averaged. The final data set consisted of 1098 independent reflections with $I > 3\sigma(I)$.

Structure Solution and Refinement

The structure could not be solved by Patterson or by direct methods; however, the Wilson plot of Multan (17) gave a strong indication of centricity.

The structure was solved by a trial method in the space group $R\bar{3}m$, by analogy to other known structures of intermetallic phases of gallium with alkali metals containing mainly icosahedra and, particularly to the rhombohedral structure of Na_7Ga_{13} determined by Schäfer (10).

We have assumed one gallium icosahedral cluster (B) to be centered around the special position $3(b)$ ($\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$) with $\bar{3}m$ symmetry and one gallium icosahedral cluster (A) to be located on the special position $9(e)$ ($\frac{1}{2}, \frac{1}{2}, 0$) with $2/m$ symmetry.

These positions allow the sequential arrangement BABABAB along the body diagonal $[1\bar{1}1]$ of the cell from $z = -\frac{1}{2}$ to $+\frac{1}{2}$ by increments of $\frac{1}{8}$, each icosahedral gallium cluster being bounded to the following one through direct intericosahedral bonds whose orientations are not far from those of the icosahedron pseudo fivefold axes, i.e., nearly in line with the body diagonal.

In this way, orientation of both types of icosahedra were well defined and coordinates of six (2 in (B) and 4 in (A)) gallium atoms could be estimated. The refinement of these positions led to a R factor of 0.52 and a subsequent Fourier synthesis showed four new gallium atoms. Refinement of ten gallium atoms led to a R factor of 0.35; at this stage a Fourier synthesis revealed all the remaining atoms. Among the 14 independent gallium atoms determined crystal-

lographically, 8 are composing a novel 28-atom polyhedron resulting from the condensation of three icosahedra.

Four sodium and two potassium independent atoms have been located. Since one gallium atom was found with partial occupancy, this leads to a K:Na:Ga ratio of 0.081:0.262:1 which is in fairly good agreement with the ratio determined by analysis.

Finally, all atomic positional parameters and anisotropic temperature factors for all atoms as well as the site occupancy for one gallium atom were refined by full-matrix least-squares minimizing the function $w(|F_0| - |F_c|)^2$ with $w^{-1} = \sigma^2(F^2)/4(F)^2 + (0.05F)^2$. After 14 of the weakest and evidently mismeasured reflections were eliminated by the criterion $\|F_c\| - |F_0|/|F_0| > 1.1$, the final agreement factors were $R(F) = 0.079$ and $R_w(F) = 0.124$.

TABLE I
FINAL ATOMIC POSITIONS AND TEMPERATURE FACTORS FOR ATOMS IN $K_4Na_{13}Ga_{49.57}$

Atom	Position ^a	Occupancy (%)	x	y	z	B_{eq} (\AA^2) ^b
Ga(1)	36(i)	100	0.8406(3)	0.3348(3)	0.0102(1)	2.34(6)
Ga(2)	36(i)	100	0.3095(2)	0.3449(2)	0.2968(1)	1.02(5)
Ga(3)	36(i)	100	0.4580(2)	0.3755(2)	0.2553(1)	1.03(5)
Ga(4)	36(i)	100	0.4504(3)	0.0875(3)	0.4856(1)	3.58(8)
Ga(5)	18(h)	100	0.2786(3)	-0.2786(3)	0.2244(1)	0.79(7)
Ga(6)	18(h)	100	0.5547(3)	-0.5547(3)	0.9497(1)	2.61(7)
Ga(7)	18(h)	100	0.8737(3)	-0.8737(3)	0.7317(1)	1.01(6)
Ga(8)	18(h)	100	0.5787(3)	-0.5787(3)	0.8200(1)	0.69(6)
Ga(9)	18(h)	100	0.2355(3)	-0.2355(3)	0.4690(1)	0.88(7)
Ga(10)	18(h)	100	0.1765(3)	-0.1765(3)	0.5276(1)	1.31(7)
Ga(11)	18(h)	100	0.2479(3)	-0.2479(3)	0.7632(1)	1.34(7)
Ga(12)	18(h)	100	0.0553(4)	-0.0553(4)	0.8297(2)	2.90(9)
Ga(13)	18(h)	19.08(1)	0.0531(16)	-0.0531(16)	0.0507(7)	1.26(14)
Ga(14)	6(c)	100	0.0	0.0	0.1113(2)	1.49(12)
K(1)	18(h)	100	0.1299(7)	-0.1299(7)	0.7574(3)	1.9(1)
K(2)	6(c)	100	0.0	0.0	0.2612(5)	1.5(2)
Na(1)	36(i)	100	0.2903(8)	0.3705(9)	0.2113(3)	2.0(2)
Na(2)	18(h)	100	0.2004(11)	-0.2004(11)	0.6758(4)	0.8(2)
Na(3)	18(h)	100	0.1112(12)	-0.1112(12)	0.6029(5)	1.5(2)
Na(4)	6(c)	100	0.0	0.0	0.3598(8)	2.0(5)

^a Number of positions and Wyckoff notation.

^b B_{eq} (\AA^2) = $8\pi^2 U_{eq}$, according to Willis and Pryor (24).

Results and Discussion

The final positional and thermal parameters are listed in Table I; main bond distances are given in Table II. The unit cell contains six formula units with three polyhedral cluster types. Of 14 independent gallium atoms Ga(1 to 4) sit in general positions $36(i)$, Ga(5 to 13) in special positions

$18(h)$ on mirror planes, Ga(14) sit in special position $6(c)$ on $3m$ axis.

Atoms Ga(1, 2, 6, 7) are coordinated to each other on the icosahedron (A) centered on $9(e)$ position with the symmetry $2/m$; Ga(5) and Ga(8) compose the icosahedron (B) located at $3(b)$ position with the symmetry $\bar{3}m$ (Fig. 1).

The remaining gallium atoms (3, 4, and 9

TABLE II
INTERATOMIC DISTANCES LESS THAN 4.0 Å

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Ga(1)		Ga(2)		Ga(3)	
Ga(7)	2.646(6)	Ga(2)	2.611(6)	Ga(11)	2.548(4)
Ga(6)	2.660(6)	Ga(3)	2.671(4)	Ga(13)	2.652(26)
Ga(2)	2.735(5)	Ga(6)	2.686(4)	Ga(2)	2.671(4)
Ga(2)	2.803(5)	Ga(1)	2.735(5)	Ga(10)	2.708(5)
Ga(1)	2.806(8)	Ga(7)	2.793(3)	Ga(3)	2.730(6)
Ga(1)	2.876(8)	Ga(1)	2.803(5)	Ga(4)	2.823(5)
Ga(4)		Ga(5)		Ga(6)	
Ga(12)	2.538(5)	Ga(6)	2.639(6)	Ga(5)	2.639(6)
Ga(4)	2.687(9)	2 Ga(5)	2.692(7)	2 Ga(1)	2.660(6)
Ga(10)	2.688(4)	3 Ga(8)	2.693(5)	2 Ga(2)	2.686(4)
Ga(11)	2.719(6)			Ga(7)	2.753(6)
Ga(9)	2.787(5)	Ga(8)		Ga(9)	
Ga(3)	2.823(5)	Ga(10)	2.566(6)	2 Ga(12)	2.600(5)
Ga(4)	3.062(9)	2 Ga(8)	2.671(5)	Ga(7)	2.632(6)
		3 Ga(5)	2.693(5)	Ga(10)	2.669(6)
Ga(7)				2 Ga(4)	2.787(5)
Ga(9)	2.632(6)	Ga(11)		Ga(12)	
2 Ga(1)	2.646(6)	Ga(14)	2.482(5)	Ga(4)	2.538(5)
Ga(6)	2.753(6)	2 Ga(3)	2.548(4)	Ga(4)	2.539(8)
2 Ga(2)	2.793(3)	Ga(13)	2.672(16)	2 Ga(9)	2.600(9)
Ga(10)		Ga(13)	2.673(19)	Ga(14)	2.615(9)
Ga(8)	2.566(6)	2 Ga(4)	2.719(6)	2 Ga(12)	2.719(11)
Ga(9)	2.669(6)	Ga(12)	2.755(8)	Ga(11)	2.755(8)
2 Ga(4)	2.688(4)	Ga(13)		Ga(14)	
2 Ga(3)	2.708(5)	Ga(13)	2.612(39)	Ga(11)	2.482(5)
		Ga(13)	2.612(38)	2 Ga(11)	2.484(5)
		Ga(14)	2.628(24)	3 Ga(12)	2.615(9)
		Ga(3)	2.652(26)	3 Ga(13)	2.628(24)
		Ga(3)	2.652(14)		
		Ga(11)	2.672(16)		
		Ga(11)	2.672(19)		
		2 Ga(13)	3.898(45)		

TABLE II—Continued

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
K(1)		Na(1)		Na(2)	
Ga(12)	3.33(1)	Ga(4)	3.04(1)	Ga(13)	3.10(3)
Ga(11)	3.36(1)	Ga(9)	3.06(1)	Ga(11)	3.38(1)
2 Ga(1)	3.43(1)	Ga(4)	3.08(1)	2 Ga(3)	3.39(1)
2 Ga(4)	3.51(1)	Ga(2)	3.10(1)	2 Ga(2)	3.51(1)
Na(2)	3.52(2)	Ga(3)	3.12(1)	K(1)	3.52(1)
2 Ga(4)	3.55(1)	Ga(7)	3.14(1)	2 Ga(3)	3.52(1)
2 Ga(9)	3.69(1)	Ga(10)	3.18(1)	2 Ga(1)	3.55(2)
2 Ga(3)	3.73(1)	Ga(8)	3.18(1)	2 Ga(2)	3.58(1)
Ga(2)	3.73(1)	Ga(8)	3.19(1)	2 Ga(13)	3.60(2)
K(2)	3.75(1)	Ga(10)	3.19(1)	Na(3)	3.62(2)
2 Ga(7)	3.75(1)	Ga(5)	3.20(1)	2 Na(2)	3.83(2)
2 Na(1)	3.88(1)	Ga(6)	3.24(1)		
		Na(1)	3.40(2)	Na(3)	
K(2)		Na(1)	3.45(2)	2 Ga(1)	3.08(2)
Na(4)	3.50(3)	Na(3)	3.49(2)	2 Ga(3)	3.11(2)
3 Ga(9)	3.58(1)	K(1)	3.88(1)	2 Ga(5)	3.17(2)
3 Ga(12)	3.59(1)			2 Ga(2)	3.18(1)
6 Ga(1)	3.59(1)	Na(4)		2 Ga(6)	3.21(1)
3 Ga(7)	3.60(1)	4 Ga(1)	3.12(1)	Ga(8)	3.25(2)
3 K(1)	3.75(1)	2 Ga(1)	3.13(1)	2 Ga(10)	3.25(2)
		3 Ga(6)	3.29(1)	Na(4)	3.43(2)
		3 Ga(5)	3.31(2)	2 Na(1)	3.49(2)
		3 Na(3)	3.43(2)	Na(2)	3.62(2)
		K(2)	3.50(3)		

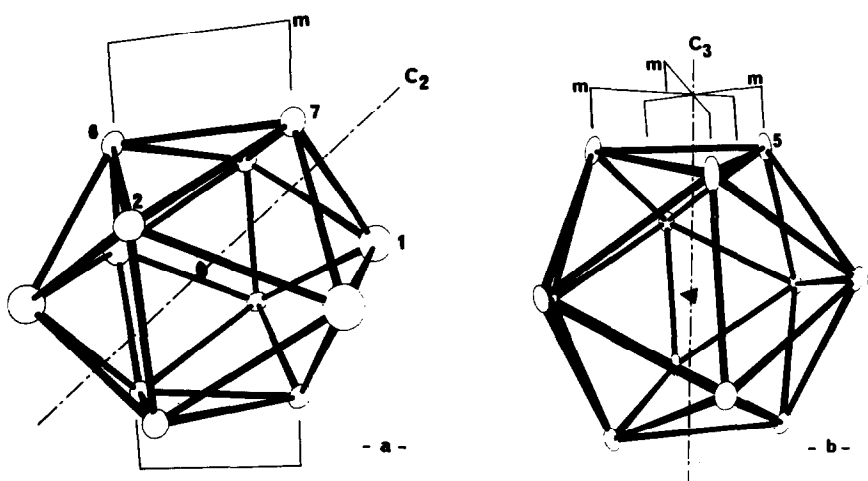


FIG. 1. The gallium icosahedra in $K_4Na_{13}Ga_{49.57}$. (a) Icosahedron (A), symmetry $2/m$. (b) Icosahedron (B), symmetry $3m$. Numbers (1 to 8) refer to gallium atoms as labeled in Table I.

to 14) are arranged on the curious 27-vertex, 28-gallium atom polyhedron (C) built on three icosahedra, each of them sharing two triangular faces with its neighbors with the global symmetry $3m$ (Fig. 2) such a polyhedron has already been encountered in the β -rhombohedral phase of boron (18).

These polyhedra are stacked in the unit cell and linked to each other through interpolyhedral direct bonds as shown in Figs. 3 and 4.

Icosahedron (A) is directly connected to $4 \times$ (A), $2 \times$ (B), and $6 \times$ (C) polyhedra; icosahedron (B) to $6 \times$ (A) and $6 \times$ (C); polyhedron (C) to $9 \times$ (A), $3 \times$ (B), and $6 \times$ (C) polyhedra.

The interpolyhedral 12-coordination for icosahedron (A) and (B) is attained, each gallium atom being hexa-coordinated. In the special case of the 28-atom polyhedron (a condensed triple icosahedron) 9-coordination is observed for the inner Ga(14) atom through only intrapolyhedral bonding; in a similar way are observed 8-coordination for Ga(11) and Ga(12), and the 7-coordination for Ga(13).

Owing to an external interpolyhedral linkage, the remaining gallium atoms Ga(3, 4, 9, 10) display 6-coordination; furthermore, Ga(4) has a polyhedral homolog at 3.062 \AA .

On polyhedron (C), the atom 13 has been

found with a partial site occupancy of 19.08%. This type of nonstoichiometry has been observed in other intermetallic phases of gallium: $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ (14), $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ (15), and $\text{LiGa}_{3.42}$ (13).

We were worried that a partial occupancy for gallium might correspond to the electronic density of a sodium atom (7e). Fortunately, the accuracy of the chemical analysis could help to solve the problem since replacing the non-stoichiometric gallium by one sodium atom would have modified the formula ratio to 0.082:0.326:1 instead of 0.081:0.262:1 for the alternative formulation which is closer to the chemical analysis result 0.082(2):0.270(7):1.

Furthermore, comparison of bonding distances from atom 13 to neighbouring gallium atoms, confirms this assignment, these distances ranging from 2.61 to 2.67 \AA are very characteristic of polyhedral gallium-gallium bonds.

In $\text{Na}_{22}\text{Ga}_{39}$ (8), the shortest distances between ionic sodium atoms and gallium atoms range from 2.93 to 3.23 \AA ; in $\text{LiGa}_{3.42}$ (13), there is an example of a gallium icosahedron where one gallium atom has been replaced by a lithium atom at distances from other gallium atoms ranging from 2.98 to 3.01 \AA .

In the intermetallic phases of gallium with alkali metals, the clusters are linked

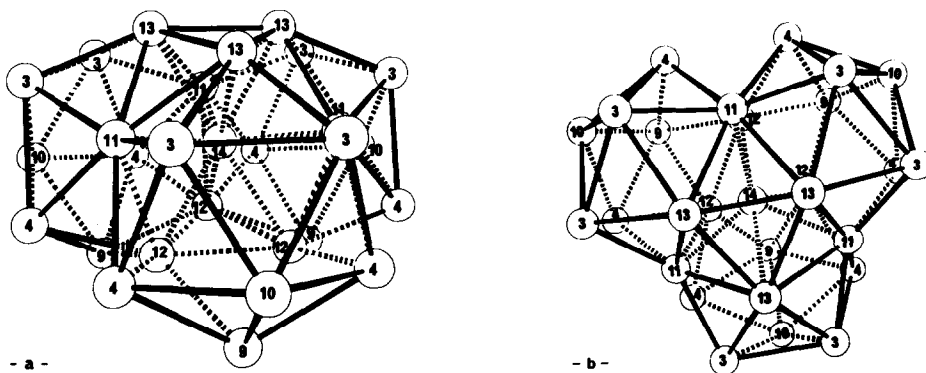


FIG. 2. The condensed triple icosahedron (C), symmetry $3m$. (a) Viewed approximately down the x axis. (b) Viewed down the z axis. Numbers (3 to 14) refer to gallium atoms as labeled in Table I.

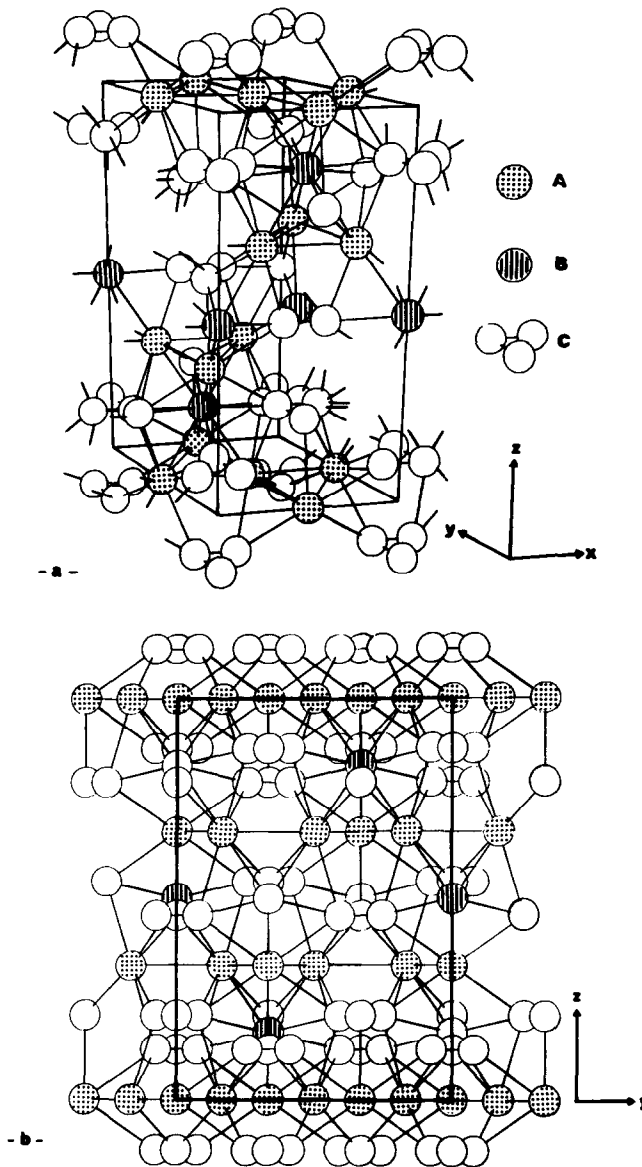


FIG. 3. Representation of the polyhedra packing in $K_4Na_{13}Ga_{49.57}$. (a) Inside the unit cell. (b) Projection down the y axis. A, B, and C, respectively, refer to (symmetries $2/m$ and $3m$) icosahedra and to ($3m$) condensed triple icosahedron.

together either directly or through isolated atoms and generally, the mean length of intraicosahedral bonds is greater than the mean length of bonds outwardly directed.

In the new phase $K_4Na_{13}Ga_{49.57}$, it is interesting to note that the linkage between

clusters is achieved through only interpolyhedral direct bonds since there is no isolated gallium atom.

In the very similar boron phases containing icosahedral units, owing to the presence of isolated atoms, the intraicosahedral bond

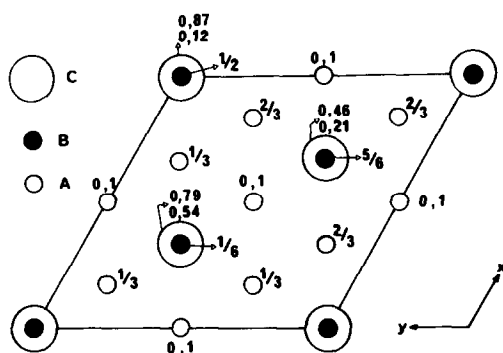


FIG. 4. Schematic representation of the projection of the unit cell down the z axis. Numbers refer to the z fractional coordinates of icosahedra A and B, and condensed triple icosahedra C.

lengths have been found to increase with the number of isolated atoms (19). This observation holds for the comparison of icosahedra (A) and (B) of this structure to the equivalent ones in $\text{Na}_7\text{Ga}_{13}$ (10) which contains some tri- and tetracoordinated isolated atoms (mean intrapolyhedral lengths are, respectively, 2.705 and 2.737 Å).

$\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$ presents a structure very close to that of $\text{Na}_7\text{Ga}_{13}$ (10) (similar parameters and icosahedra positions). The major difference comes from the existence in $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$ of a bulky 28-atom polyhedron resulting from the condensation of three icosahedra.

However the 15-vertex "hypho" cluster found in $\text{Na}_7\text{Ga}_{13}$ might roughly derive, as shown in Fig. 5, from the 28-atom polyhedron by removing of 13 (4 independent) gallium atoms, hence the interpolyhedral coordination being less in $\text{Na}_7\text{Ga}_{13}$.

In this kind of phase, the electronic contribution of the alkaline atoms to the electron deficient lattice of gallium has been shown to be fundamental. NMR measurements for $\text{Li}_3\text{Ga}_{14}$ have demonstrated the complete ionization of lithium and the stoichiometric phases could be successfully interpreted by the Wade electron-counting methods for clusters (20, 21).

For nonstoichiometric structures, this in-

terpretation is not easy, due to the difficulty in estimating the skeletal bonding electron content in polyhedra from which some gallium atoms are partially missing. Nevertheless it has been possible to give approximate interpretations for $\text{LiGa}_{3.42}$ (13), $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ (14), and $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ (15).

In this new phase, the difficulty resides in estimating the number of electrons necessary to stabilize the condensed polyhedron (C).

Each individual icosahedron (A) or (B) is linked to 12 polyhedra and the electron count for such an icosahedron is $50e$ (26 skeletal bonding electrons and 24 electrons involved in the 12 two-center, two-electron interpolyhedral bonds), so we will consider each icosahedron (A) or (B) to participate with $38e$ to the structure electron counting.

The unit cell containing 297.4 Ga (owing to the nonstoichiometry), 24 K and 78 Na atoms and in the hypothesis of the complete ionization of alkali metals, 994 valence electrons are available on the gallium lattice.

There, remain $994 - (12 \times 38) = 538$

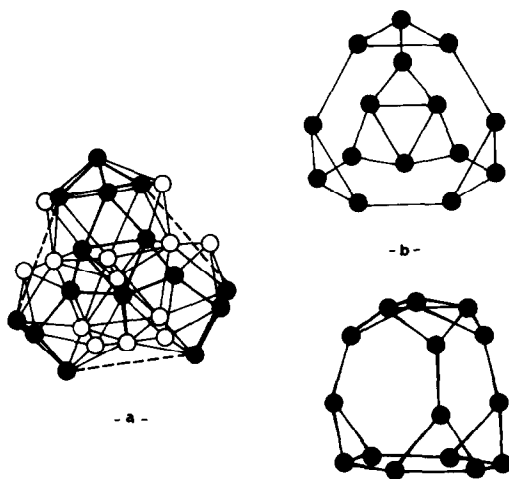


FIG. 5. Transition from the condensed triple icosahedron in $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$ to the 15-vertex "hypho" polyhedron as found in $\text{Na}_7\text{Ga}_{13}$ (or $\text{Na}_{22}\text{Ga}_{39}$). (a) The condensed triple icosahedron. (b) Top and front views of the 15-vertex "hypho" polyhedron.

electrons which are the participation of the six polyhedra (C). Each individual polyhedron (C) having eighteen interpolyhedral links, the electron count for (C) is approximately $108e$ (including skeletal and external electrons).

According to rules recently established by Teo for clusters (22), stabilization of such a polyhedron would require 360 electrons (including d electrons); a count of 350 electrons is obtained by using Teo's rules concerning close-packed, high-nuclearity metal clusters (23). Considering the nonstoichiometry, polyhedron (C) contains 25.6 Ga atoms, an electron count of $364e$ is obtained if 256 d electrons are added to the 108 electrons previously found. This number is relatively close to those calculated by Teo's rules.

Nonstoichiometric ternary intermetallic phases of gallium with alkali metals (Li, Na, K) seem to present more complicated structures than those of binary phases. The observed high-nuclearity clusters, fused double icosahedron in $Li_3Na_5Ga_{19.56}$ and in $Li_9K_3Ga_{28.83}$, fused triple icosahedron in $K_4Na_{13}Ga_{49.57}$, are incomplete polyhedra of which some vertices are statistically occupied by gallium. For such polyhedra a break up ratio could be defined as $B = (N - n)/N$ where N is the number of nuclei defining the full polyhedron and n the number of nuclei effectively present according to the stoichiometry. $B = 8.7\%$ for $K_4Na_{13}Ga_{49.57}$, 12.7% for $Li_3Na_5Ga_{19.56}$, and 15.03% for $Li_9K_3Ga_{28.83}$. In the case of the 15-vertex polyhedron encountered in Na_7Ga_{13} or $Na_{22}Ga_{39}$ and considering it as deriving from a polyhedron (C) type, the B ratio would increase to 46.4% . It is interesting to note that B increases in the same way as the ratio M/Ga ($M =$ alkali metals) which is in fact, the formal anionic charge per gallium atom: respectively 0.34, 0.41, 0.42, 0.54, and 0.56.

These ternary phases appear to be the first members of a series containing complex polyhedra resulting from the fusion of

full or partial icosahedra. Actually, the most complex polyhedron we have found is the condensed triple icosahedron, how long will it take to found a splendid tetrahedrally condensed polyhedron formed from the fusion of four icosahedra?

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