# The Crystal Structure of Ga₂Mg*

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The crystal structure of the intermetallic compound $Ga_2Mg$ has been determined by single-crystal X-ray diffraction techniques. Crystals of this material are orthorhombic with $a=6.80_2$, $b=16.34_6$, $c=4.11_1$ Å (with an estimated accuracy of about 0.2%). The unit cell contains 16 Ga atoms (in four fourfold positions) and 8 Mg atoms (in two fourfold positions). The space group as deduced from the structure analysis is *Pbam*. The calculated density is 4.76 g.cm$^{-3}$. Nearest neighbor Ga–Ga distances show approximately the same range of values, 2.556–2.835 Å, as found in elemental gallium. The shortest distance is between atoms in a $Ga_2$ pair. Ga–Mg distances average to 3.02 Å, the overall range of values being 2.80–3.31 Å. Mg–Mg interactions appear to be of lesser importance. There are holes in the structure which are almost large enough to accommodate additional Ga atoms. However, there is no evidence that these holes are even partially filled or that the phase has a range of homogeneity.

## Introduction

An investigation of the Ga–Mg system (Haucke, 1938) disclosed the existence of four binary compounds: $Ga_2Mg_5$, $GaMg_2$, $GaMg$, and $Ga_2Mg$. The crystal structures of $Ga_2Mg_5$ and $GaMg$ have been determined by Schubert, Gauzzi & Frank (1963) and that of $GaMg_2$ by Gröber & Haucke (1950). The compound most rich in gallium, $Ga_2Mg$, was recently prepared in this laboratory for use as a standard in electron microprobe analysis. No crystallographic data appear to have been reported for this material.

The present crystal structure determination may be of interest to students of the subject. A crystal, later shown to be from the $Ga_2Mg$ preparation, was inadvertently picked up in a drybox during a time when samples of $ReCl_5$ were being loaded into capillaries for structure analysis (Mucker, Smith, & Johnson, 1969). This crystal proved, naturally enough, to be different from the others, and was thought to be one of the other chlorides of rhenium or, owing to the very reactive nature of $ReCl_5$, an impurity such as an oxychloride, oxide or salt. Thus, the crystal structure of $Ga_2Mg$ was solved not just without the benefit of supplementary information such as composition, atomic sizes, known stereochemical behavior, *etc.* but it was obtained in the face of completely erroneous notions of the kind mentioned.

## Experimental

The authentic sample of $Ga_2Mg$ was prepared by standard metallurgical procedures: stoichiometric proportions of Ga and Mg (both of 99.99% purity) were sealed in a tantalum tube, and the tube was heated in a differential thermal analysis furnace assembly previously described (Wood & Cramer, 1965; Cramer &

Wood, 1967). The tube, while heated above the melting point of the sample, was rocked to effect mixing. During cooling, only one heat effect (at 284 °C) was observed. The compound thus prepared was handled in a drybox because of its sensitivity to air (reaction products become visible within 24 hours after exposure to air).

As mentioned earlier, a crystal of this material was inadvertently picked up and was thought to be a rhenium-containing compound. Oscillation and Weissenberg photographs showed the crystal to be orthorhombic. The systematic extinctions ($0kl$ for $k$ odd and $h0l$ for $h$ odd) are characteristic of the space groups *Pbam* and *Pba2* (*International Tables for X-ray Crystallography*, 1952). Lattice constants obtained from careful measurements on a single-crystal orienter using Mo $K\alpha$ radiation ($\lambda=0.7107$ Å) are: $a=6.80_2$, $b=16.34_6$, $c=4.11_1$ Å (with an estimated accuracy of about 0.2%). The calculated density for eight units of $Ga_2Mg$ per unit cell is 4.76 g.cm$^{-3}$.

Intensity measurements were carried out on a General Electric XRD–5 diffractometer equipped with a single-crystal orienter. The crystal specimen was a parallelepiped with dimensions $0.08 \times 0.12 \times 0.13$ mm. The stationary-crystal stationary-counter technique (Furnas, 1957) was used; the radiation employed was Zr-filtered Mo $K\alpha$. In all, 252 reflections were recorded up to a $2\theta$-cutoff of 40°. Reflections at $\chi=90°$ showed an intensity variation with $\varphi$ of about $\pm 30\%$ (the linear absorption coefficient for Mo $K\alpha$ radiation is 247 cm$^{-1}$). These measurements were used to obtain $\varphi$-dependent absorption corrections which were applied to all reflections. The corrected intensities were reduced to relative $|F|$'s through the application of Lorentz–polarization factors.

## Determination of structure

Because the material differed so totally from what had been anticipated, developments early in the structure

analysis were puzzling and were at times contradictory. In retrospect, the biggest obstacle was the occurrence of more 'heavy atoms' in the correct structure than could have been expected on the basis of the erroneous formulations. It may be remarked parenthetically that while a reliable, or at least an approximate, chemical formula is unquestionably of great value in structure analysis, no advance information as to composition is probably better than completely incorrect information.

It was apparent from density and volume considerations that the material was probably not $ReCl_5$. The density calculated for four units of $ReCl_5$ per unit cell is 5·28 g.cm⁻³ *vs.* densities of 3·7–4·0 g.cm⁻³ for authentic pentachlorides having generally similar formula weights (Mucker, Smith & Johnson, 1968).Similarly, use of the approximation that in closest packing each Cl atom requires a volume of ∼33 Å³ indicated that the unit cell must contain ∼14 Cl atoms. Calculated densities for the formulations $ReCl_3$ and $ReCl_4$ were 4·25 and 4·77 g.cm⁻³, respectively, four formula weights per unit cell again being assumed in both cases. $ReCl_3$ has previously been reported as rhombohedral with an observed density of 4·66 g.cm⁻³ (Cotton & Mague, 1964). Thus, the calculated density seemed too high for the phase to be $ReCl_4$, and too low for the phase to be a polymorphic form of $ReCl_3$. No density information appears to be available for the oxychlorides of rhenium.

Against this, the observed Patterson map indicated eight, and not four, Re atoms within the unit cell. This followed from large peaks in the $W=\frac{1}{2}$ as well as $W=0$ planes, for if only a single fourfold set were occupied, vector interactions in either space group would occur solely in the $W=0$ plane. An interpretation which accounted reasonably well for the largest peaks in the Patterson map placed four Re atoms in $4(g)$ positions of $Pbam$ $[\pm(x,y,0)\pm(\frac{1}{2}+x,\frac{1}{2}-y,0)]$ and four Re atoms in the $4(h)$ positions [equivalent to $4(g)$ but shifted by $\frac{1}{2}$ along $z$]. The variable parameters were: $x=0\cdot10$, $y=0\cdot07$ for Re(1) in $4(g)$ and $x=-0\cdot10$ $y=0\cdot43$ for Re(2) in $4(h)$. A structure-factor calculation based on the contribution of these two atoms gave a discouragingly high $R$ index of 78 %. Moreover, distances between prospective Cl sites in an electron density synthesis were appreciably shorter (by ∼0·8 Å) than twice the van der Waals radius of Cl.

A solution was next attempted by means of the symbolic addition procedure [see, for example, Karle & Karle (1965)]. A brief summary of the various steps is as follows: conversion of $|F|$'s to $|E|$'s by means of J. M. Stewart's *X-ray* 63 library tape (under the assumption of 8 $ReCl_5$ per unit cell), sign determination by means of H. L. Ammon's *PHASER* program (on the 82 $|E|$'s > 1·0), origin-determining signs given to 233 (+), 111 (+) and 321 (−). The first pass through *PHASER* indicated the signs of 002 and 004 as plus. In a second pass these signs were included, and the signs of 2·11·1 and 171 were permuted. The best solution, that with the signs of both 2·11·1 and 171 as minus, was used to

prepare an 82-term $E$-map. This map displayed four main peaks (heights = 100, 51, 49 and 43 on an arbitrary scale) which were interpreted as being due to Re and 3 Cl in either $4(g)$ or $4(h)$ positions of $Pbam$. A structure-factor calculation based on these atoms gave an $R$ index of 71 %, and again interatomic distances were unsatisfactory for a rhenium-chlorine compound. (It has subsequently been discovered that, due to erroneous input, criteria for not accepting a sign because of weak probabilities were bypassed in certain cases. Thus a number of signs were accepted, whereas these should have remained undetermined. On the basis of the final structure, 19 of the 82 signs were wrong; rigorous application of the *PHASER* program leaves 10 signs undetermined and 9 wrong out of 72 signs.)

It was noticed, however, that the $E$-map and the electron-density synthesis referred to above had features in common. In projection on (001), both displayed a quasi-hexagonal net as the structural motif. The essential difference, apart from a trivial shift of origin, was that one of the fourfold peaks was indicated as a Cl atom in the $E$-map, but as a Re atom in the electron-density map. It was suspected that the atomic positions were essentially correct, but that (1) identification of atom-type might be interchanged in several cases, and (2) the $z$ coordinates of some atoms might be 0 instead of $\frac{1}{2}$, and *vice versa*.

Calculated Patterson functions, *i.e.* Fourier summations with $|F_c|^2$'s as coefficients, were evaluated for both trial models. When these were compared with the observed Patterson map, there was generally good agreement with regard to *location* of peaks, but only a fair correspondence with regard to *peak heights*. Five other structure models for which atom-types and $z$ parameters were interchanged were similarly tested. Chemical compositions corresponding to these models were kept between $ReCl_4$ and $ReCl$.

Despite a substantial improvement in the quantitative fit between observed and calculated Patterson fuctions, the $R$ index remained in the range 0·57–0·68. While not all permutations had been explored, we began to develop a feeling for how changes in $z$ values and atom identification affected various peak heights in these calculated vector-maps. Four fourfold atoms were placed with $z$ coordinates which were felt to be the correct ones; it was noticed also that the agreement was better for compositions corresponding to smaller Cl/Re ratios than for larger ones. No structural pattern could be recognized for various permutations of atom-types, and indeed the interatomic distances were still unsatisfactory for a rhenium-chlorine compound. Nevertheless, there was a growing confidence in the results obtained from the calculated Patterson functions. An assumption was then made which previously would have been unthinkable, namely that all sixteen atoms were Re atoms.

The response to such a model was immediately favorable: $R$ dropped to 25 %. An electron-density map then disclosed two fourfold sites of lesser atomic number.

A least-squares refinement decreased the $R$ index to 11%, but the temperature parameters of these new atoms, identified as Cl, became negative ($-3$ Å$^2$). Refinement with these atoms identified first as Zn, then Ni and then as Cu gave $R$ values of 6·5, 5·8, and 6·0%, respectively, and temperature parameters for all atoms assumed plausible values.

It was at this point that a mixup with the Ga$_2$Mg sample was suspected. The ratio of atomic numbers of Re to Ni is almost exactly the same as Ga to Mg. Thus, a least-squares refinement with the atoms identified as Ga and Mg gave an $R$ index of 5·8%. The crystal was then positively identified as Ga$_2$Mg by comparison of single-crystal diffraction photographs with those from several genuine Ga$_2$Mg crystals.

The crystal structure having for all intents and purposes been solved, we returned to earlier attempts at a solution to see what could be learned from them. It was noted first that the preliminary models had a considerable amount of truth to them, despite the high $R$ values. For example, the two 'heavy-atom' positions deduced from the Patterson map were essentially those of two of the four 'heavy atoms' in the final structure. Similarly, three of the four main peaks in the $E$-map correspond to 'heavy atoms' in the correct model. The fourth peak is at essentially correct $x$ and $y$ values, but is at the wrong level of $z$.

An $E$-map was then synthesized using signs obtained from a rigorous application of the *PHASER* program. (As mentioned above, 9 terms out of 72 had incorrect signs.) This map tends to place the fourth peak referred to above at its correct $z$ level. Under the *a priori* assumption that the compound contained rhenium and chlorine, these peaks would undoubtedly have been interpreted as a Re atom and 3 Cl atoms. Least-squares refinement based on this composition, but with the temperature parameters held fixed, gave an $R$ index of 53%. It seems rather likely that, were the temperature parameters allowed to vary in further refinement series, the structure would have become apparent, *i.e.* the $R$ index would eventually be lowered to 5·8% corresponding to a composition of 'Re$_2$Ni'. What is at once impressive is the powerfulness of the symbolic addition procedure in providing an initial toehold even in circumstances where the chemical formulation was so grossly in error. It would seem that a knowledge of composition is not as essential to the success of the method as has been generally thought.

It appears perhaps even more likely that the structure would have been solved (*i.e.* scaled to a composition of Re$_2$Ni) by the minimum function approach. An $M_4$ superposition map (Buerger, 1959) shows well-resolved features which undoubtedly would have been interpreted as an Re atom and 5 Cl atoms (the minimum function shows, in effect, the Mg atoms). Least-squares based on on a composition of ReCl$_5$ lowers the $R$ index to 32%, and the temperature parameters of three of the fourfold 'Cl' atoms become strongly negative. Undoubtedly, heavier scattering power would

have been assigned to these atoms in subsequent cycles. Completion of the structure determination should not have been difficult.

Final refinement of the Ga$_2$Mg structure was accomplished through the full-matrix, least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 317, unpublished). The quantity minimized was $\Sigma w[|F_o| - (1/K)|F_c|]^2$ where $K$ is the scale factor relating $|F_o|$ and $|F_c|$ and the $w$'s are given by the following weighting scheme $w = F_o^{1/4}$, $F_o < A$; $w = A^{5/4}F_o^{-1}$, $F_o > A$. When the structure factors were placed on an absolute scale, $A = 68·5$. Atomic scattering factors for neutral Ga and Mg were those listed in *International Tables for X-ray Crystallography* (1962); real and imaginary anomalous dispersion corrections, although rather small in the present case, were those of Cromer (1965). Extinction corrections of the form $F_o$(corrected) $= KF_o(1 + \beta I_o)$, where $I_o$ is the raw intensity, were applied. A value of $1·0 \times 10^{-5}$ was adopted for $\beta$, and was not refined. Five cycles of least-squares refinement with isotropic temperature factors reduced the $R$ index $[= \Sigma (K|F_o| - |F_c|)/\Sigma K|F_o|]$ to 5·1% (all reflections). Changes in parameter values in the last cycle were $\leq 0·01$ times the standard deviations. A final difference map showed the maximum excursion from zero to be $< 0·9$ e.Å$^{-3}$. Details of the refinement in *Pbam* appear entirely satisfactory, and there is little reason to consider the non-centrosymmetric alternative.

Final parameters are given in Table 1. Table 2 lists observed and calculated structure factors.

Table 1. *Final parameters for* Ga$_2$Mg

All atoms in fourfold positions, e.s.d.'s in parentheses.

|  | $10^4 x$ | $10^4 y$ | $z$ | $B$ |
|---|---|---|---|---|
| Ga(1) | 4013 (4) | 4335 (2) | 0 | $0·9 \pm 0·1$ Å$^2$ |
| Ga(2) | 4097 (4) | 1902 (2) | $\tfrac{1}{2}$ | $0·8 \pm 0·1$ |
| Ga(3) | 1445 (4) | 4375 (2) | $\tfrac{1}{2}$ | $0·9 \pm 0·1$ |
| Ga(4) | 287 (4) | 1580 (2) | $\tfrac{1}{2}$ | $0·9 \pm 0·1$ |
| Mg(1) | 3241 (13) | 770 (5) | 0 | $1·0 \pm 0·2$ |
| Mg(2) | 2019 (12) | 2804 (5) | 0 | $1·0 \pm 0·2$ |

## Discussion of the structure

The structure is conveniently described in terms of two planar layers, which alternate along the **c** direction. Each layer is made up of three crystallographically distinct atoms. In one type of layer [Fig.1(*a*)] the Ga atoms form Ga$_2$ units, each atom of which is surrounded by 3 Mg atoms at the corners of a nearly equilateral triangle. The other layer [Fig.1(*b*)] is comprised solely of Ga atoms which join together to form an extended net of two- and three-connected atoms. Stacking is such that atoms of one layer fit into interstices of the other layer and *vice versa*.

Nearest neighbor Ga–Ga distances show approximately the same range of values, 2·556–2·835 Å (Table 3), as found in elemental gallium 2·484–2·788 Å (Sharma & Donohue, 1962). The shortest distance, 2·556 Å, is between Ga atoms in the Ga$_2$ dumb bells.

Ga–Ga distances in the extended net are: 2·610, 2·628, 2·644, and 2·835 Å. As in the case of elemental gallium there is no apparent reason for the fairly widespread variation in the observed distances. There is one slightly longer distance of $3·045 \pm 0·004$ Å which occurs between Ga(3) and Ga(4). While this may correspond to a rather weak bond, these atoms have not been considered in the following discussions as neighbors of one another.

The Ga–Mg distances average to 3·023 Å, the overall range of values being 2·802–3·313 Å. By way of comparison, the metallic radii of Ga and Mg are 1·41 and 1·60 Å, respectively [values from the compilation of Teatum, Gschneidner, & Waber (1959)]. Thus the sum of atomic radii agrees rather well with the average Ga–Mg distance observed. The shortest Mg–Mg distance in Ga₂Mg is 3·43 Å, some 0·23 Å longer than twice the metallic radius of Mg. It would seem that Ga–Ga and Ga–Mg interactions contribute more to the stability of the phase than do the Mg–Mg interactions.

Coordination polyhedra (C.P.'s) for the individual atoms are shown in Fig. 2. None is especially familiar except for the C.P. of Ga(2). This atom [Fig. 2(b)] has six Mg neighbors at the vertices of a trigonal prism plus three Ga neighbors along normals to rectangular faces of the prism (see also Fig. 1). This type of con-
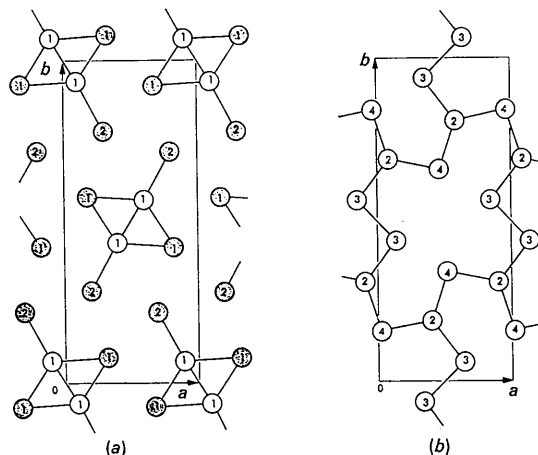


Fig. 1. The two types of planar layers which alternate along the c axis: (a) is level at $z=0$; (b) is level at $z=\frac{1}{2}$. Open circles represent Ga, shaded circles Mg. Numerals identify atoms with those of Table 1.

Table 2. *Absolute values of observed and calculated structure factors for* Ga₂Mg

| H,L= 0, 0 | | | | | | | |
|---|---|---|---|---|---|---|---|
| K FOB FCA | | | | | | | |
| 2 17 13 | | | | | | | |
| 4 69 63 | | | | | | | |
| 6 50 41 | | | | | | | |
| 8 300 290 | | | | | | | |
| 10 94 86 | | | | | | | |
| 12 68 65 | | | | | | | |
| 14 122 111 | | | | | | | |

Table 3. *Interatomic distances in* Ga₂Mg

E.s.d.'s include only uncertainties in positional parameters.

| Atom 1 | Atom 2 | Distance Å | E.s.d. Å | Atom 1 | Atom 2 | Distance Å | E.s.d. Å |
|---|---|---|---|---|---|---|---|
| Ga(1) | Ga(1) | 2·556 | 0·005 | Ga(2) | Ga(4) | 2·610 | 0·004 |
| | 2Ga(4) | 2·686 | 0·002 | | Ga(3) | 2·628 | 0·004 |
| | 2Ga(3) | 2·698 | 0·003 | | Ga(4) | 2·644 | 0·004 |
| | Mg(1) | 2·802 | 0·008 | | 2Mg(1) | 2·827 | 0·006 |
| | Mg(2) | 2·847 | 0·008 | | 2Mg(2) | 2·898 | 0·006 |
| | Mg(1) | 2·881 | 0·009 | | 2Mg(2) | 2·900 | 0·006 |
| Ga(3) | Ga(2) | 2·628 | 0·004 | Ga(4) | Ga(2) | 2·610 | 0·004 |
| | 2Ga(1) | 2·698 | 0·003 | | Ga(2) | 2·644 | 0·004 |
| | Ga(3) | 2·835 | 0·005 | | 2Ga(1) | 2·686 | 0·002 |
| | 2Mg(1) | 3·005 | 0·007 | | 2Mg(2) | 3·101 | 0·006 |
| | 2Mg(1) | 3·077 | 0·006 | | 2Mg(1) | 3·165 | 0·007 |
| | 2Mg(2) | 3·313 | 0·006 | | 2Mg(2) | 3·191 | 0·006 |
| Mg(1) | Ga(1) | 2·802 | 0·008 | Mg(2) | Ga(1) | 2·847 | 0·008 |
| | 2Ga(2) | 2·827 | 0·006 | | 2Ga(2) | 2·898 | 0·006 |
| | Ga(1) | 2·881 | 0·009 | | 2Ga(2) | 2·900 | 0·006 |
| | 2Ga(3) | 3·005 | 0·007 | | 2Ga(4) | 3·101 | 0·006 |
| | 2Ga(3) | 3·077 | 0·006 | | 2Ga(4) | 3·191 | 0·006 |
| | 2Ga(4) | 3·165 | 0·007 | | 2Ga(3) | 3·313 | 0·006 |
| | Mg(2) | 3·427 | 0·011 | | Mg(1) | 3·427 | 0·011 |
| | Mg(2) | 3·471 | 0·011 | | Mg(1) | 3·471 | 0·011 |
| | Mg(1) | 3·473 | 0·016 | | 2Mg(2) | 3·543 | 0·004 |
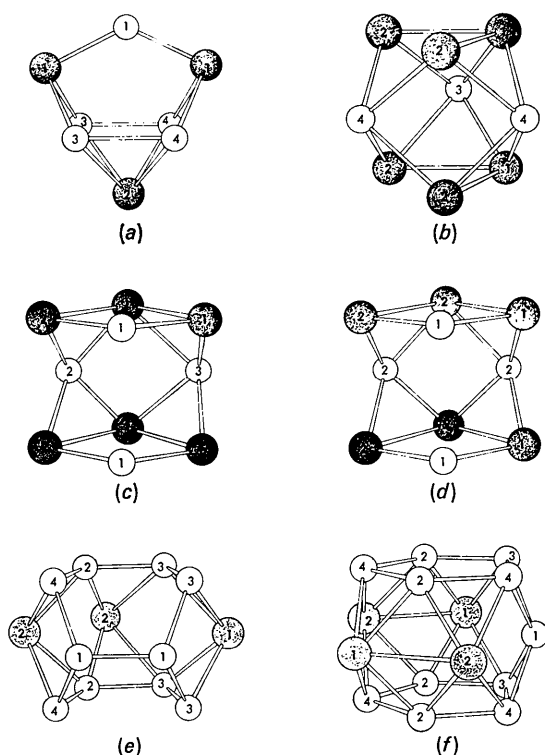
Fig. 2. Ball-and-stick drawings of coordination polyhedra for Ga(1) (a), Ga(2) (b), Ga(3) (c), Ga(4) (d), Mg(1) (e) and Mg(2) (f). In each case, the central atom is omitted for clarity. Open circles represent Ga, shaded circles Mg. Numerals identify atoms. In (a), the direction of the c axis is approximately out of the plane of the paper; in the remaining, the c axis is in the plane of the paper and vertical.

reasonable bond distances. Our final difference map, however, is negative (by $0.7$ e.$Å^{-3}$) at these points. There is thus no indication even of a partial occupancy. Additional preparations were made at 69, 70, and 75 atomic % Ga to see whether a homogeneity range might exist between 66·7 and 69·4 atomic % Ga, the latter composition corresponding to a complete filling of the 2(b) positions. In the course of these studies, we have discovered a new intermediate compound, $Ga_5Mg_2$, the crystal structure of which will be reported shortly. Powder patterns of these preparations, though complex, give no indication of changes in the lattice constants. [Were the distances from atoms in 2(b) to their Ga(1) neighbors to be at least as long as the shortest distance actually observed, the c axis repeat distance should increase by about 5%.] It may also be pointed out that, even though there appear to be holes in the structure, the calculated density of $Ga_2Mg$ is not low relative to other intermediate compounds in the system. The calculated densities of all these compounds lie on an approximately straight line which also passes through the density of Mg.

From the foregoing it is concluded that there is no evidence of the holes being even partially filled, or that the phase has a range of homogeneity.

figuration is, of course, the common one for nine-coordination, and is frequently found in borides, silicides and other gallide structures. Either atom of a pair of Ga(1) atoms has the C.P. illustrated in Fig. 2(a). This grouping of ligands approximates to a square pyramid of five Ga atoms plus a triangle of three Mg atoms. Ga(3) and Ga(4) have very similar environments. Both are surrounded by ten atoms in a configuration which resembles a cuboctahedron, but with two voids in the equatorial section. The coordination numbers of Mg(1) and Mg(2) are 13 and 15, respectively. The configuration about Mg(1) is based on the stacking of planes of 4, 5, and 4 atoms; that of Mg(2), on the stacking of three pentagons.

One unusual aspect of the structure is the appearance of holes at $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ [2(b) positions] which are nearly large enough to accommodate additional Ga atoms. Each of these points is surrounded by 4Ga(1) atoms at 2·420 Å, 2Ga(4) at 2·590 Å, 2Ga(3) at 2·625 Å, and 4Mg(1) at 3·27 Å. The distance to the 4Ga(1) atoms is some 5% shorter than the smallest Ga–Ga distance (2·556 Å) observed in the structure; otherwise the other distances would correspond to

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