

## The Intermetallic Phases of Gallium and Alkali Metals. Interpretation of the Structures according to Wade's Electron-Counting Methods

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This is a survey of the preparation and structural properties of the intermetallic phases of gallium and alkali metals. Unlike the already known phases of gallium with lithium or sodium, the structures of the recently discovered phases  $\text{Li}_3\text{Ga}_{14}$ ,  $\text{Na}_{22}\text{Ga}_{39}$ ,  $\text{KGa}_3$ ,  $\text{K}_3\text{Ga}_{13}$ ,  $\text{RbGa}_3$ ,  $\text{RbGa}_7$ , and  $\text{CsGa}_7$  are characterized by stackings of coordinated gallium polyhedra such as icosahedra, octadecahedra, dodecahedra, and undecahedra. In these phases the alkali metals stabilize the gallium framework by giving their valence electrons. On this basis, the structures are interpreted according to Wade's electron-counting procedure, bringing the Zintl phases to a more general concept and enhancing the interest on the transition forms between metallic and ionic bonding.

### Introduction

So far, apart from a few cases, structural properties of intermetallic compounds between gallium and alkali metals have been generally ignored. The interest of chemists has been restricted to alkali metals systems containing elements lying to the right of the so-called Zintl demarcation line that runs between groups III B and IV B of the periodic table. In such systems, transitions between metallic bonding and ionic bonding are observed which increase as the components exhibit greater differences in electronegativity. Zintl (1) observed that a jump occurs from intermetallic to saltlike compounds through phases having no simple anions, but rather infinite macroanions. A challenging problem remains, which is how to decide whether compounds containing

the less electronegative elements of groups III B to V B can be placed in one group or another. A first answer could be obtained from the analysis of the physical properties of the materials but it is not often sufficient if not supported by structural analysis (X ray, X-ray photoelectron spectroscopy, and particularly X-ray crystal structure determination). Klemm (2) indicated that in such systems at least four types of compound may presumably be encountered: saltlike compounds, intermetallic phases, polycompounds, and interstitial structure compounds. Zintl's previous interpretation of the NaTl structure as a diamond lattice of Tl atoms, in which the one valence electron deficiency per atom is balanced by the valence electrons of the sodium atoms, has been extended by Klemm and Busmann (3); the electropositive element transfers electrons to the electronegative element (anion former) and an anion partial lattice is

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constructed whose atomic arrangement corresponds to the element having the same number of valence electrons (Zintl–Klemm–Busmann concept). Recently, Schäfer and co-workers (4) have analyzed the application of this concept to different classes of intermetallic compounds and proposed a new definition of Zintl's phases: intermetallic compounds which display a heteropolar bonding contribution and, in agreement with an ionic formulation in their anion partial lattices, if necessary after resolution of fractional charges into nearest integral values, obey the  $(8-N)$  rule.

Making use of the published phase diagrams (5–7), we have studied the structural properties of gallium–alkali metals compounds and found a new class of phases which contain nonisolated clusters of gallium forming a pseudo three-dimensional anionic lattice bringing the Zintl phases to a more general concept.

### Experimental

The phase diagrams of systems Li–Ga, Rb–Ga, and Cs–Ga have been determined by Thümmel and Klemm and revised by Yatsenko (5, 6); those for Na–Ga and K–Ga have been described for the first time by Rinck and Feschotte (7). Referring to the phase diagrams data, we have prepared the new intermetallic compounds  $\text{Li}_3\text{Ga}_{14}$  (8),  $\text{Na}_{22}\text{Ga}_{39}$  (9),  $\text{KGa}_3$  (10),  $\text{K}_3\text{Ga}_{13}$  (11),  $\text{RbGa}_3$  (12),  $\text{RbGa}_7$ , and  $\text{CsGa}_7$  (13) and determined their crystal structures.

Intermetallic compounds of gallium with alkali metals are easily oxidized. We have obtained them by fusing the elements under an argon atmosphere in weld-sealed tantalum tubes. All these compounds differ in stoichiometry with those given as peritectic in the phase diagrams; beautiful single crystals of the gallium richest phases ( $\text{Li}_3\text{Ga}_{14}$ ,  $\text{K}_3\text{Ga}_{13}$ ,  $\text{RbGa}_7$ , and  $\text{CsGa}_7$ ) can be obtained by slow cooling of gallium concentrated mixtures followed by centrifugation at ap-

propriate temperatures to remove the excess of gallium. The alkali metal richer phases were often obtained within heterogeneous coarse crystals after cooling and annealing of fused mixtures prepared on the basis of their phase diagram stoichiometries. These coarse crystals were broken into small pieces, and crystals corresponding to the expected phases were easily distinguishable from the gallium richer phases by their tendency to slightly oxidize on their surface due to traces of oxygen contained in the argon atmosphere of the glove bag.

### Structural Description

We have determined the crystal structures of seven new intermetallic compounds of gallium:  $\text{Li}_3\text{Ga}_{14}$ ,  $\text{Na}_{22}\text{Ga}_{39}$ ,  $\text{KGa}_3$ ,  $\text{K}_3\text{Ga}_{13}$ ,  $\text{RbGa}_3$ ,  $\text{RbGa}_7$ , and  $\text{CsGa}_7$  (8–13). Unlike the already known intermetallic compounds of gallium with lithium or sodium,  $\text{Li}_2\text{Ga}$  and  $\text{Li}_3\text{Ga}_2$  (14),  $\text{Li}_5\text{Ga}_4$  (15),  $\text{LiGa}$  (16), or  $\text{NaGa}_4$  (17), these structures are characterized by stackings of coordinated gallium polyhedra, i.e., icosahedra, octadecahedra, dodecahedra, and undecahedra, as shown in Fig. 1.

Although icosahedral clusters are encountered in boron and some boron rich phases, the existence of such polyhedral clusters remains rather unusual in solid state chemistry. It is well known that physical features of gallium, such as electronegativity and covalent radius, are closer to those of boron than those of aluminum; hence, some similitude in their chemical behavior is expected, in particular, the ability of these electron poor elements to associate by sharing their electrons.

In these phases, gallium clusters are not isolated but linked to each other within a three-dimensional network through direct interpolyhedral bonding; the linkage is generally supplemented by connection with a few less coordinated satellite atoms of Ga

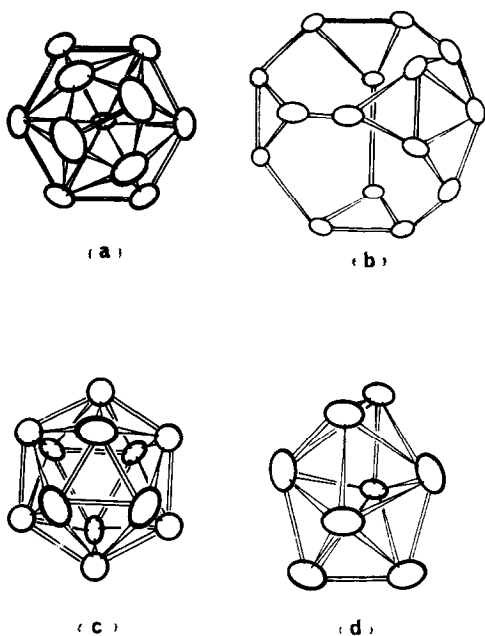


FIG. 1. (a) octadecahedron, (b) undecahedron with triangular, hexagonal and heptagonal faces, (c) icosahedron, (d) dodecahedron.

which, in complex structures like  $\text{Na}_{22}\text{Ga}_{39}$ , can also associate within some surprising opened polyhedral structures.

The  $\text{Li}_3\text{Ga}_{14}$ ,  $\text{RbGa}_7$ , or  $\text{CsGa}_7$  phases contain gallium icosahedra as shown in Figs. 2 and 3; in  $\text{Li}_3\text{Ga}_{14}$ , each icosahedron is directly linked to six adjacent homologs and its remaining vertices are connected to the neighboring icosahedra through isolated gallium atoms. The packing leaves room where the lithium can sit but the structure is lithium deficient since only half the site of lithium is occupied. In the  $\text{RbGa}_7$  gallium richer phase (Fig. 3), each icosahedron is directly linked to six adjacent homologs within three-center bonds to increase the compacity of the icosahedra packing; the cohesion of the structure is supplemented by bonding to an isolated gallium, generating parallel channels occupied by chains of the alkali metal. In fact, the original compact packing of the Ga icosahedra allows the alkali metal not to be more diluted in the

gallium network than in some gallium less rich phases. Both icosahedral and octadecahedral gallium clusters are observed in the  $\text{K}_3\text{Ga}_{13}$  phase (Fig. 4), each polyhedron is directly bonded to six neighboring polyhedra, and the linkage is supplemented by bifurcated bonding involving isolated gallium atoms; channels parallel to the crystal **b** axis contain the potassium atoms.

$\text{Na}_{22}\text{Ga}_{39}$  displays a very complex structure with a content of 244 atoms in the unit cell. Most of the Ga atoms are arranged in a noncompact framework of icosahedra (Fig. 5) linked to each other through direct bonding and to a few less coordinated satellite atoms of Ga; furthermore, one can observe that these gallium atoms are in turn arranged on noncompact 15-vertex polyhedra and the Ga packing leaves room for Na atoms to fit. The presence of large opened polyhedra owes to the richness in alkali metal which contributes to the degradation of closed polyhedra like icosahedra or octadecahedra.

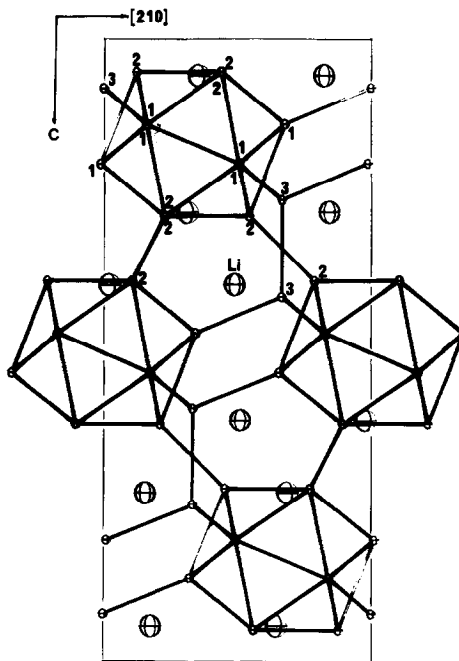


FIG. 2.  $\text{Li}_3\text{Ga}_{14}$ , trigonal,  $R\bar{3}m$  (8).

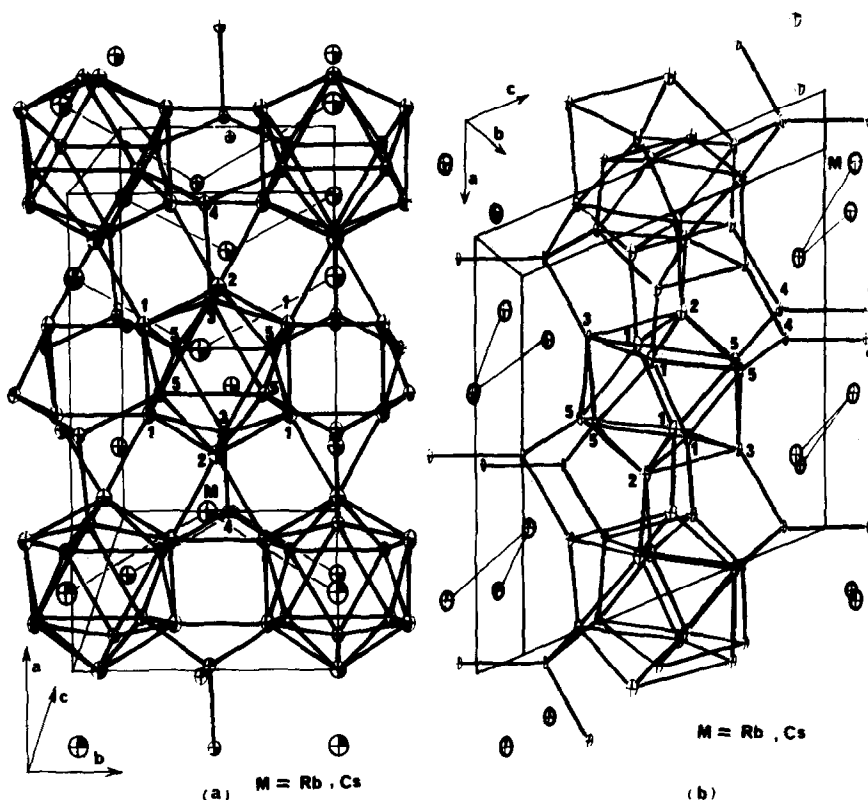


FIG. 3.  $\text{MGa}_7$  ( $M = \text{Rb}$  or  $\text{Cs}$ ), monoclinic,  $C2/m$  (13)

A new cluster (dodecahedron) is observed in the isostructural phases  $\text{RbGa}_3$  and  $\text{KGa}_3$  (Fig. 6). Due to the tetragonal symmetry, each dodecahedron is directly linked to four homologs, the remaining vertices being bonded to isolated Ga. On the other hand, the alkali atoms are arranged on a three-dimensional sublattice surrounding the polyhedra.

#### Interpretation of the Structure Using Electron-counting Methods

In these structures, the electronic contribution of the alkali atoms to the stability of the electron deficient lattice of gallium appears to be fundamental. The electronic charge of the gallium lattice, and particularly that of the gallium clusters, can be es-

timated in the same way as that used by Longuet-Higgins in interpreting the structures of  $\text{MB}_6$  ( $M = \text{Ca}, \text{Ce}$ ) and  $\text{CB}_4$  which contain, respectively, octahedra and icosahedra (18, 19), or according to the Wade electron-counting procedure generalized for boranes (20).

In fact, except for  $\text{RbGa}_7$  or  $\text{CsGa}_7$  compounds, the skeletal bonds within the polyhedra are longer than interpolyhedral bonds; the skeletal electron-counting for these polyhedra can be carried according to the counting procedure used for borane anions: a gallium icosahedron would be stabilized with 26 skeletal electrons, an octadecahedron with 24 electrons, and a dodecahedron with 18 electrons. On the other hand, an electron pair is allocated to every short two-center interpolyhedral bond. In the  $\text{RbGa}_7$  structure, the icosahedra are

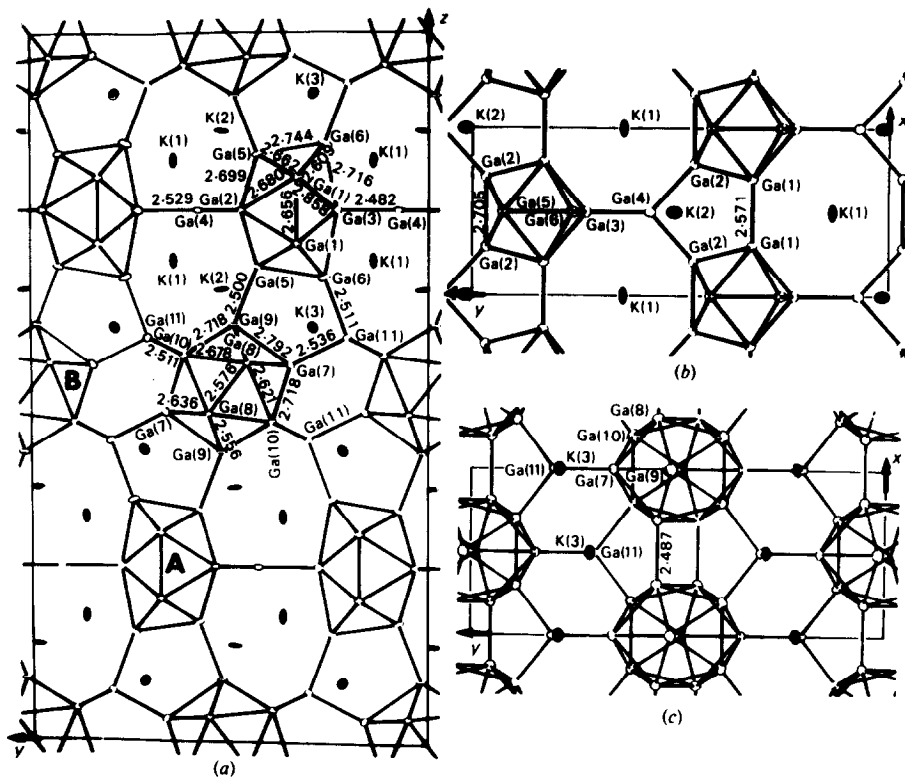


FIG. 4.  $K_3Ga_{13}$ , orthorhombic,  $Cmcm$  (11).

linked to each other through 6 three-center bonds for which interatomic distances are longer than those observed for icosahedral skeletal bonds and for intericosahedral two-center bonds; therefore one electron pair is allocated to each three-center bond.

On this basis, the structure of the  $K_3Ga_{13}$  phase can be easily interpreted. The unit cell contains 8 formula units providing 336 bonding electrons; 104 and 96 skeletal bonding electrons, respectively, are allocated to 4 icosahedra and 4 octadecahedra. A total of 48 bonding electrons are attributed to the 24 interpolyhedral two-center direct bonds and 88 electrons to the interpolyhedral bonds involving isolated atoms Ga(4) (tricoordinated) and Ga(11) (tetraordinated); therefore a total of 336 bonding electrons is required to stabilize the gallium framework which clearly confirms the

potassium valence electron transfer to the gallium lattice.

The  $RbGa_3$  unit cell contains 6 formula units comprising two dodecahedral clusters stabilized with  $2 \times 18$  skeletal bonding electrons; 8 bonding electrons are assigned to 4 interdodecahedral direct bonds and 16 bonding electrons to the 8 interdodecahedral bonds involving the outer tetraordinated Ga(3) atom. The 60 bonding electrons required for the gallium sublattice stabilization must include the 6 alkali metal valence electrons.

The  $Li_3Ga_{14}$  unit cell contains 3 icosahedra which are stabilized by  $3 \times 26 = 78$  bonding electrons; on the other hand, 18 bonding electrons are required for 9 intericosahedral direct bonds (Ga(2)–Ga(2)) and 42 bonding electrons for 21 intericosahedral links involving the outer tetraordinated

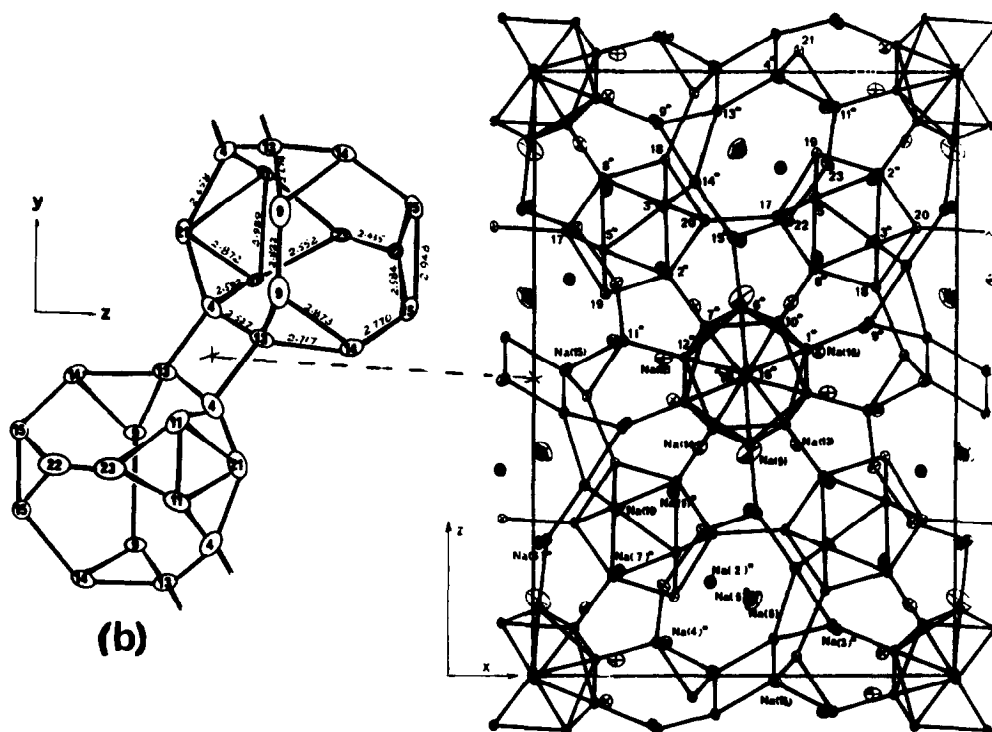


FIG. 5.  $\text{Na}_{22}\text{Ga}_{39}$ , orthorhombic,  $Pnma$  (9).

Ga(3) atoms (18 Ga(3)–Ga(1) and 3 Ga(3)–Ga(3) bonds). Beyond the 126 valence electrons provided by gallium atoms, the 138 bonding electrons required for the gallium sublattice would include 12 valence electrons provided by 12 lithium atoms; in fact, only 9 Li atoms have been found in the unit cell and this seems to be a very challenging failure, since lithium partly occupies a 18-fold position in the cell and there could still be enough room to fit 3 extra Li. The odd number of electrons in  $\text{Li}_9\text{Ga}_{42}$  is puzzling but there is, of course, absolutely no chance that the structure contains an extra Ga atom. In fact, the 6 coordination at gallium atoms on the icosahedron and the 4 coordination at the outer gallium are chemically sound. It is also highly unlikely that the structure could contain three hydrogen atoms since the starting materials have been purified and the reaction carried out in a hydrogen free atmosphere. We have

checked a few single crystals of the compound by chemical analysis which confirmed the previous Li content. On the other hand, while our publication was in press, an article from Schäfer (21) was issued which describes the same structure, in agreement with our results. Twelve Li atoms would have been congruent with the theory but, as Schäfer told us, we have to accept what nature says!

The  $\text{Na}_{22}\text{Ga}_{39}$  unit cell contains 8 icosahedra requiring 208 skeletal bonding electrons; furthermore an external pair of electrons is allocated to each of the 12 outwardly uncoordinated gallium atoms on the icosahedra (Ga(5) and (19)). Skeletal electron counting for the opened 15-vertex polyhedra (Fig. 5b) has been one of the most difficult problems in this work; as shown in Fig. 5, the unit cell contains 4 such polyhedra which are arranged along chains on both sides of inversion centers

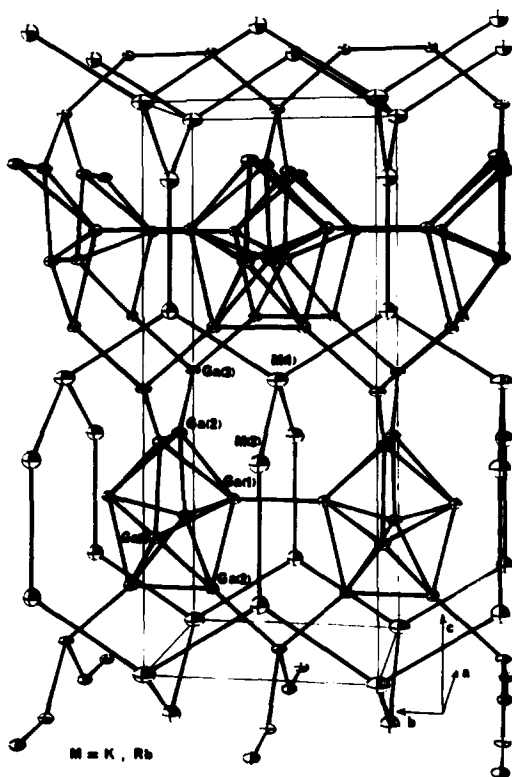


FIG. 6.  $MGa_3$  ( $M = K$  or  $Rb$ ), tetragonal,  $I\bar{4}m2$  (10, 12).

and partially coordinated to the icosahedra. As shown in Fig. 7 (e-g), this 15-vertex polyhedron can be built by fusing (g) to the (black) skullcap of (f); (f) is considered a *Hypho* 12-vertex polyhedron with a geometry deriving from the *Closo* 15-vertex polyhedron (e) and stabilized with 32 skeletal bonding electrons. On the other hand, part (g) must be considered as built with only two-center, two electron bonds. Then a resulting odd skeletal bonding charge of 43 electrons for (b) is not unreasonable since it is not isolated but, in a certain way, polymerized into infinite chains.

On the other hand, a pair of electrons is allocated to each of the two outwardly uncoordinated gallium atoms, Ga(22) and Ga(23), on these 15-vertex polyhedra; finally, 136 bonding electrons are allocated

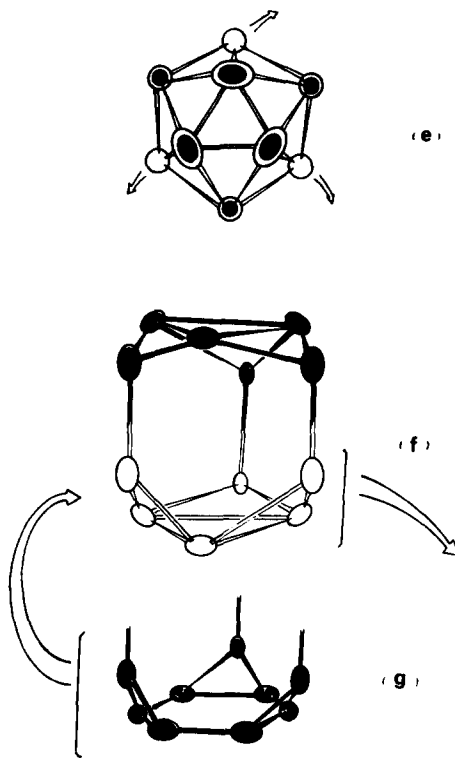


FIG. 7. (e) *Closo* triangular faces 15-vertex polyhedron, (f) *Hypho* 12-vertex polyhedron, (g) Bottom of the  $Na_{22}Ga_{39}$  opened 15-vertex polyhedron.

to the various 68 interpolyhedral bonds. The framework of gallium is then stabilized with 556 electrons, in agreement with a complete electronic contribution of the sodium atoms. Table I sums up the calculations carried out for all the gallium phases studied in this work. This rule still holds for the  $RbGa_7$  phase; one must consider 52 skeletal bonding electrons on the icosahedra, 28 bonding electrons on the 14 interpolyhedral two-center bonds, and 8 bonding electrons for the 4 three-center interpolyhedral bonds.

### Conclusion

This work points out some similitude in the chemical behavior of gallium and boron,

TABLE I  
ELECTRON-COUNTING SCHEME FOR THE INTERMETALLIC PHASES OF GALLIUM

Intermetallic phases—Bonding electrons	$\text{Li}_3\text{Ga}_{14}$	$\text{Na}_{27}\text{Ga}_{39}$	$\text{K}_3\text{Ga}_{13}$	$M\text{Ga}_3$ ( $M = \text{Rb}, \text{Cs}$ )	$M\text{Ga}_7$ ( $M = \text{Rb}, \text{Cs}$ )
Icosahedra skeletons	78	208	104		52
Octadecahedra skeletons			96		
Dodecahedra skeletons				36	
Undecahedra skeletons		172			
Lone pairs		40			
Interpolyhedra 2-center- $2e$ bonds	60	136	136	24	28
Interpolyhedra 3-center- $2e$ bonds					8
Total	138	556	336	60	88
Gallium valence electrons	126	468	312	54	84
Alkali metals valence electrons	9	88	24	6	4
Electronic deficit	3	0	0	0	0

particularly their ability to arrange into compact polyhedra.

While the various modifications of elemental boron and boron rich phases are characterized by a three-dimensional skeleton of boron atoms built from icosahedral units, such associations are not observed in the numerous phases of elemental gallium but only in some of its combinations with electropositive elements like alkali metals; moreover, such combinations allow gallium a larger variety of associations. In the gallium phases discussed above, the alkali metals appear essential to the formation of the covalent gallium skeleton; they fill the holes inside the gallium framework and their valence electrons contribute to the stabilization of the structures. The interpretation of these structures according to Wade's rules works perfectly for gallium phases containing large and very electropositive alkali atoms but fails for  $\text{Li}_3\text{Ga}_{14}$

and generally for most interstitial compounds of boron (22). This interpretation must be considered as just a guideline and should not be taken too literally; actually, these phases are probably far from having pure saltlike structures and the electron contribution of the alkali atoms may have been overestimated in the electron-counting procedure. Nevertheless, these results represent a new step in bringing the Zintl phases to a more general concept and emphasize the transition forms between metallic and ionic bonding.

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