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Synthesis and Structure Determination of the New Intermetallic Compound $RbGa_7$

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Abstract. $RbGa_7$, monoclinic, space group $C2/m$, $a = 11{\cdot}432\,(3)$, $b = 6{\cdot}603\,(2)$, $c = 10{\cdot}259\,(3)$ Å, $\beta = 111{\cdot}85\,(2)°$, $V = 718{\cdot}7$ Å^3, $Z = 4$. Diffraction data with $0 < 2\theta < 60°$ (Mo $K\alpha$ radiation) were collected on a Nonius CAD-4 automatic diffractometer within the octants $h\bar{k}l$ and $\bar{h}\bar{k}l$. The structure was solved in space group $C2$ by direct methods and finally refined in $C2/m$ by full-matrix least squares to a final $R(F)$ of 0·058 for 584 independent reflections with $I > 3\sigma(I)$. The structure can be described in terms of a packing of icosahedra (Ga atoms) arranged around inversion centers in a sheet-like non-compact netting leaving channels where Rb atoms reside to form zig-zag chains parallel to the y axis.

Introduction. The system Rb–Ga was investigated (DTA) by Thümmel & Klemm (1970); the phase diagram was not complete, but revealed the existence of two compounds: $RbGa_4$ and Rb_5Ga_8. The diagram by Yatsenko (1977) revealed the existence of two different compounds, $RbGa_5$ and $RbGa_2$. On the other hand, Bruzzone (1969) had previously analyzed the behavior of alkaline metals Na, K, Rb and Cs to give MX_4 phases with Group II to IV*b* elements, displaying the tetragonal $D1_3$ ($BaAl_4$) structure type; such phases were found for $NaGa_4$, KIn_4 and $RbIn_4$. Recently, we have found a new phase (K_3Ga_{13}) with orthorhombic symmetry (Belin, 1980).

We have reinvestigated the system Rb–Ga through X-ray diffraction methods and found two novel compounds: $RbGa_3$ and $RbGa_7$; the first is very unstable and oxidizable, the second fairly stable. Its crystal structure will be described and discussed below.

Alusuisse gallium was used while rubidium was prepared in the laboratory through reduction of the chloride by pure calcium and subsequent purification through several distillations under vacuum. Referring to Klemm's phase diagram, a 95 mol % gallium mixture was prepared by weighing the elements in a dry box filled with argon. The mixture was then fused and heated up to 873 K in a tantalum tube which had previously been sealed by welding in an argon atmosphere and then allowed to cool slowly to room temperature. The resulting grey mass was centrifuged as described before (Belin, 1980) in order to separate the crystals.

The crystals were examined under an optical microscope inside a glove bag filled with argon. It was not possible to find any crystal exhibiting well-defined edges or faces so several were mounted in Lindemann-glass capillaries, using a cyanoacrylate ester adhesive to hold them in position, and tested through preliminary oscillation and Weissenberg photographs.

Monoclinic symmetry was found and systematic extinctions suggested the following space groups: $C2$, Cm, $C2/m$. The crystal which gave the best diffraction spots was selected and mounted on an Enraf–Nonius CAD-4 automatic diffractometer. Accurate lattice constants were determined by least-squares refinement of the angular positions of 24 reflections collected and centered on the diffractometer.

Integrated diffraction intensities were collected at room temperature (293K) in the range $0 < 2\theta < 60°$ within the two octants $h\bar{k}l$ and $\bar{h}\bar{k}l$ using graphite-monochromated Mo $K\alpha$ radiation; the profile analysis of a few low-angle reflections indicated that an ω–2θ scan method was the most appropriate for data collection. During data collection, the intensities of three standard reflections were checked after every 50 reflections and no substantial loss in intensity was observed. The data were corrected for background and Lorentz–polarization effects. Once the composition of the compound was known, the data were corrected for the effects of absorption by Gaussian integration (Busing & Levy, 1957) with a linear absorption coefficient $\mu = 34{\cdot}2$ mm^{-1} and the approximation that the crystal was square prismatic with dimensions $0{\cdot}04 \times 0{\cdot}04 \times 0{\cdot}1$ mm. The final data set consisted of 1133 independent reflections of which 584 with $I > 3\sigma(I)$ were used in refinement.

The structure was solved by direct methods. Although the Wilson plot of *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) gave a strong indication of centricity, the program failed to give a solution in the space group $C2/m$ and the solution was obtained in the lower space group $C2$.

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The output from the Fourier step of *MULTAN* contained eight peaks of high and almost equal weight; all these peaks, except one, having distances in the order of Ga—Ga bonds, were attributed to Ga atoms while the remaining peak was attributed to an Rb atom.

After a few cycles of positional and isotropic thermal-parameter refinement of these positions in the space group $C2$, $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0{\cdot}081$ and a subsequent difference Fourier map with residual peaks less than 6 e Å^{-3} contained no obvious extra Ga or Rb atoms. Once the distribution of the Ga and Rb atoms appeared to be centric, the space group $C2/m$ was chosen; thus the number of Ga atoms was reduced from seven to five, two of them occurring in general positions 8(j) and the other three in special positions 4(i) while the Rb atom occurs in position 4(i). Finally, all atomic positional parameters and anisotropic temperature factors were refined by full-matrix least squares minimizing the function $W(|F_o| - |F_c|)^2$ with $W^{-1} = \sigma^2(F^2)_{\text{count}}/4F^2 + (0{\cdot}01F)^2$. The final agreement factors were $R(F) = 0{\cdot}058$ and $R_w(F) = 0{\cdot}068$; the goodness-of-fit, defined as $[\sum w(|F_o| - |F_c|)^2/(N - M)]^{1/2}$, where N is the number of observations (584) and M the number of parameters varied (43), was 0·994. The final difference Fourier map was flat except for some spurious peaks close to Ga atoms of height $<2{\cdot}4$ e Å^{-3}. In the final cycle of refinement, the shifts in atom positional parameters were $<0{\cdot}052\sigma$. The uncertainties in Ga and Rb atoms range from 0·0030 to 0·0044 Å.

Corrections for the anomalous-dispersion effects were included in the neutral-atom scattering factors (Doyle & Turner, 1968). The crystallographic programs used in this work were *MULTAN* (Main *et al.*, 1974), *DRF* (a modification of the Zalkin Fourier program), *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinements, *ORFFE* (Busing, Martin & Levy, 1964) for molecular and error functions and *ORTEP* II (Johnson, 1971), the thermal ellipsoid program for molecular plots.

Table 1. *Final positional* ($\times 10^4$) *and thermal parameters for atoms in* $RbGa_7$

B_{eq} defined according to Willis & Pryor (1975).

	N*	x	y	z	B_{eq} (Å^2)
Ga(1)	8(j)	1193 (3)	3019 (5)	5561 (3)	1·35 (6)
Ga(2)	4(i)	1823 (4)	0	4438 (4)	1·37 (8)
Ga(3)	4(i)	2169 (4)	0	7321 (4)	0·84 (7)
Ga(4)	4(i)	4561 (4)	0	8679 (4)	0·73 (7)
Ga(5)	8(j)	−73 (2)	−2095 (4)	2684 (2)	0·82 (5)
Rb	4(i)	1949 (4)	0	842 (4)	1·71 (7)

* N = Number of positions and Wyckoff notation.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* $RbGa_7$

Ga(1)–1Ga(1)	2·535 (6)	Ga(1)–1Ga(5)	2·639 (4)
Ga(1)–1Ga(2)	2·537 (4)	Ga(1)–1Ga(3)	2·642 (4)
Ga(1)–1Ga(1)	2·616 (6)	Ga(1)–1Ga(5)	2·828 (3)
Ga(1)–1Ga(2)	2·618 (5)	Ga(1)–1Rb	3·742 (4)
Ga(2)–2Ga(1)	2·537 (4)	Ga(2)–1Ga(3)	2·834 (5)
Ga(2)–2Ga(1)	2·619 (5)	Ga(2)–1Rb	3·746 (6)
Ga(2)–2Ga(5)	2·635 (4)		
Ga(3)–1Ga(4)	2·566 (5)	Ga(3)–1Ga(2)	2·834 (5)
Ga(3)–2Ga(1)	2·642 (4)	Ga(3)–1Rb	3·713 (5)
Ga(3)–2Ga(5)	2·765 (5)	Ga(3)–2Rb	3·749 (2)
Ga(4)–1Ga(4)	2·517 (7)	Ga(4)–1Rb	3·833 (5)
Ga(4)–1Ga(3)	2·566 (5)	Ga(4)–2Rb	3·842 (3)
Ga(4)–2Ga(5)	2·566 (4)		
Ga(5)–1Ga(4)	2·566 (4)	Ga(5)–1Ga(1)	2·828 (3)
Ga(5)–1Ga(2)	2·635 (4)	Ga(5)–1Rb	3·718 (4)
Ga(5)–1Ga(1)	2·639 (4)	Ga(5)–1Rb	3·748 (4)
Ga(5)–1Ga(3)	2·765 (5)	Ga(5)–1Rb	3·753 (5)
Ga(5)–1Ga(5)	2·767 (6)		
Rb–1Ga(3)	3·713 (5)	Rb–2Ga(5)	3·753 (5)
Rb–2Ga(5)	3·718 (4)	Rb–1Ga(4)	3·833 (5)
Rb–2Ga(1)	3·742 (4)	Rb–2Ga(4)	3·842 (3)
Rb–1Ga(2)	3·746 (6)	Rb–2Rb	4·134 (5)
Rb–2Ga(5)	3·748 (4)	Rb–Rb	4·137 (8)
Rb–2Ga(3)	3·749 (2)		
Ga(1)–Ga(1)–Ga(5)	58·6 (1)	Ga(3)–Ga(1)–Ga(5)	63·1 (1)
Ga(5)–Ga(1)–Ga(2)	58·5 (1)	Ga(5)–Ga(1)–Ga(1)	66·2 (1)
Ga(2)–Ga(1)–Ga(3)	66·3 (1)		
Ga(3)–Ga(2)–Ga(1)	58·6 (1)	Ga(5)–Ga(2)–Ga(5)	63·3 (1)
Ga(1)–Ga(2)–Ga(5)	66·3 (1)		
Ga(5)–Ga(3)–Ga(5)	60·0 (1)	Ga(1)–Ga(3)–Ga(2)	55·1 (1)
Ga(5)–Ga(3)–Ga(1)	58·4 (1)		
Ga(3)–Ga(4)–Ga(4)	120·1 (2)	Ga(5)–Ga(4)–Ga(4)	120·5 (1)
Ga(3)–Ga(4)–Ga(5)	96·7 (1)	Ga(5)–Ga(4)–Ga(5)	96·7 (2)
Ga(1)–Ga(5)–Ga(1)	55·1 (1)	Ga(5)–Ga(5)–Ga(2)	58·3 (1)
Ga(1)–Ga(5)–Ga(3)	58·5 (1)	Ga(2)–Ga(5)–Ga(1)	55·2 (1)
Ga(3)–Ga(5)–Ga(5)	60·0 (1)		
Rb–Rb–Rb	106·0 (2)	Rb–Rb–Rb	105·9 (1)

Discussion. The final positional and thermal parameters are listed in Table 1,* bond distances and some angles are given in Table 2. Two views of the unit cell are shown in Fig. 1. The structure is characterized by a non-compact packing of interconnected icosahedra of gallium, each icosahedron being located near an inversion center. Each contains Ga atoms (1, 2, 3, 5); the crystal symmetry reproduces Ga(1) and Ga(5) four times through a mirror plane and inversion center while Ga(3) and Ga(2), lying in special position (x,0,z), are reproduced twice with respect to the inversion center. This icosahedron is fairly distorted from the regular one as indicated by Ga—Ga—Ga angles (Table 2); Ga—Ga distances within the polyhedron range from 2·535 to 2·834 Å. Furthermore, each polyhedron is linked to its homologues, produced by C centering, on a sheet-like lattice parallel to the plane (001) through 12

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP36161 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

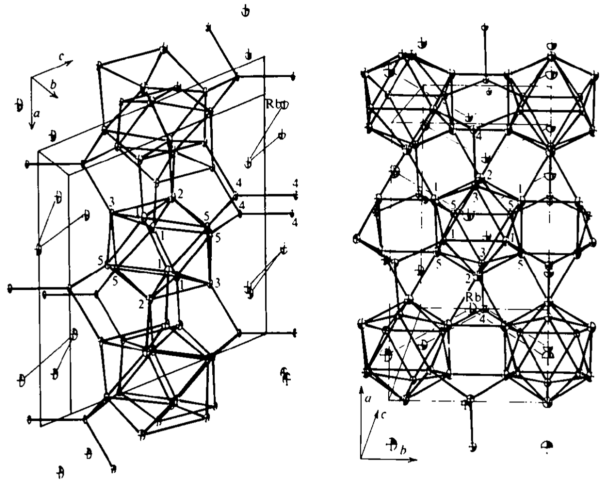

Fig. 1. Two different views of the unit cell of RbGa$_7$, with thermal ellipsoids shown at the 50% probability level.

direct Ga–Ga bonds occurring between Ga(1) and Ga(2); the linkage between adjacent sheets is ensured, along the z axis, by double bifurcated bonds involving Ga(4) as centers and occurring between Ga(3) and Ga(5). Ga(1) and Ga(2) have seven, Ga(3) and Ga(5) have six and Ga(4) has four coordinating Ga atoms at less than 3·5 Å. Ga(4) is coordinated to its four neighboring Ga atoms (3, 4 and 5) nearly tetrahedrally (120·1, 96·7, 120·5 and 96·7°).

Rb atoms occupy vacant channels parallel to the y axis and bordered by Ga atoms (3, 4 and 5). These alkaline atoms form zig-zag chains parallel to the y axis with mean Rb–Rb distance and angle of 4·135 Å and 106°; their contact distances with Ga atoms range from 3·713 (3) to 3·842 (3) Å.

In conclusion, this structure presents some analogies with that of K$_3$Ga$_{13}$ (Belin, 1980). Although in the latter, both the concentration of the alkaline-metal atoms and the symmetry of the crystal are higher, Ga atoms have the ability to coordinate to each other within icosahedra arranged around inversion centers. However, in K$_3$Ga$_{13}$ the structure is more complex since Ga atoms are also coordinated within 11 vertex polyhedra. In both structures, connections between such polyhedra are ensured through direct and bifurcated Ga–Ga bonds; the stacking of Ga atoms is not compact, leaving holes where the alkaline-metal atoms can reside.

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The Structure of Tetrakis(tricarbonyl-μ_3-hydroxo-rhenium)–Benzene (1:2)

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Abstract. [Re(CO)$_3$OH]$_4$.2C$_6$H$_6$, M_r = 1305·18, cubic, $Pn3m$, a = 11·343 (2) Å, V = 1454·42 Å^3, Z = 2, d_c = 2·96, d_o = 3·0 Mg m^{-3}, μ(Mo $K\alpha$) = 16·9 mm^{-1}. Final weighted R = 0·029 for 225 observed independent reflections. The structure consists of discrete tetramers, four Re and four O atoms occupy-

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