Table 3. *Details of the hydrogen bonds*

| | | | |
|---|---|---|---|
| O(1) ···O(4) | 2·71$_4$ Å | O(15) ···O(24) | 2·78$_8$ Å |
| H(11)···O(4) | 2·27 | H(151)···O(24) | 1·97 |
| O(1) ···O(38)* | 3·24$_4$ | O(1)—H(11) ···O(4) | 114° |
| H(12)···O(38)* | 2·17 | O(1)—H(12) ···O(38)* | 157 |
| | | O(15)–H(151)···O(24) | 148 |

* O(38) at equivalent position $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

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# The Crystal Structure of $V_8Ga_{41}$

BY K. GIRGIS, W. PETTER AND G. PUPP*

*Institut für Kristallographie und Petrographie, ETH Zürich, Sonneggstrasse 5, CH-8006 Zürich, Switzerland*

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The structure of $V_8Ga_{41}$ has been determined by trial-and-error methods. In the space group $R\bar{3}$ a rhombohedral unit cell with $a=9{\cdot}456$ Å, $\alpha=94{\cdot}958°$, contains one $Ga(VGa_5)_8$ formula unit. One Ga is in the centre of a cuboctahedron of Ga atoms, whose triangular faces are each shared by a face of a $[VGa_{10}]$ polyhedron. This $[VGa_{10}]$ polyhedron is formed by ten triangular and three almost-square faces and can be described as consisting of half an icosahedron and half a cube. The structure has been refined anisotropically with 2457 unique reflexions to $R=0{\cdot}044$.

## Introduction

This work is part of a programme of study of Ga-rich compounds to gain understanding of the crystal chemistry of the Ga metal (Girgis, 1970). The V–Ga system (Girgis, 1969) is of interest because $V_3Ga$ is a superconductor with a relatively high critical temperature. The Ga-richest phase in this system is $V_8Ga_{41}$ (formerly called '$VGa_{\sim 5}$') (Girgis, Laves & Reinmann, 1966).

## Preparation of the crystals

Earlier experiments to obtain single crystals of '$VGa_5$' by cooling from the melt resulted in twinned crystals (Girgis, Laves & Reinmann, 1966). Untwinned single crystals were prepared by one of us (K.G.) by the following procedure. A cylindrical vanadium sheet was dipped in gallium in a quartz tube, which was then evacuated and sealed. This ampoule was heated to 450 °C. After four months the gallium had fully reacted with the vanadium sheet, which had been converted to '$VGa_5$'. Crystals from the lower part of this sheet were used in this investigation. The chemical analysis of these crystals showed a ratio $V:Ga=1:5{\cdot}17\pm0{\cdot}05$.

* Present address: Institut für Mineralogie, Kristallographie und Strukturchemie, TH Wien, Getreidemarkt 9, A-1060 Wien, Austria.

The space group as determined from precession photographs is $R3$ or $R\bar{3}$.

The cell dimensions determined from Guinier powder photographs (Jagodzinsky camera, Cu $K\alpha_1$, $\lambda = 1{\cdot}5405$ Å, 123 reflexions, Si as standard) are:

$a_H = 13{\cdot}9382\ (6)$ Å, $c_H = 14{\cdot}8924\ (12)$ Å — hexagonal setting

$a_R = 9{\cdot}4560\ (4)$ Å, $\alpha = 94{\cdot}958\ (3)°$ — rhombohedral setting.

The measured density of 6·49 (5) g cm$^{-3}$ leads to $147 \pm 2$ atoms per hexagonal unit cell. The structure determination led to 147 atoms (24 V and 123 Ga) and to a calculated density of 6·533 g cm$^{-3}$. Comparing this density with those of V and Ga shows that $V_8Ga_{41}$ is more dense than both metals: $D_{calc}$ of V = 6·09, $D_{calc}$ of Ga = 5·907 g cm$^{-3}$.

## Data collection

2457 unique reflexions were collected on a Picker 4-circle automatic diffractometer (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, graphite monochromator, $2\theta$ up to 70°, scan width 1·5°, scan speed 1° min$^{-1}$). With a limit of $3\sigma$, 1909 reflexions were classified as observed. The crystal had the dimensions $0{\cdot}20 \times 0{\cdot}14 \times 0{\cdot}10$ mm$^3$. The intensities were corrected for absorption ($\mu = 335$ cm$^{-1}$) by assuming a spherical crystal of the same volume. Statistical tests led to the centrosymmetric space group $R\bar{3}$.

| | $V_8Ga_{41}$ | Centric | Acentric |
|---|---|---|---|
| $\langle\|E\|\rangle$ | 0·765 | 0·798 | 0·886 |
| $\langle\|E^2-1\|\rangle$ | 1·035 | 0·968 | 0·736 |

## Structure determination

The rhombohedral indices of 35 of the 49 largest $E$ values ($E \geq 2{\cdot}5$) are either all even or all odd. This face-centred pseudosymmetry led to difficulties in applying direct methods. The Patterson projection of the hexagonal cell showed 6 distinct layers of maxima parallel to the $bc$ plane and 9 parallel to $ab$. We therefore chose as a starting model the cubic close-packed atomic

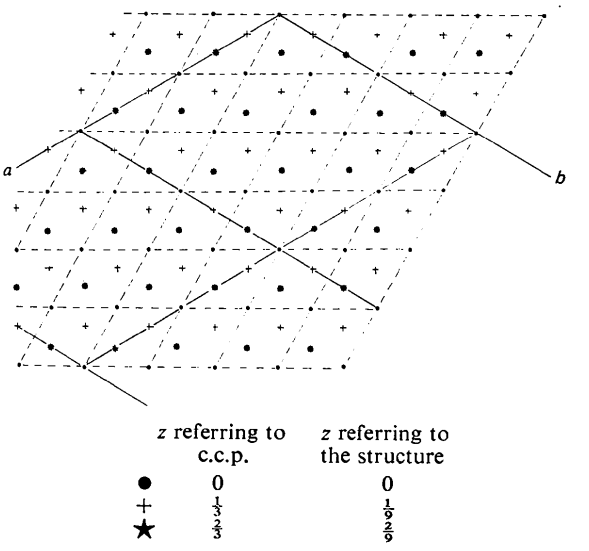


Fig. 1. Starting model based on c.c.p. atomic arrangement.

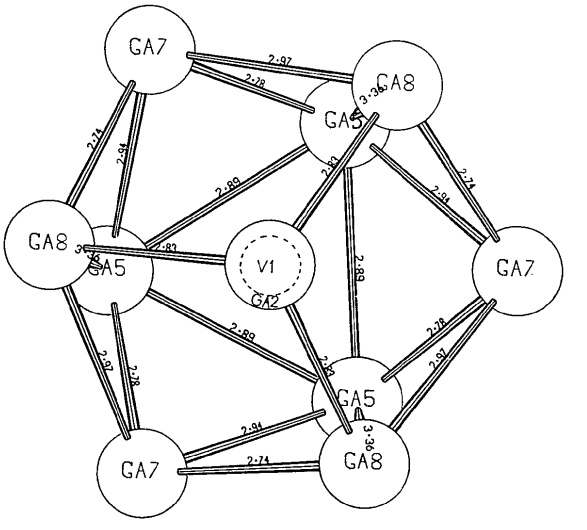


Fig. 2. The coordination polyhedron [$VGa_{10}$] around V(1) in the c direction. The three 'cube' faces intersect at Ga(2). V(1) bonding to the Ga atoms is not drawn.

Table 1. *Atomic and thermal parameters with standard deviations in parentheses*

Values are $\times 10^4$.

| | Equipoint | $x$ | $y$ | $z$ | $u_{11}$ | $u_{22}$ | $u_{33}$ | $u_{12}$ | $u_{13}$ | $u_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Ga(1) | 3(*a*) | 0 | 0 | 0 | 126 | 126 | 161 (15) | 63 (5) | 0 | 0 |
| Ga(2) | 3(*b*) | 0 | 0 | 5000 | 134 | 134 | 95 (13) | 67 (5) | 0 | 0 |
| Ga(3) | 9(*d*) | 5000 | 0 | 5000 | 68 (8) | 141 (9) | 121 (7) | 55 (7) | 21 (6) | −5 (7) |
| Ga(4) | 18(*f*) | 1116 (1) | 2426 (1) | 35 (1) | 123 (6) | 256 (8) | 111 (5) | 124 (6) | −22 (5) | −1 (5) |
| Ga(5) | 18(*f*) | 1154 (1) | 1235 (1) | 1647 (1) | 132 (7) | 130 (6) | 248 (7) | 72 (5) | 82 (6) | 85 (6) |
| Ga(6) | 18(*f*) | 3102 (1) | 3196 (1) | 2670 (1) | 128 (6) | 118 (6) | 66 (5) | 62 (5) | −6 (4) | −2 (4) |
| Ga(7) | 18(*f*) | 8 (1) | 1832 (1) | 2846 (1) | 126 (6) | 80 (6) | 133 (6) | 65 (5) | 11 (5) | 18 (5) |
| Ga(8) | 18(*f*) | 1698 (1) | 1566 (1) | 3864 (1) | 74 (6) | 86 (5) | 125 (6) | 17 (5) | −11 (5) | −24 (5) |
| Ga(9) | 18(*f*) | 1827 (1) | 3187 (1) | 4938 (1) | 88 (6) | 122 (6) | 119 (6) | 66 (5) | 21 (4) | 2 (5) |
| V(1) | 6(*c*) | 0 | 0 | 3140 (2) | 41 | 41 | 76 (12) | 20 (4) | 0 | 0 |
| V(2) | 18(*f*) | 2956 (2) | 3100 (2) | 987 (1) | 49 (7) | 50 (7) | 4729 (7) | 27 (6) | −3 (6) | −3 (6) |

arrangement with a layer spacing of $c/9$. The orientation of $a$ is shown in Fig. 1. The atomic distances within a layer of this packing are as large as 4·02 Å but are only 2·85 Å between atoms of neighbouring layers. This model gave rise to 108 atoms per hexagonal unit cell, so we further filled two general positions of the space group $R\bar{3}$ to obtain 144 atoms per unit cell. These positions were chosen so that the additional atoms were equally distributed over the unit cell with interatomic distances about 2·7 Å. The resulting model had additional layers at $3c/18$, $9c/18$ and $15c/18$. This model was investigated by least-squares refinement, interatomic distance calculations and difference syntheses. Atoms which showed unacceptably small distances to other atoms or very high temperature factors were removed. The missing atoms were finally found by Fourier methods. The structure was refined aniso-

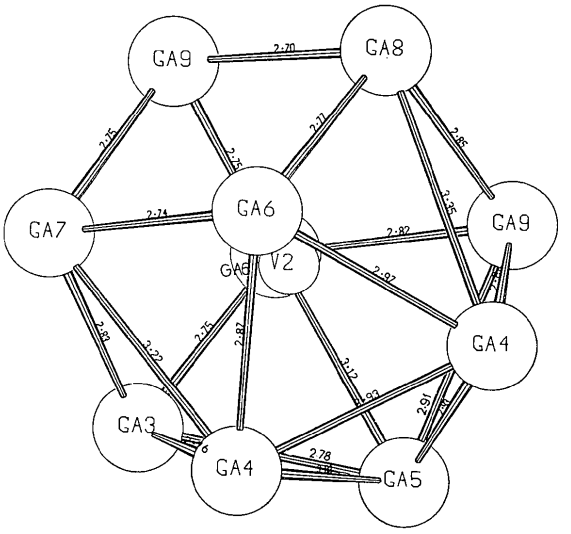


Fig. 3. The coordination polyhedron [$VGa_{10}$] around V(2) in the **c** direction. The three 'cube' faces intersect at Ga(9) on the left side of the figure. V(2) bonding to the Ga atoms is not shown.

Table 2. *Interatomic distances* (Å)

Only distances less than 3·5 Å are listed.

| | | | |
|---|---|---|---|
| V(1)–3Ga(8) | 2·518 (2) | Ga(6)–V(2) | 2·512 (2) |
| 3Ga(7) | 2·579 (1) | V(2) | 2·535 (2) |
| Ga(2) | 2·764 (3) | Ga(7) | 2·741 (2) |
| 3Ga(5) | 2·774 (3) | Ga(3) | 2·747 (1) |
| V(2)–Ga(6) | 2·512 (2) | Ga(9) | 2·752 (2) |
| Ga(3) | 2·515 (1) | Ga(8) | 2·770 (2) |
| Ga(6) | 2·533 (2) | Ga(9) | 2·816 (2) |
| Ga(8) | 2·538 (2) | Ga(4) | 2·874 (2) |
| Ga(9) | 2·970 (2) | Ga(4) | 2·970 (2) |
| Ga(7) | 2·585 (2) | Ga(5) | 3·117 (2) |
| Ga(9) | 2·590 (2) | Ga(7)–V(1) | 2·579 (1) |
| Ga(4) | 2·652 (2) | V(2) | 2·584 (2) |
| Ga(4) | 2·684 (2) | Ga(8) | 2·739 (2) |
| Ga(5) | 2·732 (3) | Ga(6) | 2·741 (2) |
| Ga(1)–6Ga(4) | 2·926 (2) | Ga(9) | 2·754 (2) |
| 6Ga(5) | 2·962 (2) | Ga(5) | 2·778 (2) |
| Ga(2)–2V(1) | 2·764 (3) | Ga(3) | 2·830 (2) |
| 6Ga(8) | 2·833 (2) | Ga(5) | 2·937 (2) |
| Ga(3)–2V(2) | 2·513 (1) | Ga(8) | 2·970 (2) |
| 2Ga(6) | 2·746 (1) | Ga(4) | 3·224 (2) |
| Ga(4) | 2·757 (2) | Ga(8)–V(1) | 2·518 (2) |
| Ga(4) | 2·758 (2) | V(2) | 2·539 (2) |
| Ga(5) | 2·779 (2) | Ga(9) | 2·696 (1) |
| Ga(5) | 2·780 (2) | Ga(7) | 2·739 (2) |
| Ga(7) | 2·830 (1) | Ga(6) | 2·770 (2) |
| Ga(7) | 2·832 (1) | Ga(2) | 2·833 (2) |
| Ga(4)–V(2) | 2·652 (2) | Ga(9) | 2·850 (2) |
| V(2) | 2·684 (2) | Ga(7) | 2·970 (2) |
| Ga(3) | 2·756 (2) | Ga(4) | 3·349 (2) |
| Ga(9) | 2·823 (2) | Ga(5) | 3·359 (2) |
| Ga(6) | 2·873 (2) | Ga(9)–V(2) | 2·570 (2) |
| Ga(1) | 2·926 (2) | V(2) | 2·591 (2) |
| 2Ga(4) | 2·928 (2) | Ga(8) | 2·696 (1) |
| Ga(5) | 2·930 (2) | Ga(7) | 2·754 (2) |
| Ga(6) | 2·969 (2) | Ga(6) | 2·754 (2) |
| Ga(5) | 3·034 (2) | Ga(6) | 2·816 (2) |
| Ga(7) | 3·223 (2) | Ga(4) | 2·823 (2) |
| Ga(8) | 3·348 (2) | Ga(8) | 2·850 (2) |
| Ga(5)–V(2) | 2·732 (3) | Ga(5) | 2·908 (2) |
| V(1) | 2·774 (3) | | |
| Ga(7) | 2·778 (2) | | |
| Ga(3) | 2·779 (2) | | |
| 2Ga(5) | 2·885 (3) | | |
| Ga(9) | 2·908 (2) | | |
| Ga(4) | 2·930 (2) | | |
| Ga(7) | 2·937 (2) | | |
| Ga(1) | 2·962 (2) | | |
| Ga(4) | 3·034 (2) | | |
| Ga(6) | 3·117 (2) | | |
| Ga(8) | 3·359 (2) | | |

Table 3. *Interatomic distances for coordination spheres up to* 7·413 Å

| | Number of atoms in the first sphere | 2·512–2·630 | 2·630–2·753 | 2·753–2·884 | 2·884–3·019 | 3·019–3·163 | 3·163–3·311 | 3·311–3·467 | 3·467–3·630 | 3·630–3·803 | 3·803–3·982 | 3·982–4·170 | 4·170–4·366 | 4·366–4·527 | 4·527–4·785 | 4·785–5·011 | 5·011–5·248 | 5·248–5·496 | 5·496–5·755 | 5·755–6·026 | 6·026–6·310 | 6·310–6·607 | 6·607–6·918 | 6·918–7·245 | 7·245–7·413 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
| Ga(1) | 12 | | | | 12 | | | | | | | | | 6 | 8 | 18 | | | | 12 | 18 | | | 18 | |
| Ga(2) | 8 | | | 8 | | | | | | | 6 | 6 | | | | 12 | | 6 | 12 | | 6 | 24 | | 12 | 12 |
| Ga(3) | 10 | 2 | 2 | 6 | | | | | | | 4 | | 6 | 6 | 4 | 2 | 4 | 2 | 4 | 4 | 6 | 18 | 16 | 14 | 6 |
| Ga(4) | 13 | | 2 | 3 | 5 | 1 | 1 | 1 | | | | 1 | 2 | 4 | 8 | 2 | 5 | 5 | 8 | 9 | | 8 | 19 | 12 | 7 |
| Ga(5) | 13 | | 1 | 3 | 6 | 2 | | 1 | | | | 1 | 2 | 2 | 8 | 3 | 6 | 8 | 8 | 6 | | 7 | 17 | 15 | 6 |
| Ga(6) | 10 | 2 | 3 | 3 | 1 | 1 | | | | 1 | 2 | 4 | 1 | 3 | 7 | 6 | 3 | 1 | 7 | 3 | 10 | 10 | 18 | 14 | 1 |
| Ga(7) | 10 | 2 | 2 | 3 | 2 | | 1 | | | 2 | 3 | 2 | | 5 | 7 | 3 | 3 | 4 | 5 | 6 | 10 | 8 | 18 | 12 | 4 |
| Ga(8) | 10 | 2 | 2 | 3 | 1 | | | 2 | | | 4 | 5 | 1 | | 5 | 8 | 3 | 3 | 4 | 6 | 15 | 9 | 10 | 18 | 3 |
| Ga(9) | 9 | 2 | 1 | 5 | 1 | | | | | 1 | 6 | | 1 | 5 | 4 | 8 | 2 | 5 | 3 | 5 | 11 | 8 | 14 | 13 | 6 |
| V(1) | 10 | 6 | | | 4 | | | | | | | | | 3 | 10 | 9 | 9 | 6 | 4 | | 12 | 6 | 3 | 21 | 6 |
| V(2) | 10 | 7 | 3 | | | | | | | | | | | 6 | 9 | 6 | 11 | 7 | | 3 | 10 | 5 | 11 | 13 | 9 |

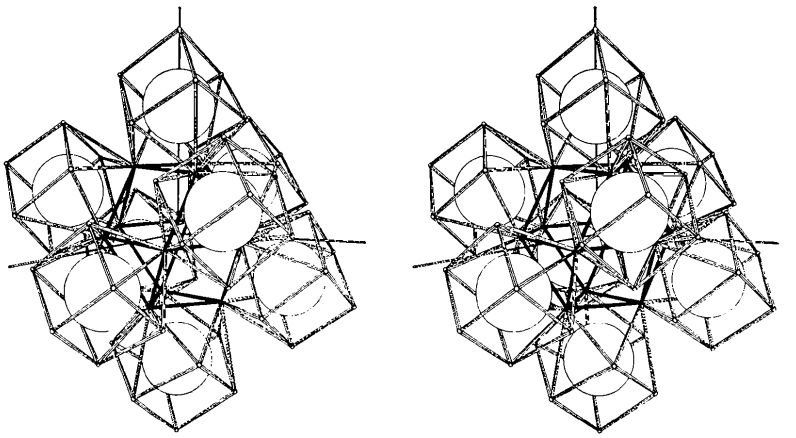

Fig. 4. Stereographic view of a $GaGa_{12}$ cuboctahedron surrounded by eight $VGa_{10}$ polyhedra (central atoms V given as spheres, *c* nearly vertical).

tropically to an $R$ of 4·4%. Positional and thermal parameters and interatomic distances are given in Tables 1 and 2.*

## Discussion of the structure

The structure can be described by the packing of coordination polyhedra. The coordination numbers were defined by the method of largest gaps in the atomic distance sequence (Brunner & Schwarzenbach, 1971) (Table 3).

It is remarkable that Ga(1) has 12 Ga neighbours which form a cuboctahedron. The polyhedra around V(1) and V(2) are each formed by 10 Ga atoms and can be described as a combination of half an icosahedron and half a cube (Figs. 2, 3). The V(1) polyhedron is slightly more symmetric since it has a threefold axis passing through its centre and the corner where the three cube faces intersect, but it is topologically equivalent to the V(2) polyhedron. This structure can be completely described by just 2 types of coordination polyhedra (cuboctahedron and V-polyhedron). The centre of a $GaGa_{12}$ cuboctahedron is at one of the symmetry centres of a $\bar{3}$ axis which passes through 2 of its 8 triangular faces. Both faces are shared with a V(1) polyhedron [$VGa_{10}$], which is oriented so that the vertex where the 'cube' faces meet is opposite the shared triangular face. The other 6 triangular faces are shared with V(2) polyhedra [$VGa_{10}$] in the same way as that described above (Fig. 4).

Two [$VGa_{10}$] polyhedra meet at each vertex of the cuboctahedron. Each of its 12 Ga atoms therefore belongs to 3 polyhedra; the central Ga atom belongs to the cuboctahedron alone. Each of the 10 Ga atoms in a [$VGa_{10}$] polyhedron is shared by another [$VGa_{10}$] polyhedron, but 3 of them (forming a triangular face) also belong to the cuboctahedron. The structure formula can therefore be written as

$$(GaGa_{12/3})\,(VGa_{3/3}Ga_{7/2})_8 \quad \text{or} \quad Ga(VGa_{10/2})_8.$$

Thus each V polyhedron shares only one of its ten triangular faces with a cuboctahedron and all ten corners with other V polyhedra. Fig. 4 shows the arrangement of these polyhedra.

The coordination numbers of the Ga atoms at the vertices of the V(1) and V(2) polyhedra are, according to Brunner & Schwarzenbach (1971): Ga(2) 8, Ga(3) 10, Ga(4) 13, Ga(5) 13, Ga(6) 10, Ga(7) 10, Ga(8) 10, Ga(9) 9.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30607 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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