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Structure of the Intermetallic Compound $Na_{22}Ga_{39}$ (~36·07% Na)

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Abstract

$Na_{22}Ga_{39}$ is orthorhombic, space group *Pnma*, with $a = 15.585$ (4), $b = 14.948$ (6), $c = 21.632$ (6) Å, $Z = 4$, $V = 5039.53$ Å^3. Diffraction data with $0 < 2\theta < 50°$ (Mo $K\alpha$ radiation) were collected on a Nonius CAD-4 automatic diffractometer within the octant *hkl*. The structure was solved by direct methods and refined by full-matrix least squares to a final $R(F)$ of 3·9% for 1722 independent reflections with $I > 3\sigma(I)$. $Na_{22}Ga_{39}$ displays a complex structure with 244 atoms in the unit cell. Most of the Ga atoms are arranged in a non-compact framework of icosahedra linked to each other through direct bonding and to a few less-coordinated satellite atoms of Ga. The Ga packing leaves room for Na atoms to fit.

Introduction

The system sodium–gallium was investigated, by means of DTA, by Rinck & Feschotte (1961); the phase diagram displays the compounds $NaGa_4$ and Na_5Ga_8. These results were recently confirmed by Yatsenko (1977). In the meantime, Bruzzone (1969) had shown $NaGa_4$ to display the tetragonal $D1_3$ ($BaAl_4$) structure type. After our work on potassium and rubidium–gallium systems and the structure determination of three new compounds: K_3Ga_{13} (Belin, 1980), $RbGa_7$ (Belin, 1981) and $RbGa_3$ (Belin & Ling, 1981), we have reinvestigated the sodium–gallium system by means of X-ray diffraction and determined the crystal structure of a new compound $Na_{22}Ga_{39}$ whose stoichiometry is somewhat different from that of Na_5Ga_8.

Experimental

The metals used were Alusuisse gallium and Merck sodium; the latter was purified through several fractional recrystallizations. Referring to the Rinck & Feschotte (1961) phase diagram, a 62 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 900 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 ingots were broken into small pieces. As the compound is very oxidizable, the crystals were mounted under an argon atmosphere inside a Lindemann-glass capillary and checked through preliminary oscillation and Weissenberg photographs. They were shown to possess orthorhombic symmetry and systematic extinctions indicated the two possible space groups *Pnma* and $Pn2_1a$. A wedge-shaped crystal of dimensions $0.35 \times 0.20 \times 0.25$ mm which gave the best diffraction spots was selected and mounted on an Enraf–Nonius CAD-4 automatic diffractometer. Accurate lattice parameters were determined by least-squares refinement of the angular positions of 18 reflections collected and centered on the diffractometer. Integrated diffraction intensities were collected at room temperature (293 K) in the range $0 < 2\theta < 50°$, within one octant, using graphite-monochromated Mo $K\alpha$ radiation. (The profile analysis of a few low-angle reflections indicated that an ω–$\frac{1}{3}\theta$ 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 loss of 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 $\mu = 21.6$ mm^{-1}. The final data set consisted of 4929 independent reflections of which 1722 with $I > 3\sigma(I)$ were used in the refinement.

Structure solution and refinement

The structure was solved by direct methods. The Wilson plot gave a strong indication of centricity, so an attempt was made to solve the structure in the space group *Pnma* which proved later on to be appropriate. The output from the Fourier step of *MULTAN* (Main *et al.*, 1980) contained 23 peaks of high weight which

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were attributed to Ga atoms. After a few cycles of positional- and isotropic-thermal-parameter refinement, $R = \sum||F_o| - |F_c||/\sum |F_o| = 0{\cdot}20$, 15 Na-atom positions were deduced from a subsequent difference Fourier map. 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 $w^{-1} = \sigma^2_{\rm count}(F^2)/4(F)^2 + (0{\cdot}03F)^2$ and using the data set corrected for absorption. The final agreement factors were $R(F) = 0{\cdot}039$ and $R_w(F) = 0{\cdot}045$; the goodness-of-fit, defined as $[\sum w(|F_o| - |F_c|)^2/(N - M)]^{1/2}$ where N is the number of observations (1722) and M the number of parameters varied (298), was 0·71. The final difference Fourier map was flat except for residual peaks less than 1·0 e Å^{-3}. In the final cycle of refinement, the shifts in atom positional parameters were zero, while the shifts in temperature factors were zero for Ga and <0·04σ (e.s.d.) for Na atoms.

The crystallographic programs used were *MULTAN* (Main *et al.*, 1980), *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 and equivalent isotropic thermal parameters* ($\times 10^4$) *for atoms in* $Na_{22}Ga_{39}$

$B_{\rm eq} = 8\pi^2 U_{\rm eq}$ according to Willis & Pryor (1975). N = number of positions and Wyckoff notation.

	N	x	y	z	$B_{\rm eq}$ (Å^2)
Ga(1)	8(*d*)	8563 (2)	4211 (2)	438 (2)	1·15 (7)
Ga(2)		1846 (2)	6610 (2)	1660 (2)	1·10 (7)
Ga(3)		1896 (2)	5955 (2)	2817 (2)	1·11 (7)
Ga(4)		5694 (2)	5926 (2)	−73 (2)	1·34 (7)
Ga(5)		8366 (2)	5959 (2)	2934 (2)	1·22 (7)
Ga(6)		116 (2)	4245 (2)	1124 (1)	1·17 (6)
Ga(7)		961 (2)	5777 (2)	809 (2)	1·11 (7)
Ga(8)		8391 (2)	6600 (2)	1754 (2)	1·09 (7)
Ga(9)		7079 (2)	3444 (3)	859 (2)	1·43 (7)
Ga(10)		9225 (2)	5740 (2)	881 (1)	1·14 (7)
Ga(11)		7101 (2)	6500 (2)	−573 (2)	1·27 (7)
Ga(12)		1446 (2)	4264 (2)	288 (1)	1·11 (7)
Ga(13)		5694 (2)	4443 (2)	621 (2)	1·31 (7)
Ga(14)		1202 (2)	4400 (3)	3178 (2)	1·31 (7)
Ga(15)		293 (2)	3486 (3)	2276 (2)	1·46 (7)
Ga(16)		9976 (2)	3357 (2)	42 (2)	1·20 (6)
Ga(17)	4(*c*)	4241 (3)	7500	2378 (2)	1·08 (9)
Ga(18)		6915 (3)	7500	1452 (2)	1·04 (9)
Ga(19)		3332 (3)	7500	1333 (2)	1·27 (10)
Ga(20)		5955 (3)	7500	2445 (2)	1·08 (10)
Ga(21)		6236 (3)	7500	345 (2)	1·18 (10)
Ga(22)		1006 (3)	7500	7429 (2)	1·64 (10)
Ga(23)		6933 (3)	7500	−1522 (2)	1·68 (10)
Na(1)	8(*d*)	3306 (7)	4338 (9)	3055 (6)	2·0 (3)
Na(2)		4182 (7)	4237 (8)	1583 (5)	1·9 (3)
Na(3)		7187 (7)	5613 (9)	786 (15)	1·7 (2)
Na(4)		3112 (7)	5636 (9)	563 (6)	2·3 (3)
Na(5)		5147 (8)	6265 (8)	1301 (6)	2·5 (3)
Na(6)		107 (7)	5593 (9)	2225 (5)	2·1 (2)
Na(7)		2017 (7)	4398 (9)	1769 (5)	2·0 (3)
Na(8)	4(*c*)	4774 (12)	7500	8736 (10)	3·6 (4)
Na(9)		103 (15)	7500	1283 (10)	7·5 (8)
Na(10)		3280 (10)	7500	4592 (8)	1·6 (4)
Na(11)		7988 (11)	7500	7227 (8)	2·3 (4)
Na(12)		1948 (12)	7500	285 (8)	2·5 (5)
Na(13)		8790 (11)	7500	8863 (8)	1·9 (4)
Na(14)		6064 (12)	7500	6199 (8)	2·3 (4)
Na(15)		9254 (10)	7500	4914 (8)	1·9 (4)

Results and discussion

The final positional and thermal parameters with e.s.d.'s are listed in Table 1,* bond distances are given in Table 2. The structure described in Fig. 1 is relatively complex. The unit cell contains four formula units; of 23 independent Ga atoms, Ga(1 to 16) sit in general positions 8(*d*) and Ga(17 to 23) in the special positions 4(*c*), on mirror planes. Ga atoms (1, 6, 7, 10, 12, 16) are coordinated to each other around inversion centers [4(*a*) positions] on nearly regular icosahedra (*A*). On the other hand, Ga (2, 3, 5, 8, 17, 18, 19, 20) are arranged on the second set of icosahedra (*B*) with *m* symmetry. The nine remaining Ga atoms, whose coordination is lower, lie around those icosahedra and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36486 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

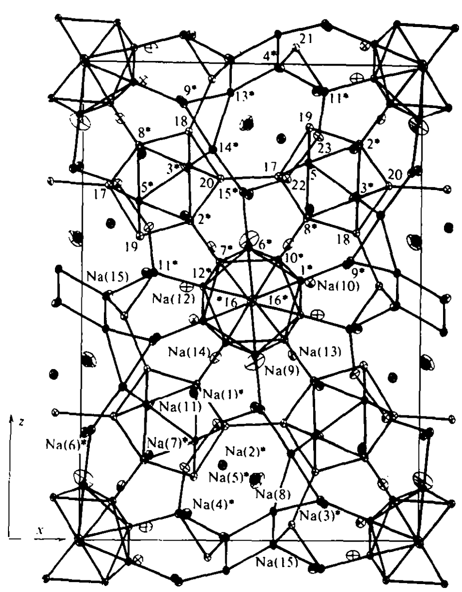

Fig. 1. Projection of the crystal packing down the y axis. Thermal ellipsoids are shown at the 50% probability level. Numbers 1 to 23 refer to Ga atoms; atoms marked with asterisks occur twice in the projection at x,y,z and $x, \frac{1}{2} - y, z$. Ga—Ga bond drawing was computed up to 4 Å, and no distance was found in the range 3 to 4 Å. For clarity, bonds involving Na atoms are not represented on the figure.

Table 2. *Interatomic distances less than* 4·0 Å *in* $Na_{22}Ga_{39}$

Neighbor	Distance
Ga(1)	
1 Ga(10)	2·684 (5)
1 Ga(16)	2·686 (5)
1 Ga(9)	2·737 (5)
1 Ga(12)	2·767 (5)
1 Ga(7)	2·796 (5)
1 Ga(6)	2·840 (4)
1 Na(3)	3·09 (1)
1 Na(14)	3·10 (1)
1 Na(12)	3·10 (1)
1 Na(1)	3·29 (1)
1 Na(4)	3·40 (1)
Ga(2)	
1 Ga(7)	2·617 (5)
1 Ga(2)	2·661 (7)
1 Ga(3)	2·687 (5)
1 Ga(5)	2·707 (4)
1 Ga(20)	2·728 (5)
1 Ga(19)	2·763 (5)
1 Na(9)	3·13 (2)
1 Na(12)	3·26 (2)
1 Na(7)	3·33 (1)
1 Na(6)	3·34 (1)
1 Na(4)	3·41 (1)
Ga(3)	
1 Ga(14)	2·679 (5)
1 Ga(2)	2·687 (5)
1 Ga(8)	2·688 (4)
1 Ga(20)	2·794 (4)
1 Ga(18)	2·799 (4)
1 Ga(5)	2·809 (4)
1 Na(3)	3·10 (1)
1 Na(6)	3·12 (1)
1 Na(7)	3·25 (1)
1 Na(1)	3·31 (1)
1 Na(5)	3·36 (1)
Ga(4)	
1 Ga(13)	2·527 (4)
1 Ga(11)	2·592 (4)
1 Ga(2)	2·658 (4)
1 Ga(13)	2·678 (5)
1 Na(3)	3·02 (1)
1 Na(5)	3·13 (1)
1 Na(4)	3·17 (1)
1 Na(15)	3·27 (1)
1 Na(2)	3·28 (1)
1 Na(8)	3·77 (2)
Ga(5)	
1 Ga(2)	2·707 (4)
1 Ga(8)	2·727 (5)
1 Ga(17)	2·761 (4)
1 Ga(19)	2·796 (5)
1 Ga(3)	2·809 (4)
1 Na(2)	3·05 (1)
1 Na(6)	3·16 (1)
1 Na(7)	3·21 (1)
1 Na(1)	3·23 (1)
1 Na(5)	3·26 (1)
1 Na(4)	3·31 (1)
Ga(6)	
1 Ga(10)	2·682 (5)
1 Ga(16)	2·699 (5)
1 Ga(7)	2·728 (5)
1 Ga(15)	2·751 (5)
1 Ga(12)	2·752 (4)
1 Ga(1)	2·840 (4)
1 Na(13)	3·12 (1)
1 Na(6)	3·12 (1)
1 Na(14)	3·20 (1)
1 Na(7)	3·28 (1)
1 Na(1)	3·34 (1)
Ga(7)	
1 Ga(2)	2·617 (5)
1 Ga(12)	2·636 (5)
1 Ga(16)	2·683 (5)
1 Ga(10)	2·711 (4)
1 Ga(6)	2·728 (5)
1 Ga(1)	2·796 (5)
1 Na(9)	3·08 (1)
1 Na(12)	3·21 (1)
1 Na(6)	3·35 (1)
1 Na(7)	3·36 (1)
1 Na(4)	3·40 (1)
Ga(8)	
1 Ga(10)	2·627 (5)
1 Ga(17)	2·662 (5)
1 Ga(3)	2·688 (4)
1 Ga(8)	2·692 (7)
1 Ga(5)	2·727 (5)
1 Ga(18)	2·744 (5)
1 Na(9)	3·16 (2)
1 Na(3)	3·17 (1)
1 Na(10)	3·21 (2)
1 Na(6)	3·23 (1)
1 Na(1)	3·41 (1)
Ga(9)	
1 Ga(13)	2·674 (5)
1 Ga(1)	2·737 (5)
1 Ga(9)	2·822 (8)
1 Ga(14)	2·873 (5)
1 Na(12)	3·23 (2)
1 Na(15)	3·24 (2)
1 Na(3)	3·25 (1)
1 Na(11)	3·28 (2)
1 Na(14)	3·30 (2)
1 Na(1)	3·31 (1)
1 Na(8)	3·33 (2)
1 Na(4)	3·38 (1)
Ga(10)	
1 Ga(8)	2·627 (5)
1 Ga(6)	2·682 (5)
1 Ga(1)	2·684 (5)
1 Ga(7)	2·711 (4)
1 Ga(16)	2·713 (5)
1 Ga(12)	2·735 (4)
1 Na(9)	3·09 (1)
1 Na(10)	3·18 (1)
1 Na(3)	3·19 (1)
1 Na(6)	3·22 (1)
1 Na(1)	3·43 (1)
Ga(11)	
1 Ga(23)	2·552 (5)
1 Ga(4)	2·592 (4)
1 Ga(12)	2·610 (4)
1 Ga(21)	2·827 (5)
1 Ga(11)	2·989 (7)
1 Na(2)	3·16 (1)
1 Na(10)	3·18 (1)
1 Na(4)	3·21 (1)
1 Na(7)	3·22 (1)
1 Na(3)	3·23 (1)
1 Na(6)	3·26 (2)
Ga(12)	
1 Ga(11)	2·610 (4)
1 Ga(7)	2·636 (5)
1 Ga(16)	2·715 (5)
1 Ga(10)	2·735 (4)
1 Ga(6)	2·752 (4)
1 Ga(1)	2·767 (5)
1 Na(10)	3·07 (1)
1 Na(3)	3·16 (1)
1 Na(13)	3·24 (1)
1 Na(7)	3·33 (1)
1 Na(4)	3·36 (1)
Ga(13)	
1 Ga(4)	2·527 (4)
1 Ga(9)	2·674 (5)
1 Ga(4)	2·678 (5)
1 Ga(14)	2·717 (5)
1 Na(3)	2·93 (1)
1 Na(2)	3·16 (1)
1 Na(4)	3·17 (1)
1 Na(5)	3·21 (1)
1 Na(15)	3·28 (1)
1 Na(8)	3·30 (1)
Ga(14)	
1 Ga(3)	2·679 (5)
1 Ga(13)	2·717 (5)
1 Ga(15)	2·770 (5)
1 Ga(9)	2·873 (5)
1 Na(2)	3·20 (1)
1 Na(6)	3·22 (1)
1 Na(11)	3·23 (1)
1 Na(3)	3·27 (1)
1 Na(1)	3·29 (1)
1 Na(7)	3·30 (1)
1 Na(5)	3·43 (1)
1 Na(8)	3·44 (1)
Ga(15)	
1 Ga(22)	2·584 (5)
1 Ga(6)	2·751 (5)
1 Ga(14)	2·770 (5)
1 Ga(15)	2·948 (7)
1 Na(6)	3·17 (1)
1 Na(13)	3·21 (2)
1 Na(7)	3·21 (1)
1 Na(2)	3·22 (1)
1 Na(11)	3·24 (2)
1 Na(1)	3·42 (1)
1 Na(14)	3·48 (2)
1 Na(8)	3·49 (2)
Ga(16)	
1 Ga(16)	2·562 (6)
1 Ga(7)	2·683 (5)
1 Ga(1)	2·686 (5)
1 Ga(6)	2·699 (5)
1 Ga(10)	2·713 (5)
1 Ga(12)	2·715 (5)
1 Na(9)	3·14 (2)
1 Na(10)	3·16 (1)
1 Na(14)	3·24 (2)
1 Na(13)	3·31 (2)
1 Na(12)	3·34 (2)
Ga(17)	
2 Ga(8)	2·662 (5)
1 Ga(19)	2·667 (7)
1 Ga(20)	2·676 (6)
2 Ga(5)	2·761 (4)
1 Na(9)	3·19 (2)
2 Na(6)	3·27 (1)
2 Na(5)	3·29 (1)
Ga(18)	
1 Ga(21)	2·617 (7)
1 Ga(20)	2·618 (7)
2 Ga(8)	2·744 (5)
2 Ga(3)	2·799 (4)
1 Na(10)	3·10 (2)
2 Na(3)	3·19 (1)
2 Na(5)	3·33 (1)
Ga(19)	
1 Ga(17)	2·667 (7)
2 Ga(2)	2·763 (5)
2 Ga(5)	2·796 (5)
1 Na(15)	3·06 (2)
1 Na(12)	3·13 (2)
2 Na(4)	3·26 (1)
2 Na(5)	3·38 (1)
Ga(20)	
1 Ga(18)	2·618 (7)
1 Ga(17)	2·676 (6)
2 Ga(2)	2·728 (5)
2 Ga(3)	2·794 (4)
1 Na(9)	3·05 (2)
2 Na(6)	3·22 (1)
2 Na(5)	3·34 (1)
Ga(21)	
1 Ga(18)	2·617 (7)
2 Ga(4)	2·658 (4)
2 Ga(11)	2·827 (5)
1 Na(15)	3·14 (2)
1 Na(10)	3·19 (2)
2 Na(5)	3·25 (1)
1 Na(3)	3·33 (1)
Ga(22)	
1 Ga(23)	2·435 (7)
2 Ga(15)	2·584 (5)
1 Na(14)	2·97 (2)
1 Na(8)	3·17 (2)
1 Na(11)	3·18 (2)
2 Na(2)	3·19 (1)
2 Na(1)	3·24 (1)
Ga(23)	
1 Ga(22)	2·435 (7)
2 Ga(11)	2·552 (5)
1 Na(13)	3·01 (2)
2 Na(2)	3·13 (1)
1 Na(11)	3·17 (2)
2 Na(7)	3·32 (1)
1 Na(8)	3·41 (2)
Na(1)	
1 Ga(5)	3·23 (1)
1 Ga(22)	3·24 (1)
1 Ga(14)	3·29 (1)
1 Ga(1)	3·29 (1)
1 Ga(3)	3·31 (1)
1 Ga(9)	3·31 (1)
1 Na(14)	3·33 (2)
1 Ga(6)	3·34 (1)
1 Ga(8)	3·41 (1)
1 Ga(15)	3·42 (1)
1 Ga(10)	3·43 (1)
1 Na(7)	3·33 (2)
1 Na(6)	3·33 (2)
1 Na(11)	3·46 (2)
1 Na(2)	3·47 (2)
1 Na(3)	3·60 (2)
Na(2)	
1 Ga(5)	3·05 (1)
1 Ga(23)	3·13 (1)
1 Na(8)	3·14 (2)
1 Ga(13)	3·16 (1)
1 Ga(11)	3·16 (1)
1 Ga(22)	3·19 (1)
1 Ga(14)	3·20 (1)
1 Ga(15)	3·22 (1)
1 Ga(4)	3·28 (1)
1 Na(7)	3·41 (1)
1 Na(5)	3·44 (2)
1 Na(4)	3·47 (2)
1 Na(1)	3·47 (2)
1 Na(6)	3·58 (2)
Na(3)	
1 Ga(13)	2·93 (1)
1 Ga(4)	3·02 (1)
1 Ga(1)	3·09 (1)
1 Ga(3)	3·10 (1)
1 Ga(12)	3·16 (1)
1 Ga(8)	3·17 (1)
1 Ga(10)	3·19 (1)
1 Ga(18)	3·19 (1)
1 Ga(11)	3·23 (1)
1 Ga(9)	3·25 (1)
1 Ga(14)	3·27 (1)
1 Ga(21)	3·33 (1)
1 Na(10)	3·40 (2)
1 Na(4)	3·50 (2)
1 Na(5)	3·51 (2)
1 Na(1)	3·60 (2)
Na(4)	
1 Ga(13)	3·17 (1)
1 Ga(4)	3·17 (1)
1 Ga(11)	3·21 (1)
1 Ga(19)	3·26 (1)
1 Ga(5)	3·31 (1)
1 Ga(12)	3·36 (1)
1 Na(12)	3·38 (2)
1 Ga(9)	3·38 (1)
1 Ga(1)	3·40 (1)
1 Ga(7)	3·40 (1)
1 Ga(2)	3·41 (1)
1 Na(15)	3·46 (2)
1 Na(2)	3·47 (2)
1 Na(3)	3·50 (2)
1 Na(7)	3·62 (2)
1 Na(5)	3·67 (2)
Na(5)	
1 Ga(4)	3·13 (1)
1 Ga(13)	3·21 (1)
1 Ga(21)	3·25 (1)
1 Ga(5)	3·26 (1)
1 Ga(17)	3·29 (1)
1 Ga(18)	3·33 (1)
1 Ga(20)	3·34 (1)
1 Na(6)	3·34 (2)
1 Ga(3)	3·36 (1)
1 Ga(19)	3·38 (1)
1 Ga(14)	3·43 (1)
1 Na(2)	3·44 (2)
1 Na(15)	3·50 (2)
1 Na(3)	3·51 (2)
1 Na(4)	3·67 (2)
1 Na(5)	3·69 (2)
Na(6)	
1 Ga(3)	3·12 (1)
1 Ga(6)	3·12 (1)
1 Ga(5)	3·16 (1)
1 Ga(15)	3·17 (1)
1 Ga(14)	3·22 (1)
1 Ga(20)	3·22 (1)
1 Ga(10)	3·22 (1)
1 Ga(8)	3·23 (1)
1 Ga(17)	3·27 (1)
1 Ga(2)	3·34 (1)
1 Na(5)	3·34 (2)
1 Ga(7)	3·35 (1)
1 Na(1)	3·43 (2)
1 Na(9)	3·50 (2)
1 Na(2)	3·58 (2)
1 Na(7)	3·61 (2)
Na(7)	
1 Ga(5)	3·21 (1)
1 Ga(15)	3·21 (1)
1 Ga(11)	3·22 (1)
1 Ga(3)	3·25 (1)
1 Ga(6)	3·28 (1)
1 Ga(4)	3·30 (1)
1 Ga(23)	3·32 (1)
1 Ga(2)	3·33 (1)
1 Ga(12)	3·33 (1)
1 Ga(7)	3·36 (1)
1 Na(13)	3·39 (2)
1 Na(2)	3·41 (1)
1 Na(1)	3·43 (2)
1 Na(11)	3·57 (2)
1 Na(6)	3·61 (2)
1 Na(4)	3·62 (2)
Na(8)	
1 Na(15)	3·03 (3)
2 Na(2)	3·14 (2)
1 Ga(22)	3·17 (2)
2 Ga(13)	3·30 (1)
2 Ga(9)	3·33 (2)
1 Ga(23)	3·41 (2)
2 Ga(14)	3·44 (1)
1 Na(11)	3·48 (3)
2 Ga(15)	3·49 (2)
2 Ga(4)	3·77 (2)
Na(9)	
1 Ga(20)	3·05 (2)
2 Ga(7)	3·08 (1)
2 Ga(10)	3·09 (1)
2 Ga(2)	3·13 (2)
2 Ga(16)	3·14 (2)
2 Ga(8)	3·16 (2)
1 Ga(17)	3·19 (2)
1 Na(10)	3·41 (3)
2 Na(6)	3·50 (2)
1 Na(12)	3·60 (3)
Na(10)	
2 Ga(12)	3·07 (1)
1 Ga(18)	3·10 (2)
2 Ga(16)	3·16 (1)
2 Ga(11)	3·18 (1)
2 Ga(10)	3·18 (1)
1 Ga(21)	3·19 (2)
2 Ga(8)	3·21 (2)
2 Na(3)	3·40 (2)
1 Na(9)	3·41 (3)
1 Na(13)	3·44 (2)
Na(11)	
1 Ga(23)	3·17 (2)
1 Ga(22)	3·18 (2)
2 Ga(14)	3·23 (1)
2 Ga(15)	3·24 (2)
2 Ga(9)	3·28 (2)
2 Na(1)	3·46 (2)
1 Na(8)	3·48 (3)
2 Na(7)	3·57 (2)
1 Na(14)	3·73 (2)
1 Na(13)	3·75 (2)
Na(12)	
2 Ga(1)	3·10 (1)
1 Ga(19)	3·13 (2)
2 Ga(7)	3·21 (1)
2 Ga(9)	3·23 (2)
2 Ga(2)	3·26 (2)
2 Ga(16)	3·34 (2)
2 Na(4)	3·38 (2)
1 Na(14)	3·49 (3)
1 Na(9)	3·60 (3)
1 Na(15)	3·62 (2)
Na(13)	
1 Ga(23)	3·01 (2)
2 Ga(6)	3·12 (1)
2 Ga(15)	3·21 (2)
2 Ga(12)	3·24 (1)
2 Ga(11)	3·26 (2)
2 Ga(16)	3·31 (2)
2 Na(7)	3·39 (2)
1 Na(10)	3·44 (2)
1 Na(14)	3·55 (2)
1 Na(11)	3·75 (2)
Na(14)	
1 Ga(22)	2·97 (2)
2 Ga(1)	3·09 (1)
2 Ga(6)	3·20 (1)
2 Ga(16)	3·24 (2)
2 Ga(9)	3·30 (2)
2 Na(1)	3·33 (2)
2 Ga(15)	3·48 (2)
1 Na(12)	3·49 (3)
1 Na(13)	3·55 (2)
1 Na(11)	3·73 (2)
Na(15)	
1 Na(1)	3·03 (3)
1 Ga(19)	3·06 (2)
1 Ga(21)	3·14 (2)
2 Ga(9)	3·24 (2)
2 Ga(4)	3·27 (1)
2 Ga(13)	3·28 (1)
2 Na(4)	3·46 (2)
2 Na(5)	3·50 (2)
1 Na(12)	3·62 (2)

maintain the overall cohesion. Icosahedron (A) is linked to two adjacent homologs through Ga(16)–Ga(16) bonding and to four type (B) icosahedra through Ga(10)–Ga(8) and Ga(7)–Ga(2) bonds; the linkage is supplemented by six connections with the satellites Ga(9, 11, 15). In a similar way, icosahedron (B) is linked to two adjacent (B) homologs, through two Ga(17)–Ga(20) bonds and to four type (A) icosahedra, through Ga(2)–Ga(7) and Ga(8)–Ga(10) bonds; three connections occur with satellites Ga(14, 14, 21). In fact, if in (A) all atoms are six-coordinated, in (B) three Ga atoms (19, 5, 5) are restricted to five-coordination.

The distribution of the icosahedra inside the unit cell nearly conforms to tetragonal symmetry; this is not surprising because of the pseudo-equality of the a and b lattice parameters. On the other hand, the survey of the mean values of the intensities, according to the different parity groups of reflections, clearly reveals some character of a body-centered cell, due to the distribution of the Ga atoms. In fact the center of the centrosymmetric icosahedron (A) is, of course, located on the special position 0,0,0, while the center of icosahedron (B) is close to the position $\frac{3}{4},\frac{3}{4},\frac{1}{4}$. If we assume the equivalence of icosahedra (A) and (B), then their centers are approximately located on special positions 8(c) of a tetragonal unit cell, space group $I4_1/amd$ (No. 141), as shown in Fig. 2(a). Furthermore, the ratio $c:a$ or b between lattice parameters is close to $\sqrt{2}$, so one could imagine an approximate distribution of the icosahedra on an F-centered cubic lattice, close to space group $Fd3c$ (No. 228b) and built on the pseudo-tetragonal unit cell as shown in Fig. 2(b), where they would occupy half the special positions 32(c). This high symmetry is also, of course, lowered by the distribution in the cell of the satellite Ga and Na atoms. Between the icosahedra, there is room for the Na atoms to fit; the shortest distances between Ga and Na atoms range from 2·93 to 3·23 Å. The coordinations around Ga and Na atoms respectively range from 10 to 12 and 14 to 16. Na(8) is coordinated to Na(15) and to Na(2) atoms within relatively short distances (3·03 and 3·14 Å) in an approximate trigonal-like arrangement; for remaining Na atoms, their shortest contact distances are somewhat larger (3·38 to 3·49 Å). Na(9) shows an abnormally high temperature factor which could indicate either a defect of structure or some disorder. Attempts to vary the occupancy of Na(9) gave no satisfactory results, even when this parameter and the isotropic thermal parameter were varied in alternate cycles of refinement. Convergence was only obtained using the normal occupancy and refining the thermal parameter. Although the coordination around Na(9) is approximately the same as for other Na atoms, its thermal ellipsoid seems to indicate more important thermal motion or some slight disorder which, unfortunately, could not be resolved.

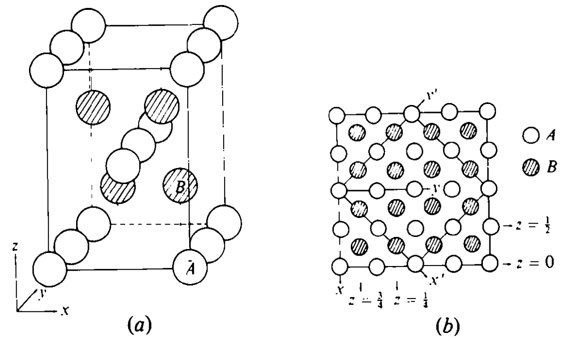

Fig. 2. (a) Perspective view of type (A) and (B) icosahedra distribution inside the pseudo-tetragonal unit cell. (b) Distribution of the icosahedra inside the F-centered cubic supercell built on four adjacent tetragonal units.

In the compound $NaGa_4$, whose structure was described by Bruzzone (1969), the Ga atoms are arranged, rather, on a regular three-dimensional netting and exhibit no trend to clustering, unlike $Na_{22}Ga_{39}$ and the earlier structural studies of K_3Ga_{13} (Belin, 1980), $RbGa_7$ (Belin, 1981) and $RbGa_3$ (Belin & Ling, 1981). Such gallium icosahedra are encountered in K_3Ga_{13}, associated with 11 vertex polyhedra; they are bound to each other through direct and bifurcated Ga–Ga bonds where K atoms occupy some vacant holes.

$RbGa_7$ is only characterized by icosahedra clustering and Rb-atom channel occupation while in $RbGa_3$, with tetragonal symmetry, the clustering is restricted to 8 vertex polyhedra.

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