

α -Gallium: An Alternative to the Boron Structure

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The well-known α -Ga structure is attributed to a structure which is built up from open polyhedral fragments, and is strongly related to the closed polyhedral boron clusters B_n . The one short Ga–Ga bond corresponds to the terminal bonds in closo-boranes. Extended Hückel calculations support this model and show that also the α -Ga structure is an appropriate covalent three-electron arrangement and is not electron-deficient.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

It is generally accepted that the structures of the Group 13 elements of the Periodic Table below boron are mainly classical metal structures. Only the structure of the semi-conducting modifications of boron are decisively determined by covalent bonding. Icosahedral B_{12} -clusters form the fundamental structural units. From the chemistry of the boranes it is known that these clusters are especially stable as 38 electron systems, as in the case of the decaborane(12) anion $[B_{12}H_{12}]^{2-}$. According to Wade,¹ the central B_{12} icosahedron requires 12 electrons for the 12 peripheral B–H bonds, and a 26 further electrons for the internal bonds of the B_{12} cage. In elemental boron, the two additional electrons of the anion are missing. This problem is solved by the structure of α -rhombohedral boron in the following way: (1) only six of the B atoms form peripheral σ -bonds to neighbouring B_{12} cages; (2) the remaining six B atoms participate in six three-centre bonds with the corresponding B atoms of the other neighbouring B_{12} cages. Therefore, all the peripheral bonds only need $6 + 2 \times (6/3) = 10$ electrons per cage, leaving exactly 26 electrons remaining, which is precisely the number that the B_{12} cage needs for its skeletal bonds. In this way all valence electrons are in localized electronic states, corresponding to the physical properties.

Abrupt alterations characterize the higher homologues. Aluminium and thallium form simple fcc structures, typical of metals. The tetragonal indium structure is understood as a deformation variant of the fcc structure, whose deformation is quantitatively deduced by the electron theory of metals. The α -gallium structure resists this analysis, and a clear relationship to the metal structures cannot be recognized. Although pseudopotential theory provides for structural and energetic arguments² for the stability of α -Ga compared to fcc-Ga the close relationship to boron structures has not been found.

Systematic investigations of the Zintl phases in recent years have led to the discovery of semiconducting compounds like Li_3Ga_{14} , Na_7Ga_{13} and $Na_{22}Ga_{39}$, whose structures contain discrete cluster anions Ga_{12}^{2-} and Ga_8^{2-} .^{3–5} These cluster anions are direct analogues of the well-known units B_{10}^{2-} , B_8^{2-} , B_6^{2-} etc. observed in Li_3B_{14} and Li_2B_6 .⁶ Obviously, only a few additional electrons are needed to form with Ga the covalently bonded E_n cages that are typical of boron compounds.

In this context we again inspected the α -Ga structure after we had doubts concerning our explanations of the well-known structure model in the course of a seminar. Recall the low melting point at 303 K and the high boiling temperature of about 2510 K, showing that the condensed phase exists over a large temperature region.

In a recent publication, Parrinello and co-workers have investigated the structural relationships of the α -gallium, β -gallium, fcc-gallium and the Ga-II modifications by means of *ab initio* SCF calculations.⁷ This leads to a description of the α -Ga structure as a 'molecular metal' with Ga_2 dumb-bells as covalently bonded central molecular units, corresponding to the short Ga–Ga distance (see below). A comparison of the total energy and volume dependence clearly shows that all four structures are energetically very close to each other. The differences between α -Ga and the Ga-II, β - and fcc-phases have been determined as 4, 9 and 11 kJ mol⁻¹, respectively. On this basis the low melting point of Ga at 303 K can be interpreted by a continuous transition between the competing structures in smaller or larger domains. The high boiling point ensures that the strong chemical bonding is not affected by the melting process, and that pair formation is only part of the total chemical bonding.

The α -Ga structure is shown in Fig. 1. The orthorhombic unit cell contains eight equivalent Ga atoms, each coordinated by (1+6) nearest neighbours: space group $Cmca$

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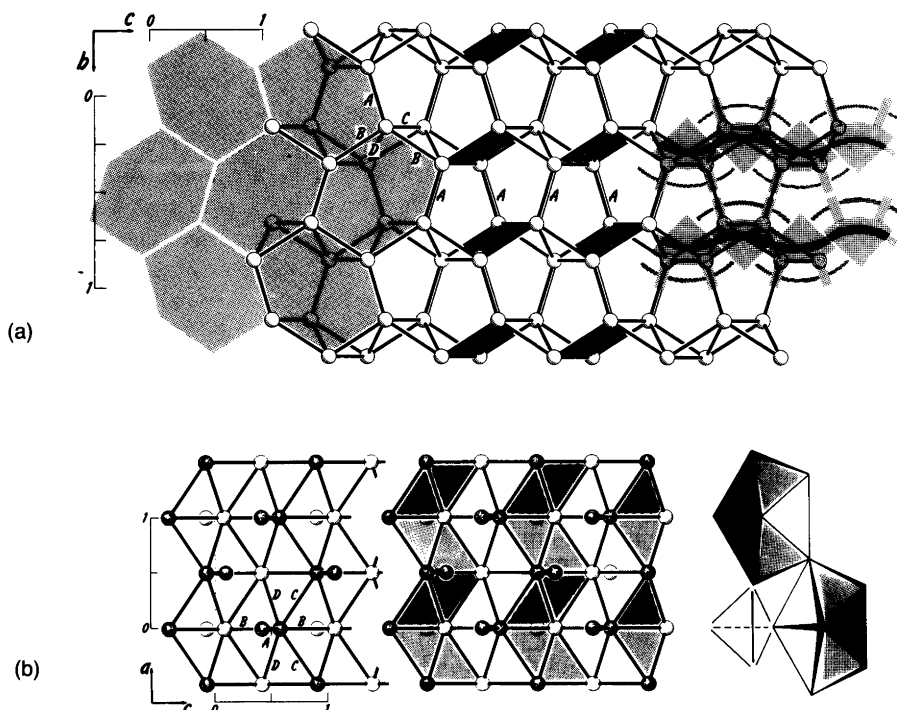


Fig. 1. The α -gallium structure parallel to [100] (a) and parallel to [010] (b). The four different bond types A, B, C, and D are indicated. (a) The central part shows the interatomic connections emphasizing the short bonds of type A which interconnect the corrugated layers at $y = 1/4$ and $y = 3/4$. Shadows indicate the different orientations of the zigzag ribbons along [100] formed by double triangles. The hexagonal shadows on the left-hand side give an impression of the graphite-like network in the planes at $x = 0$ and $x = 1/2$. This fragment represents the basis of classical descriptions of the α -gallium structure,⁸ but our calculations show that this fragment will not become important until more than three electrons per atom are present (cf. text). The right-hand part represents the idea of a two-dimensional network of condensed open polyhedral fragments alternately oriented upwards and downwards, with respect to the mean planes at $y = 1/4$ and $y = 3/4$. The short type A bonds act as 'terminal' bonds. (b) Corrugated layer centred at $y = 1/4$ with some atoms of adjacent layers connected by short A bonds. Dark spheres are above $y = 1/4$, light spheres below. The central part shows the zig-zag ribbons of double triangles running along [100]. In the right-hand part, sections of the structural pattern are transformed by small positional shifts into condensed icosahedral fragments and tetrahedra. This demonstrates the similarity of the α -gallium structure to that of boron polyhedra (cf. text).

(No. 64), $a = 4.519(2)$, $b = 7.658(3)$ and $c = 4.526(2)$ Å at 298 K; atomic position $8f$ $0yz$ with $y = 0.1549(6)$, $z = 0.0806(8)$;[†] bond lengths $d(\text{Ga-Ga})$: type A = 2.482 (1 \times), type B = 2.691 (2 \times), type C = 2.732 (2 \times), type D = 2.786 (2 \times) Å (± 0.010 Å). The corresponding Pauling bond orders are PBO = 1.00, 0.45, 0.38 and 0.30 at $d_1 = 2.48$ Å. The total bond order is $\Sigma\text{PBO} = 3.26$, close to the valency of 3. Usually the structure is described as a stacking of strongly deformed hexagonal nets⁹ (Fig. 1). The hexagons are formed by two bonds of type A and four bonds of type B. Therefore, each Ga atom exhibits $\Sigma^*\text{PBO} = 1.90$ in the hexagonal network, and a residue of about $\Sigma'\text{PBO} = 1.36$ remains to connect the two-dimensional network with the neighbouring one.

However, the experiences with the Zintl phases of boron and gallium, as well as the structures of the above-cited boranes, directed our attention towards the **one short distance of type A**. It is that short distance which is directly

comparable with the terminal bonds of the E_n cages, whereas the internal multicentre cage bonds are characterized by larger interatomic distances (cf. the bond distances in the $\frac{1}{2}[\text{B}_6^{2-}]$ net of CaB_6). How can one interpret the short Ga-Ga distance of the α -Ga structure? One may think about this in the following way: the formation of E_n cages only represents one solution of the general problem of separating two interaction types in space: it is merely the formation of drops. An equivalent solution is given by the formation of wavy layers as indicated in Fig. 1 (top right). Therefore, the idea is to interpret the α -Ga structure in terms of open polyhedral fragments, which are oriented alternately upwards and downwards with respect to the (010) plane and have their short 'terminal' bonds along [101]. Following this model, each Ga atom exhibits $\Sigma^{**}\text{PBO} = 2.26$ in the wavy layers, to form the internal multicentre bonds in the arrangement of polyhedral fragments. The remaining 'terminal' bond has PBO = 1.0, and both PBO values correspond largely to those of the boron cluster compounds.

In order to substantiate this idea, we have probed the

[†] Lattice parameters and positional parameters are mean values taken from the last determination, cf. Ref. 8.

chemical bonding in α -gallium by the extended Hückel method, using the crystal orbital overlap population (COOP) scheme in a rigid-band model¹⁰ [$H_{ii}(\text{Ga},4s) = 14.58$ eV, $\zeta(\text{Ga},4s) = 1.77$, $H_{ii}(\text{Ga},4p) = -6.75$ eV, $\zeta(\text{Ga},4p) = 1.55$]. The COOP values are measures of relative bonding strength, and can be evaluated separately for individual atom pairs and for different electron counts. Thus they give local bonding information in real space derived from band structure calculations. As expected, the overlap population increases with continuous filling of electrons for all Ga–Ga bonds more or less in a parallel way, and the magnitude of the populations corresponds to the inverse distances. The maximum of the total overlap population is reached exactly at 3 electrons per Ga atom, which supports our model in which the α -Ga structure is not electron-deficient, but an adequate covalent solution for the electronic problem.

Interestingly, new unforeseen partial structures appear during further filling in of electrons. At $26 e^-$ per unit cell, or $3.25 e^-$ per atom, the two longest distances of 2.732 and 2.786 Å (types C and D) show a reduction of the covalent bonding strength, while that of the shorter ones of 2.482 and 2.691 Å (type A and B) still increases. The latter two contacts, however, form a substructure of the graphite type as discussed above (cf. Fig. 1). In other words, going from three to four electrons per Ga atom, a graphite-like arrangement appears (!). Filling in even more electrons without relaxation of the structure only favours the bond strength of the short type-A bond up to $28 e^-$ per unit cell (cf. the N_2 molecule). A further increase of valence electrons above $28 e^-$ then weakens all bonds simultaneously.

There is no doubt that the structure of α -gallium can be described as a Ga_2 molecular metallic crystal, as Parrinello and co-workers have done.⁷ However, in our opinion there seems to be much more quasi-localized bonding in this structure, which is not only manifested in the Ga–Ga pairs, but also in the polyhedral fragments forming the strongly puckered layers parallel to (110) (Fig. 1). Therefore, α -gallium can be understood as an inorganic polymer, strongly related to the boron structures. The metallic behaviour seems to be a minor effect on top of the more localized bonding, and the calculation of boron with the α -Ga structure could well yield a semiconductor.

In a recent publication, Burdett and Canadell¹¹ pointed out that "in fact the only extended system built from edge-shared deltahedra of which we are aware is MgB_4 . The structure of MgB_4 consists of one-dimensional chains of edge-sharing nido pentagonal bipyramids vertex linked into a three dimensional structure". α -Gallium, however, is another example of this type in which polyhedra like icosahedra are dissected and the fragments are condensed via edge-sharing. One might wonder how many other examples have been overlooked in the past, because the condensation of nido, arachno or hypho deltahedra had not really been considered as an electronically adequate replacement of closo clusters.

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