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Distribution of the *M*—*M* Distances in the Oxides of the Group 13 Elements and their Spinels and Delafossites

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Abstract

An analysis of the distribution of the *M*—*M* distances (*M* = Al, Ga, In, Tl) in all their binary, ternary and quaternary oxides, contained in the Inorganic Crystal Structure Database (ICSD95), shows that the *M*—*M* distances are not distributed uniformly, but present maxima at values which are near the corresponding distances in pure metals. As for boron, this feature reflects the tendency of these elements to form aggregates in their compounds. These metal aggregates maintain distances and, in many instances, also the topology of the elemental structures, as is illustrated here with two families of structures, *i.e.* spinels and delafossites. In spinels, the group 13 cations form a 3D (three-dimensional) network of truncated tetrahedra, which are also found in the Zintl phases of these elements. In $MgAl_2O_4$ the Al subnet is identical, in topology and dimensions, to that of $CaAl_2$ and both reproduce exactly half of the *f.c.c.* (face-centred cubic) net of Al metal.

1. Introduction

In previous works (Vegas *et al.*, 1990, 1991; Vegas & Martínez-Ripoll, 1992; Martínez-Cruz *et al.*, 1994; Vegas *et al.*, 1995; Ramos-Gallardo & Vegas, 1995*a*) we have reported examples of how the cationic substructure, in many compounds, can be related to the structure of the parent metal, maintaining both topology and distances of the respective elemental structure. Although the examples given are varied, involving elements as different as alkaline earths, lanthanides, Sc, Al, In and Tl, a general trend cannot be deduced from them.

One way of obtaining information about the degree of occurrence of this feature is to evaluate the distribution of the *M*—*M* distances in all the compounds of a given element. In connection with this we have advanced elsewhere (Isea & Vegas, 1995) in a study of the distribution of the *M*—*M* distances in all the compounds of Mg, Ca and Sr, showing that these distances are not distributed uniformly, but they present maxima which are coincident with the *M*—*M* distances of the different elemental phases. In that work, the coincidence was quite good for Mg and Ca. However, for Sr a maximum appeared, centered at 3.82 Å, which did not match the considered phases of Sr. The possible existence of a high-pressure (HP) *b.c.c.* phase of Sr (a_{bcc} = 3.82 Å) was speculated. Now, the existence of a HP phase (a_{bcc} = 4.43 Å) is ensured (McWhan & Jayaraman, 1963); the Sr maximum coincides with the first-neighbor distance (3.84 Å) of this *b.c.c.*-Sr.

In this article the study is extended to the elements of group 13 (B, Al, Ga, In, Tl) to see if they show a behavior similar to that of Mg, Ca and Sr. In this case, however, only the oxygen-containing compounds are considered, avoiding intermetallic phases in which the appearance of metal aggregates should be more likely. An exception to this is the distribution of the B—B distances, for which all the compounds have been taken into account. As an example of the investigated behavior, data are given on two families of structures, *i.e.* spinels and delafossites containing group 13 elements, in which cations form aggregates which can be related to the structures of the parent metals.

2. Data processing

The rough data were obtained from the Inorganic Crystal Structure Database [ICSD95 (Kirschhoff *et al.*, 1995)] and further processed with the aid of a program (*BICSD*) written in Turbo Pascal 7.0 for this purpose. It runs on a PC with at least 1 Mb RAM.

A set of searching processes, varying the element count (ELC command of ICSD) from two (binary compounds) to four (quaternary compounds), was carried out. For each set, all the *M*—*M* distances up to 4.5 Å (5.0 Å for Tl) were calculated (PDIST command of ICSD). These data were read by *BICSD*, reduced and then written in two sets of files. The first contain all the crystallographic information for each ELC value. The second contain all the *M*—*M* distances.

The data were reduced using the following criteria:

(i) Entries for which the occupancy factor of the involved atom was not 1.0 were eliminated.

(ii) For multiple structure determinations of a given compound, that with the lowest *R* value was selected. The

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others were eliminated. If no R value was given, the entry was not considered.

(iii) Duplicated entries corresponding to the same compound but formulated in different ways were also eliminated, except when entries corresponded to different crystallographic phases of the same compound.

(iv) In compounds in which the atom involved occupies two or more crystallographically independent

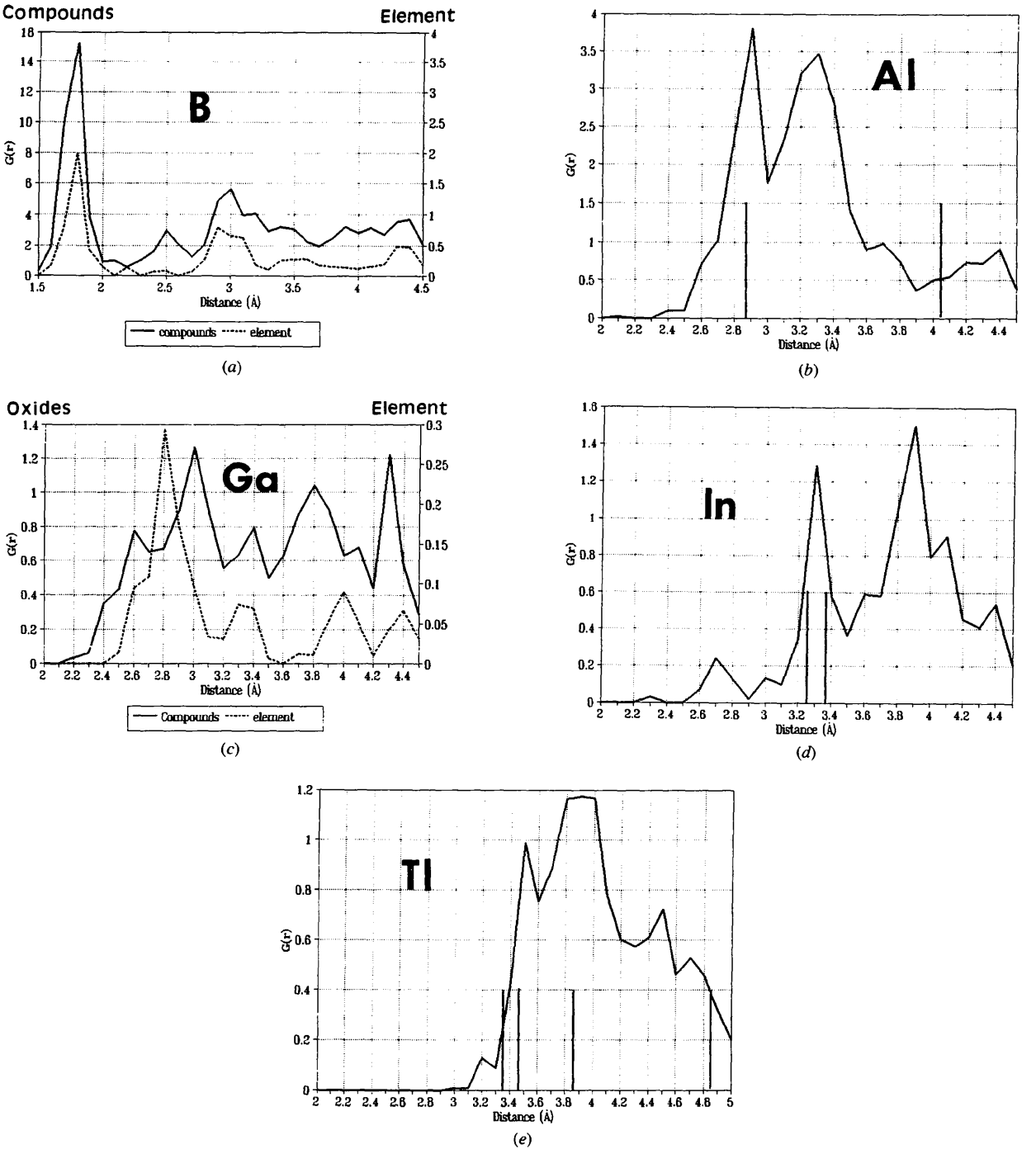

Fig. 1. Density functions [$G(r) = N_d/4\pi r^2$] of the M—M distances for B, Al, Ga, In and Tl in boron compounds and in Al-, Ga-, In- and Tl-containing oxides. In the curves corresponding to B and Ga, the density functions of the elemental phases have been represented with dotted lines and the values of $G(r)$ are represented on the scale at the right-hand side. In the remaining curves the M—M distances in the pure elements are represented by vertical lines.

sites, the *M*—*M* distances involving atoms at different sites appear duplicated. However, duplicated distances were not eliminated because the aim was to compute the coordination spheres rather than the distances themselves.

Data from a total of 1015 B-containing compounds (12 706 distances), 506 Al-containing compounds (4189 distances), 356 Ga-containing compounds (2618 distances), 312 In-containing compounds (1832 distances) and 275 Tl-containing compounds (2516 distances) were selected. The final result was a file containing the frequency (N_d) of distances at each interval of d (Å) denoted as r. The interval width can be selected as the input parameter. In our case a value of 0.1 Å was selected. Finally, the values of the density function, $G(r) = N_d/4\pi r^2$, were computed and plotted against r in Fig. 1(*a*)–(*e*) for B, Al, Ga, In and Tl, respectively. These functions are equivalent to radial distribution functions.

3. Discussion

As shown in Fig. 1, all the *M*—*M* distances in the oxides and the *B*—*B* distances in all the B-containing compounds are not distributed uniformly, but the density functions present maxima which can be identified using the corresponding values in the pure elements.

In the case of B (Fig. 1*a*) two density functions are shown: that of the B compounds (solid line) and that of the elemental boron (dotted line), for which the seven phases of boron contained in the ICSD have been taken into account. As can be seen, both functions are quite similar, presenting a maximum at 1.7 Å which corresponds to the B—B distance in elemental boron. This coincidence should be expected in view of the great tendency of boron to form aggregates (octahedra, pyramids, chains *etc.*), in which the B—B distances are maintained as in the element and this behavior is reflected in Fig. 1(*a*).

The density function of the Al-containing oxides is shown in Fig. 1(*b*). It presents two maxima, one at 2.90 Å and the other at 3.30 Å. The first one coincides with the shortest Al—Al distance in *f.c.c.*-Al (2.86 Å), indicating that it is maintained in many of the oxides. Examples of this behavior are the aluminum oxides, hydroxides and oxyhydroxides previously reported (Ramos-Gallardo & Vegas, 1995*b*, 1996) and the spinels and delafossites which will be discussed below. The second maximum, however, is not related to elemental *f.c.c.*-Al. It can be identified with the distribution of distances (Al···Al) between two Al atoms bridged by a single O atom. From this observation, O'Keeffe & Hyde (1981) assigned a value of 1.62 Å to the nonbonded or 'one-angle' radius. An example of this behavior is $NaAlO_2$, in which the AlO_4 tetrahedra share corners to form a 3D array where the Al—Al distances are 3.21 Å.

Fig. 1(*c*) shows the density function for both Ga-containing oxides and elemental Ga. As is well known, Ga presents several phases (five contained in ICSD), some of which are far from being the closest-packed structures, which give rise to a great variety of distances ranging from 2.6 to 3.3 Å. For this reason, the Ga—Ga distances have been represented by a density function, as for boron. Note that the two functions of Fig. 1(*c*) are on different scales. Both functions present similarities, but they are not coincident. For the Ga-containing oxides, the highest peak appears at 3.00 Å, which is displaced 0.2 Å from the corresponding peak in the curve of elemental Ga. However, it should be noticed that values close to 3.00 Å appear in several phases of Ga; β-Ga (Bosio *et al.*, 1969) has Ga—Ga distances of 2.92 Å; especially in Ga-III (Weir *et al.*, 1971) which has a body-centered tetragonal (*b.c.t.*) In-type structure and where each Ga atom has four nearest neighbors at 2.81 Å and eight second-nearest neighbors at 2.99 Å. This structure is a distortion of a *f.c.c.* net and because fragments of a *f.c.c.* net appear in the structures of spinels and delafossites, *b.c.t.*-Ga could well be the reference with which to compare the Ga subarray in the oxides.

The distribution of the In—In distances is represented in Fig. 1(*d*). As indicated above, the maximum centered at 3.30 Å agrees with the first- and second-nearest neighbors in *b.c.t.*-In (a = 3.252, c = 4.946, d = 8 × 3.376 Å). It should be outlined that the first coordination sphere in *b.c.t.*-In has four nearest neighbors at 3.252 Å and eight second-nearest neighbors at 3.376 Å, the mean value being 3.335 Å. The small peak centered at 2.70 Å is produced by the In—In distances in mixed In and Mo oxides, as in $In_5Mo_{13}O_{28}$, in which all cations are separated by distances ranging from 2.65 to 2.84 Å, equivalent to the Mo—Mo distance in *b.c.c.*-Mo (d = 2.725 Å). Examples of In-containing compounds showing In—In distances as in the pure metal are the cubic sesquioxide In_2O_3 (Ramos-Gallardo & Vegas, 1995*a*) and the spinels which will be discussed below.

In the case of thallium the distribution of the Tl—Tl distances is more uniform, showing wider maxima. Nevertheless, the density function has a maximum at 3.50 Å, which is close to the first neighbor distance in *b.c.c.*-Tl (3.36 Å) and very close to the corresponding distance in *h.c.p.*- and *f.c.c.*-Tl (d = 3.44 Å). This maximum indicates that a non-negligible number of distances reproduce the values of those in the pure metal. The second maximum, centered at 3.90 Å, agrees with the unit-cell dimension of *b.c.c.*-Tl (a = 3.87 Å). Examples of this behavior are C-Tl_2O_3 of the bixbyite-type (Ramos-Gallardo & Vegas, 1995*a*), showing Tl—Tl distances of 3.52 Å, and the delafossite $AgTlO_2$ with Tl—Tl distances of 3.56 Å.

4. The cation array in spinels

Spinels, AB_2O_4, are cubic, $Fd\bar{3}m$, Z = 8, with A cations occupying site (8*a*) ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$), B cations at (16*d*) ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and the oxygens situated at (32*e*) (x, x, x) (with

$x \simeq \frac{3}{8}$). Traditionally, the structure has been described as an almost cubic close-packed array of O atoms in which $\frac{1}{8}$ of the tetrahedral holes are occupied by the A cations and half the octahedral holes occupied by the 16 B cations. The first analysis of the cation array in spinels was published by Gorter (1954). More recently, a complete description of the spinel structure based on the cation arrays has been reported (O'Keeffe & Hyde, 1985), pointing out how the AB_2 substructure is of the $MgCu_2$-type.

In terms of polyhedra, the AB_2 cation array is described as a space-filling array of empty B_4 tetrahedra and filled truncated tetrahedra AB_{12}. The B_4 tetrahedra are corner-sharing and form a net similar to that of the ideal high cristobalite. This ideal net gives rise to the formation of B_{12} truncated tetrahedra, where the A cations are lodged. In fact, the B subarray is just one half of a *f.c.c.* array, the other half being identical and interpenetrating the first (O'Keeffe & Hyde, 1985). The relationship between the *f.c.c.* array and the truncated tetrahedra can be easily deduced from Fig. 2. Here, the B subarray could be described as a *f.c.c.* net in which the B_4 tetrahedra, inserted in the B_{12} truncated tetrahedra, are missing (see Fig. 2) and would have been replaced by the A cations. It should be recalled that the *f.c.c.* net can also be reconstructed from the B cation array, as described previously (Ramos-Gallardo & Vegas, 1996). The normal AB_2O_4 (B = Al, Ga, In) spinels are collected in Table 1, together with their unit-cell parameters and B—B distances. The mean values of the latter are 2.857, 2.945 and 3.241 Å for the Al, Ga and In spinels, respectively, and are in good agreement with the respective M—M distances in the pure metals, *i.e.* 2.857 Å for *f.c.c.*-Al, 2.985 Å for Ga-III and 3.252 Å for *b.c.t.*-In. In the case of AAl_2O_4 the Al atoms reproduce exactly half the *f.c.c.* structure of the pure metal and could be considered as a giant Al cluster. In the case of AGa_2O_4 and AIn_2O_4 compounds the oxides stabilize half a *f.c.c.* structure, which, on the one hand, is not very far from the *b.c.t.* net of both Ga-III and In.

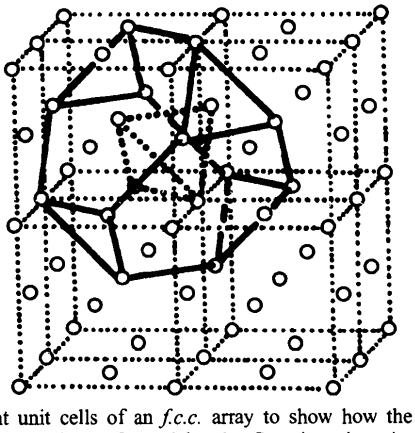

Fig. 2. Eight unit cells of an *f.c.c.* array to show how the truncated tetrahedra (full lines) formed by the B cations in spinels can be derived from it. A tetrahedron, formed by the four atoms centering the hexagonal faces of the truncated tetrahedron, has been depicted with dotted lines. This tetrahedron is missing in the cation array of spinels.

Table 1. *AB_2O_4 (B = Al, Ga, In) spinels*

In the first column the unit-cell parameters are given. In the second column the B—B distances are listed. All values are given in Å. N and I denote normal and inverse spinels. The remaining entries have different degrees of inversion.

	Compound	a	B—B	References
N	$MgAl_2O_4$	8.075	2.86	Yamanaka & Takeuchi (1983)
	$FeAl_2O_4$	8.152	2.88	Larsson *et al.* (1994)
	$CoAl_2O_4$	8.095	2.86	Toriumi *et al.* (1978)
I	$NiAl_2O_4$	8.053	2.85	Cooley & Reed (1972)
	$CuAl_2O_4$	8.078	2.86	Cooley & Reed (1972)
	$(Cu,Ni)Al_2O_4$	8.053	2.85	Otero-Areán & Viñuela (1985)
N	$ZnAl_2O_4$	8.088	2.86	Cooley & Reed (1972)
	$MgGa_2O_4$	8.278	2.93	García-Casado & Rasines (1982)
	$MnGa_2O_4$	8.458	2.99	García-Casado & Rasines (1982)
	$FeGa_2O_4$	8.363	2.96	Oles (1966)
	$CoGa_2O_4$	8.307	2.94	Lensen & Michel (1958)
	$NiGa_2O_4$	8.261	2.92	Otero-Areán & Trobajo-Fernández (1985)
I	$CuGa_2O_4$	8.390	2.97	Rubio-González & Otero-Areán (1985)
N	$ZnGa_2O_4$	8.330	2.95	Hornstra & Keulen (1972)
	$CdGa_2O_4$	8.602	3.04	Datta & Roy (1968)
I	$MgIn_2O_4$	8.864	3.13	Pokrovskii *et al.* (1972)
	$MnIn_2O_4$	9.007	3.18	Pokrovskii *et al.* (1972)
N	$CdIn_2O_4$	9.166	3.24	Rasines (1974)

5. Cation array in the delafossite-type structures

Another family of structures which contribute to the maxima of the density functions represented in Fig. 1 is the delafossite, ABO_2, where A is a monovalent cation (Ag^+ or Cu^+) and B is a trivalent cation (in this case Al^{3+}, Ga^{3+}, In^{3+} or Tl^{3+}). The compounds of these elements are collected in Table 2.

The structure has been described as double layers of close-packed O atoms with the B cations occupying the octahedral holes. The A atoms are situated between two of these double layers in such a way that they are coordinated linearly by two O atoms of two layers. In this structure the cation subarray is formed by alternate 3^6 planar nets of A and B cations (Rogers *et al.*, 1971). They are perpendicular to **c** and the M—M distances are the same for both the A and B cations (coincident with the $\mathbf{a}_h$ parameter of the hexagonal unit cell). It has been pointed out (Rogers *et al.*, 1971) how the first coordination sphere of the A cation contains not only two anions, but also six additional A cations. Thus, the structure can also be regarded as consisting of layers of A cations, one atomic dimension in thickness and metallic in nature, which are sandwiched by two layers of octahedrally coordinated B cations (Rogers *et al.*, 1971). It should be added, however, that the B cations also form the same 3^6 net and, as mentioned above, with the same dimensions as the A cations. Moreover, from the data collected in Table 2 it can be concluded that the B cations (Al^{3+},

Table 2. *ABO_2 (B = Al, Ga, In, Tl) delafossites*

The first column collects the $\mathbf{a}_h$ parameters of either the trigonal or hexagonal cells which correspond to the *A—A* and *B—B* distances in the $\mathbf{3}^6$ planar nets. The second column gives the shortest *M—M* distances in the pure metals Al, Ga, In and Tl.

Compound	$\mathbf{a}_h$ (Å)	*M—M* (Å)	References
$CuAlO_2$	2.858	2.857	Köhler & Jansen (1983)
$CuGaO_2$	2.977	2.808, 2.985	Köhler & Jansen (1986)
$AgAlO_2$	2.896	2.857	Brachtel & Jansen (1981)
$AgGaO_2$	2.989	2.808, 2.985	Shannon *et al.* (1971)
$AgInO_2$	3.277	3.25, 3.376	Köhler & Jansen (1987)
$AgTlO_2$	3.568	3.44	Shannon *et al.* (1971)

Ga^{3+}, In^{3+} or Tl^{3+}) maintain the B—B distances as in the pure metals. On the contrary, the *A* cations seem to be more flexible as they adjust to accommodate the B—B distances. Thus, a difference of 0.67 Å is found between the Ag—Ag distances in $AgAlO_2$ and $AgTlO_2$. It is noteworthy that the elemental Al—Al and Ag—Ag distances (2.86 and 2.89 Å, respectively) are quite similar and that both are reproduced in $AgAlO_2$.

Finally, it should be mentioned that whereas Ag-containing delafossites are formed with the four group 13 elements, the copper compounds have only been synthesized with Al and Ga. Failure to obtain $CuTlO_2$ has been reported elsewhere (Doumerc *et al.*, 1992), but there is no mention of $CuInO_2$ whose synthesis should be of interest to check the constancy of this feature.

6. Conclusions

In the same manner that boron forms aggregates which maintain the B—B distances of the elemental structures in its compounds, the distribution functions of Fig. 1 indicate that in the oxides of Al, Ga, In and Tl are also present aggregates of these metals, intergrown with other metal lattices and/or anionic networks.

The two families of compounds described (spinels and delafossites) are additional examples of this behavior to be added to the aluminum oxides, hydroxides and oxyhydroxides (Ramos-Gallardo & Vegas, 1996), and GaOOH and InOOH (Vegas & Isea, 1997) reported previously. They have been selected because of their significant contribution to the distribution functions of Fig. 1.

It is noteworthy, however, that these features are not restricted to oxides, which means that the topologies and distances observed in the cation aggregates cannot be regarded merely as a consequence of the holes occupied by cations in the more or less distorted close-packed anionic arrays. Similar topologies and distances are also observed in compounds which are far from being described in this manner. As examples we can cite AlB_2Fe_2 in which $\mathbf{4}^4$ planar nets of Al atoms, as those forming the (100) planes of *f.c.c.*-Al, are intergrown with Fe clusters and boron chains, and $LiAlB_{14}$ in which linear chains of Al atoms, separated at distances of 2.92 Å, coexist with Li^+ and the boron clusters.

Another example is $CaAl_2$, a Laves phase of the $MgCu_2$ type, in which the Ca atoms are at the center of the Al-truncated tetrahedra with Al—Al distances of 2.84 Å (Novotny & Mohrheim, 1939), which is the topology and dimensions found in the Al-containing spinels (see previously). The difference is that spinels are 'ionic' compounds, where the Al atoms are 'cations' and $CaAl_2$ is an intermetallic compound at the Zintl border. Although $CaAl_2$ adopts a structure which is not consistent with the Zintl–Klemm concept, it is believed that its Al subnet is a charge acceptor with a partial anionic character. The degree of charge transfer is difficult to assess, but theoretical calculations indicate that the planar **3636** nets (kagome net) forming the truncated tetrahedra show stability for a valence electron count (v.e.c.) of 3.2–3.7 electrons per Al atom (Miller, 1996). Surprisingly, 'cations' and 'anions' would behave structurally in the same manner. The results would be equally surprising if $CaAl_2$ is considered as a true intermetallic compound in which the Al atoms have a more neutral character.

An alternative interpretation of bonding in these compounds is due to Nesper (1991), who considers the alloys as 'electrides' and the corresponding oxide as a stuffed alloy with the O atoms situated at the sites occupied by the electrons in the alloy. Thus, in $CaAl_2$ the eight valence electrons would be situated in pairs at the center of Al_3Ca tetrahedra, just the equivalent position of the O atoms in $MgAl_2O_4$. The problem that we see in this interpretation is that $CaAl_2$ does not form the corresponding $CaAl_2O_4$ spinel and that the $MgAl_2$ alloy is not of the $MgCu_2$ type.

Similarly, the truncated tetrahedra of the spinels can also be found in Zintl phases of Ga, In and Tl. They appear as structural units in complex polyanions (Samson polyhedra) such as those existing in $Na_{96}In_{97}Ni_2$ (Sevov & Corbett, 1993) and in $K_{49}Tl_{108}$ and $Li_{13}Cu_6Ga_{21}$ (Eisenmann & Cordier, 1996).

In the case of the $\mathbf{3}^6$ planar nets in the delafossites, there seems to be no contradiction. In the other compounds showing this type of net, *i.e.* AlB_2 and the high-pressure polymorph of $LiAlO_2$, a cationic character is assumed for the Al atoms. The same theoretical calculations indicate that this net, which is a fragment of *f.c.c.*-Al (in $MAlO_2$), should be stable for a v.e.c. less than 3 (Miller, 1996). Consequently, the formation of the $\mathbf{3}^6$ nets, as well as other metallic fragments, should be understood as the result of an incomplete electron transfer from the group 13 elements to the O atoms, in such a way that the nontransfered electrons should be involved in the formation of *M—M* interactions.

The Tl compounds deserve a special comment. It could be asked if the oxidation state of Tl (I or III) can exercise any influence on the formation of metal aggregates. A brief inspection of the Tl compounds

indicates that Tl—Tl distances, as in the pure metal, are observed in Tl^{III} compounds as Tl_2O_3 (Ramos-Gallardo & Vegas, 1995*a*) and $AgTlO_2$ (this work), as well as in Tl^{I} compounds as $Tl_2Cu(SO_3)_2$, $Tl_2SnGe_3O_9$ and $TlBePO_4$. Both types of compounds contribute to the maximum of Fig. 1(*e*). The lone-pair electrons assigned to Tl^{I} seem to have no influence on the formation of these metal aggregates.

The results discussed here indicate that the appearance of metal aggregates is more general than believed and that it is not restricted to the classical cluster-forming compounds. They are also present in compounds with saturated valences, considered as 'ionic' in nature.

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