

Intermetallic Phases of Gallium and Alkali Metals: Synthesis and Structure of the Nonstoichiometric Phase $K_3Li_9Ga_{28.83}$

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The nonstoichiometric phase $K_3Li_9Ga_{28.83}$ has been obtained by reduction of Li_3Ga_{14} by potassium. The crystal is orthorhombic, space group $Cmcm$ with $a = 25.794(6)$ Å, $b = 18.911(5)$ Å, and $c = 13.497(3)$ Å, $Z = 8$. Diffraction data with $4^\circ \leq 2\theta \leq 50^\circ$ (MoK α 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 4.7% for 1096 independent reflections with $I > 3\sigma(I)$. $K_3Li_9Ga_{28.83}$ displays a very intricate structure built on incomplete icosahedral clusters of gallium arranged on a three-dimensional anionic lattice. The structure is stabilized by alkaline cations filling holes and channels. The nonstoichiometry has been interpreted in terms of geometrical and electronic considerations according to Wade's electron-counting procedure for clusters.

Introduction

Crystal structures of new intermetallic phases of gallium with alkali metals have recently been determined: Li_3Ga_{14} (1, 2), $Na_{22}Ga_{39}$ (3) or Na_7Ga_{13} (4, 5), K_3Ga_{13} (6), KGa_3 (7), $RbGa_3$ (8), and $RbGa_7$ (9). As described by Schäfer and co-workers (10) a few years ago, such compounds can be considered as Zintl phases.

They are composed of nonisolated clusters of gallium arranged on a three-dimensional anionic lattice leaving holes or channels in which the alkali metal cations can sit.

Some of these phases are favorable to the insertion of lithium atoms by chemical or electrochemical methods. This work will describe the crystal structure determination of a nonstoichiometric phase in the ternary system Li-K-Ga.

Experimental

The compound has been obtained after reduction of the Li_3Ga_{14} phase by potassium. The metals used were Alusuisse gallium, lithium, and potassium from Merck Laboratories. Li_3Ga_{14} was obtained by heating a 95 mole % gallium mixture to 400°C in an evacuated pyrex tube, and allowing it to cool slowly (14°/hr) to 150°C. The product was immediately centrifuged and filtered through silica cotton within the same tube to separate the Li_3Ga_{14} crystals from the unreacted gallium.

Li_3Ga_{14} was reduced by potassium under an argon atmosphere in a weld-sealed tantalum tube heated at 600°C for several days, then cooled slowly to room temperature. The heterogeneous product was examined by the use of a microscope inside a glove box filled with argon. Needles of the well-

known K_3Ga_{13} phase were easily distinguished from small and relatively oxidizable coarse ingots. These were broken into small pieces which were mounted inside Lindemann-glass capillaries and checked by preliminary oscillation and Weissenberg photographs. The crystals were shown to possess orthorhombic symmetry and systematic extinctions suggested the following space groups: $Cmcm$, $Ama2$, or $Cmc2_1$. Since all phases in the Li–Ga and K–Ga systems are well established and their crystal structure determined, its lattice parameters, together with its symmetry, indicated that the material was probably a novel phase in the Li–K–Ga ternary system. A wedge-shaped crystal of dimensions $0.10 \times 0.12 \times 0.09$ 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 25 reflections collected and automatically centered on the diffractometer ($a = 25.794(6)$ Å, $b = 18.911(5)$ Å, and $c = 13.497(3)$ Å). Integrated diffraction intensities were collected at room temperature (22°C) in the range $4^\circ \leq 2\theta \leq 50^\circ$ within one octant, using graphite-monochromated $MoK\alpha$ radiation. The profile analysis of a few low-angle reflections indicated that an ω – θ scan method was the most appropriate for data collection. During data collection, the intensities of three standard reflections were checked after every 40 reflections and no loss in intensities 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 effect of absorption by Gaussian integration (11) with $\mu = 247 \text{ cm}^{-1}$. The final data set consisted of 3052 independent reflections of which 1096 with $I > 3\sigma(I)$ were used in the refinement.

Since, in such a compound, the lithium content is poorly determined by X-ray dif-

fraction, the lithium and potassium ratio was checked by flame spectrometry of a few single crystals (Li:K mole ratio 3.01:1).

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 $Cmcm$. The output from the Fourier step of Multan (12) contained 18 peaks of high weight which were attributed to gallium atoms. After a few cycles of positional and isotropic thermal parameter refinement, $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.17$. A subsequent difference map clearly indicated the potassium atoms but revealed three additional peaks of various heights which, when refined as gallium atoms, exhibited fairly large temperature factors.

Interatomic distance calculations involving these peaks implied that they were not potassium atoms but their electron density was far too high to attribute them to lithium atoms. They were finally refined as gallium atoms with partial site occupancies.

In the last stages of refinement, the positions of Li atoms could be located from a difference Fourier map in addition to a peak with an electron density approximately twice that corresponding to a lithium atom. This position was first refined as a lithium atom but its resulting temperature factor was strongly negative. Refinement of the peak as a gallium atom with a site occupancy which converged at 16.3% gave a more satisfactory result.¹

¹ On the suggestion of one of the referees, a second set of reflections was recorded using the condition $I > \sigma(I)$ instead of the previous $I > 3\sigma(I)$, which gave about 50% more data. This larger data set, comprising weak reflections, made no difference to the conclusions already drawn from the first set, in particular the impossibility of attributing the partially occupied gallium site (Ga(10)) to a lithium atom with full site occupancy.

Finally, all atomic positional parameters and anisotropic temperature factors for gallium and potassium (isotropic temperature factors for lithium) were refined by full-matrix least squares, minimizing the function $W(|F_o| - |F_c|)^2$ with $W^{-1} = \sigma_{\text{count}}^2(F)^2 + (0.05 F)^2$ by using the data set corrected for ab-

sorption. Corrections for the anomalous dispersion effects were included in the gallium scattering factors (13). The final agreement factors were $R(F) = 0.047$ and $RW(F) = 0.060$; the goodness of fit, defined as $[\sum W(|F_o| - |F_c|)^2 / (N - M)]^{1/2}$, where N is the number of observations (1096) and M the

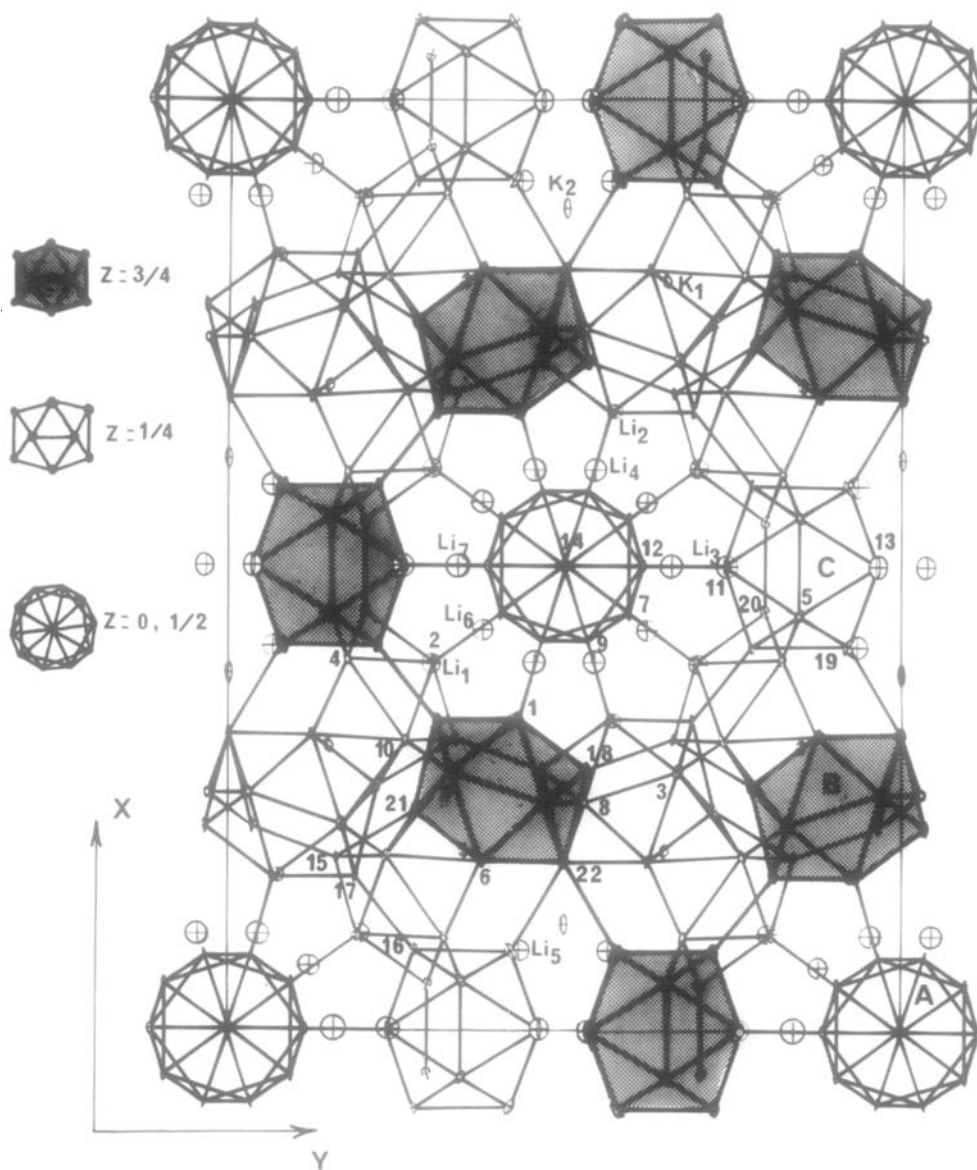


FIG. 1. Projection of the crystal packing of $K_3Li_9Ga_{28.83}$ down the z axis. Numbers 1 to 22 refer to Ga atoms; Ga-Ga bond drawing was computed up to 4 Å and no distance was found in the range 3 to 4 Å

TABLE I
FINAL POSITIONAL AND THERMAL PARAMETERS FOR ATOMS IN $K_3Li_9Ga_{28.83}$

Positions		Occupancies (%)	x	y	z	B_{eq} (\AA^2)
Ga(1)	16(h)	100	0.8358(1)	0.0670(2)	0.6538(3)	0.71(7)
Ga(2)	16(h)	100	0.1028(1)	0.1939(2)	0.3495(3)	0.78(7)
Ga(3)	16(h)	100	0.7789(2)	0.1691(2)	0.5807(3)	1.12(8)
Ga(4)	16(h)	100	0.0991(1)	0.3227(2)	0.4165(3)	0.75(7)
Ga(5)	16(h)	100	0.9476(2)	0.3474(2)	0.5858(3)	0.91(8)
Ga(6)	16(h)	100	0.1823(1)	0.3752(2)	0.3482(3)	0.77(7)
Ga(7)	16(h)	100	0.0495(1)	0.0946(2)	0.4143(3)	1.18(8)
Ga(8)	16(h)	100	0.7449(1)	0.0301(2)	0.5857(3)	0.65(6)
Ga(9)	16(h)	100	0.0794(1)	0.0340(2)	0.5858(3)	1.51(8)
Ga(10)	16(h)	16.3	0.3119(7)	0.2644(9)	0.5773(12)	0.7(3)
Ga(11)	8(f)	100	0	0.2364(2)	0.6536(4)	0.80(8)
Ga(12)	8(f)	100	0	0.1152(2)	0.5863(5)	1.32(8)
Ga(13)	8(f)	75.6	0	0.4644(2)	0.6481(3)	1.37(9)
Ga(14)	8(f)	23.1	0	-0.0021(9)	0.6619(12)	0.6(3)
Ga(15)	8(g)	100	0.1858(2)	0.1612(2)	0.250	0.65(7)
Ga(16)	8(g)	100	0.9139(2)	0.2773(2)	0.750	0.60(7)
Ga(17)	8(g)	100	0.8346(2)	0.1902(2)	0.750	0.79(8)
Ga(18)	8(g)	100	0.2194(2)	0.0349(3)	0.250	0.75(8)
Ga(19)	8(g)	100	0.9155(2)	0.4219(3)	0.750	1.54(9)
Ga(20)	8(g)	100	0.0482(2)	0.2973(3)	0.250	0.86(8)
Ga(21)	8(g)	100	0.2364(2)	0.2776(3)	0.250	0.78(7)
Ga(22)	8(g)	51.7	0.1807(4)	0.4998(5)	0.750	0.8(1)
K(1)	16(h)	100	0.1935(3)	0.3510(4)	0.6092(6)	1.2(1)
K(2)	8(e)	100	0.6147(5)	0	0	1.7(2)
Li(1)	16(h)	100	0.396(2)	0.302(3)	0.434(4)	2(1)
Li(2)	16(h)	100	0.334(2)	0.426(3)	0.561(4)	1.3(9)
Li(3)	8(f)	100	0	0.240(5)	0.425(7)	3(2)
Li(4)	8(g)	100	0.397(4)	0.455(5)	0.750	3(2)
Li(5)	8(g)	100	0.085(4)	0.434(5)	0.250	3(2)
Li(6)	8(g)	100	0.432(4)	0.378(5)	0.250	3(2)
Li(7)	4(c)	100	0.500	0.341(3)	0.750	1.9(9)

number of parameters varied (203), was 1.21 ($R(F) = 0.068$, using the larger data set comprising weak reflections with no improvement in the standard deviations of the positional and temperature factors parameters). The final difference Fourier map was flat except for residual peaks less than $2.0e^{-A^{-3}}$ near gallium atoms which could not be in any case assigned to extra lithium atoms.

Seven independent lithium atoms have been found with full site occupancy, making a total of 68 atoms in the unit cell. The

chemical analysis indicates that in fact, at least 72 lithium atoms are present; however, the four extra lithiums cannot be found in special positions and they are presumed to partly fill positions which are statistically occupied by atoms Ga(13) and Ga(22) to nearly 75 and 50%.

Distances between these atoms and the nearest gallium atoms are in the order of 2.70 \AA and are not incompatible with other Ga-Li distances observed in the structure.

On the other hand, it appears impossible to avoid the statistical distribution of atoms

TABLE II
 INTERATOMIC DISTANCES LESS THAN 3.7 Å IN $K_3Li_9Ga_{28.83}$

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Ga(1)					
Ga(9)	2.453(5)			Ga(14)	2.39(1)
Ga(1)	2.596(8)			Ga(1)	2.453(5)
Ga(8)	2.612(5)			Ga(7)	2.551(5)
Ga(3)	2.619(5)			Ga(12)	2.560(4)
Ga(17)	2.668(5)			Ga(9)	2.649(9)
Ga(18)	2.723(6)			Ga(7)	2.695(6)
Li(2)	2.91(6)			Li(4)	2.74(6)
Li(2)	2.95(5)			Li(6)	2.78(6)
Li(4)	2.95(9)			Li(2)	3.05(5)
Li(6)	2.99(9)			Li(2)	3.09(6)
Li(1)	3.15(6)			Li(1)	3.18(6)
Ga(2)					
Ga(7)	2.487(5)			Ga(2)	2.54(2)
Ga(10)	2.54(2)			Ga(3)	2.62(2)
Ga(4)	2.599(4)			Ga(15)	2.72(2)
Ga(15)	2.603(6)			Ga(21)	2.76(2)
Ga(2)	2.687(8)			Ga(4)	2.83(2)
Ga(20)	2.758(5)			Ga(6)	2.83(2)
Li(1)	2.92(7)			Ga(3)	2.96(2)
Li(3)	2.97(5)			Li(1)	2.98(6)
Li(2)	3.04(5)			Li(2)	3.11(5)
Li(7)	3.05(2)			K(1)	3.33(2)
Li(4)	3.12(9)			K(1)	3.49(2)
Ga(3)					
Ga(10)	2.62(2)			Ga(12)	2.465(6)
Ga(1)	2.619(5)			Ga(11)	2.60(1)
Ga(21)	2.727(5)			2Ga(5)	2.560(5)
Ga(17)	2.729(5)			2Ga(16)	2.687(6)
Ga(8)	2.772(5)			2Li(1)	3.03(7)
Ga(6)	2.799(5)			2Li(6)	3.07(9)
Ga(10)	2.96(2)			Li(3)	3.08(11)
Li(2)	2.99(6)			Ga(12)	
Li(1)	3.07(6)			Ga(14)	2.44(2)
K(1)	3.401(9)			Ga(11)	2.465(6)
K(1)	3.534(8)			2Ga(9)	2.560(4)
Ga(4)					
Ga(6)	2.537(5)			2Ga(7)	2.678(7)
Ga(2)	2.599(5)			2Li(6)	2.82(6)
Ga(5)	2.625(5)			2Li(1)	3.13(6)
Ga(20)	2.646(5)			Li(3)	3.21(10)
Ga(10)	2.83(2)			Ga(13)	
Li(3)	3.00(5)			2Ga(19)	2.700(7)
Li(5)	3.10(7)			2Ga(15)	2.727(7)
Li(1)	3.11(6)			Ga(13)	2.75(2)
K(2)	3.560(3)			2Li(5)	3.23(9)
K(1)	3.603(8)			2K(2)	3.63(1)
Ga(5)					
Ga(4)	2.625(5)				
Ga(11)	2.660(5)				
Ga(5)	2.706(8)				
Ga(16)	2.725(5)				
Ga(13)	2.727(7)				
Ga(19)	2.753(5)				
Li(1)	3.14(6)				
Li(3)	3.26(9)				
K(2)	3.500(7)				
K(1)	3.652(8)				
Ga(6)					
Ga(4)	2.537(5)				
Ga(8)	2.571(5)				
Ga(6)	2.651(8)				
Ga(21)	2.668(6)				
Ga(22)	2.709(9)				
Ga(3)	2.800(5)				
Ga(10)	2.83(2)				
Li(5)	3.04(9)				
K(1)	3.564(9)				
K(2)	3.577(7)				
Ga(7)					
Ga(14)	2.40(1)				
Ga(2)	2.487(5)				
Ga(9)	2.551(5)				
Ga(7)	2.554(8)				
Ga(12)	2.678(7)				
Ga(9)	2.695(6)				
Li(4)	2.77(6)				
Li(7)	2.83(3)				
Li(3)	3.04(9)				
Li(2)	3.05(6)				
Li(1)	3.16(6)				
Ga(8)					
Ga(6)	2.571(5)				
Ga(8)	2.578(7)				
Ga(1)	2.612(5)				
Ga(18)	2.697(5)				
Ga(3)	2.772(5)				
Ga(22)	2.828(7)				
Li(2)	3.04(5)				
Li(2)	3.15(6)				
K(2)	3.60(1)				
K(1)	3.651(8)				

TABLE II—Continued

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Ga(14)		Ga(20)		Ga(16)	2.94(6)
Ga(14)	2.38(4)	Ga(20)	2.49(1)	Ga(17)	2.95(7)
2Ga(9)	2.39(1)	2Ga(4)	2.646(5)	Ga(10)	2.98(7)
2Ga(7)	2.40(2)	Li(5)	2.75(9)	Li(6)	3.03(9)
Ga(12)	2.44(2)	2Ga(2)	2.758(5)	Ga(11)	3.03(7)
2Li(4)	3.01(10)	2Li(3)	2.88(10)	Ga(3)	3.07(6)
2Li(6)	3.15(9)	Li(7)	2.90(7)	Ga(4)	3.11(6)
Li(7)	3.19(8)			Ga(12)	3.13(6)
Ga(15)		Ga(21)		Ga(5)	3.14(6)
Ga(18)	2.542(7)	Ga(15)	2.560(7)	Ga(1)	3.15(6)
Ga(21)	2.560(7)	Ga(17)	2.604(7)	Ga(7)	3.16(6)
2Ga(2)	2.603(6)	2Ga(6)	2.667(6)	Ga(9)	3.18(6)
2Ga(10)	2.72(2)	2Ga(3)	2.727(5)	Li(2)	3.31(8)
Li(4)	3.07(10)	Ga(10)	2.76(2)	Li(3)	3.39(9)
2Li(2)	3.07(6)	2K(1)	3.578(9)		
2K(1)	3.655(9)	Ga(22)		Li(2)	
Ga(16)		Ga(18)	2.66(1)	Ga(1)	2.91(6)
Ga(17)	2.627(7)	2Ga(6)	2.709(9)	Ga(1)	2.95(5)
2Ga(11)	2.687(6)	Li(5)	2.76(10)	Ga(3)	2.99(6)
2Ga(5)	2.725(5)	2Ga(8)	2.828(7)	Ga(18)	2.99(6)
Ga(19)	2.736(7)	Ga(19)	2.89(1)	Ga(2)	3.04(6)
2Li(1)	2.94(6)	2K(1)	2.41(1)	Ga(8)	3.04(6)
Li(6)	2.98(9)	K(1)		Ga(9)	3.05(6)
Ga(17)		Ga(10)	3.33(2)	Ga(7)	3.05(6)
Ga(21)	2.604(7)	Ga(3)	3.401(9)	Ga(15)	3.07(6)
Ga(16)	2.627(7)	Ga(22)	3.41(1)	Li(4)	3.08(9)
2Ga(1)	2.667(5)	Ga(10)	3.49(2)	Ga(9)	3.09(6)
2Ga(3)	2.729(5)	Ga(3)	3.534(8)	Ga(10)	3.11(5)
Li(6)	2.84(10)	Ga(6)	3.564(9)	Ga(8)	3.15(6)
2Li(1)	2.95(7)	Ga(21)	3.578(9)	Li(2)	3.25(11)
2K(1)	3.659(8)	Ga(4)	3.602(8)	Li(1)	3.31(8)
Ga(18)		Ga(16)	3.637(9)	Li(3)	
Ga(15)	2.542(7)	Ga(19)	3.647(9)	Li(7)	2.82(11)
Ga(22)	2.66(1)	Ga(18)	3.650(9)	2Ga(20)	2.88(10)
2Ga(8)	2.697(5)	Ga(8)	3.651(8)	2Ga(4)	2.97(5)
2Ga(1)	2.723(6)	Ga(5)	3.652(8)	2Ga(7)	3.04(9)
2Li(2)	2.99(6)	Ga(15)	3.656(9)	Ga(11)	3.08(11)
Li(4)	3.02(10)	Ga(17)	3.659(8)	Ga(12)	3.21(10)
2K(1)	2.650(9)	K(2)		2Ga(5)	3.26(9)
Ga(19)		2Ga(5)	3.500(7)	2Li(1)	3.39(9)
2Ga(13)	2.700(7)	2Ga(4)	3.560(3)	Li(4)	
Li(5)	2.73(9)	2Ga(6)	3.578(7)	2Ga(9)	2.74(6)
Ga(16)	2.736(7)	2Ga(8)	3.598(11)	2Ga(7)	2.77(6)
2Ga(5)	2.753(5)	2Ga(13)	3.634(11)	2Ga(1)	2.95(9)
Ga(22)	2.89(1)	2Li(5)	3.68(4)	2Ga(14)	3.01(10)
2K(1)	3.648(9)	Li(1)		Ga(18)	3.02(10)
		Ga(2)	2.92(7)	Ga(15)	3.07(10)
				2Li(2)	3.08(9)
				2Ga(2)	3.12(9)

TABLE II—Continued

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Li(6)	3.28(14)	2K(2)	3.68(4)	2Ga(14)	3.15(9)
Li(7)	3.41(11)			Li(4)	3.27(14)
				Li(6)	3.49(20)
		Li(6)			
	Li(5)	2Ga(9)	2.78(6)	Li(7)	
Ga(19)	2.73(9)	2Ga(12)	2.82(6)	2Li(3)	2.82(12)
Ga(20)	2.75(10)	Ga(17)	2.84(10)	4Ga(7)	2.83(3)
Ga(22)	2.76(10)	Ga(16)	2.98(10)	2Ga(20)	2.90(7)
2Ga(6)	3.04(9)	2Ga(1)	2.99(9)	4Ga(2)	3.05(2)
2Ga(4)	3.10(7)	2Li(1)	3.03(9)	2Ga(14)	3.19(8)
2Ga(13)	3.23(9)	2Ga(11)	3.07(9)	2Li(4)	3.41(11)

Ga(10), Ga(13), Ga(14) and Ga(22) representing, respectively, nearly 3, 6, 2, and 4 atoms in the unit cell, since the other two possible noncentrosymmetric space groups have only general and special positions of multiplicity 8 and 4, which is incompatible with the above results.

The stoichiometry found for the compound $K_3Li_9Ga_{28.83}$ is very close to that expected from the reduction reaction:



The difference in gallium content is within the standard deviation of the site occupancy for galliums Ga(10), Ga(13), Ga(14), and Ga(22).

Results and Discussion

The final positional and thermal parameters with esd's are listed in Table I; bond distances are given in Table II. The structure described in Fig. 1 is relatively complex. The unit cell contains four formula units of 22 independent Ga atoms: Ga(1 to 10) sit in general positions 16(*h*), Ga(11 to 14) in 8(*f*), and Ga(15 to 22) in 8(*g*), on mirror planes. Atoms Ga(7, 9, 12, 14) are coordinated to each other around inversion centers (4(*a*) positions) on nearly regular icosahedra (A). On the other hand, Ga(1, 3, 6, 8, 17, 18, 21, and 22) are arranged on the

second set of icosahedra (B) centered on a 8(*g*) position and displaying *m* symmetry. The third set of icosahedra (C) is built on gallium(5, 11, 13, 16, 19); each icosahedron is centered around a 4(*c*) position and displays *mm* symmetry. The remaining gallium atoms (2, 4, 10, 15, 20) are arranged, as shown in Fig. 2, on a 11-vertex polyhedron which shares a triangular face with icosahedron (B). Figure 3 represents the stacking of the icosahedra inside the unit cell; icosahedron (A) is directly connected to the 8 neighboring icosahedra $2 \times (A)$, $4 \times (B)$, $2 \times (C)$; icosahedron (B) to the six neighbors $3 \times (A)$, $2 \times (B)$ and $1 \times (C)$; and icosahedron (C) to the six $2 \times (A)$, $4 \times (B)$ icosahedra. The coordination of icosahedra (A) and (B) is extended to 12 by connections to gallium atoms (2, 4, 10, 15) while the coordination of icosahedron (C) is restricted to 10 since two of its vertices, gallium(13), are not outwardly coordinated.

The nonstoichiometry of the compound arises from the fact that gallium atoms (10, 13, 14, and 22) are not fully occupying their site (their occupancy factors are given in Table I). Ga(10) partially caps the pentagonal faces (2, 4, 6, 21, 15) of a 9-vertex polyhedron (20, 2, 2, 4, 4, 15, 6, 6, 21) (Fig. 2); this polyhedron has approximately C_{3v} symmetry; thus its pentagonal face (20, 4, 6, 6, 4) is nearly equivalent to faces (2, 4, 6,

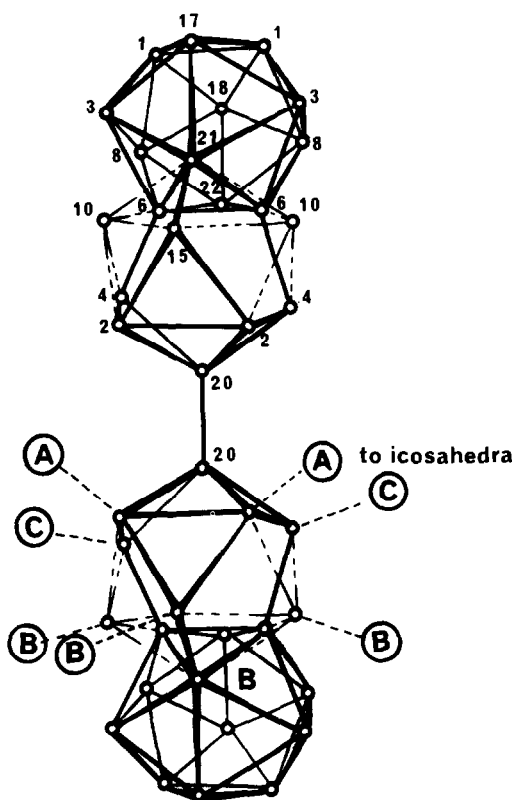


FIG. 2. Detail of the composite polyhedron (B) viewed along the y axis. Linkages to adjacent icosahedra are indicated.

21, 15), but no trace of a capping atom similar to Ga(10) has been found on the difference Fourier map. It becomes clear that this polyhedron corresponds to a partly dismantled icosahedron. Ga(14) partially occupies the icosahedron (A) vertices along z axis and this is confirmed by shorter than usual interatomic distances inside the icosahedron as well as shorter intericosahedral distances. Ga(13) is partially missing from its two sites on icosahedron (C) while Ga(22) is partially occupying one vertex of icosahedron (B). Except for the largely dismantled icosahedron (A), the interatomic distances inside the icosahedra are similar to those observed in the $\text{Li}_3\text{Ga}_{14}$, $\text{Na}_{22}\text{Ga}_{39}$, and K_3Ga_{13} (1–6) phases containing icosahedra: it is worth noting that intraico-

sahedral gallium distances are generally longer than the intericosahedral ones. The packing of the icosahedra leaves room where the alkali atoms can sit and stabilize the structure. Potassium atoms K(1) and K(2) have been found, respectively, in general positions 16(h) and 8(e), in the holes between icosahedra (B) and (C). The lithium atoms are located on a double crown around icosahedron (A) inside the channel parallel to the z axis and bordered by icosahedra (B) and (C). A few lithium atoms are, as discussed above, located on icosahedra (B) and (C), instead of the nonstoichiometric gallium atoms Ga(13) and Ga(22).

In this kind of compound, the electronic contribution of the alkali atoms to the electron-deficient lattice of gallium has been shown (14) to be fundamental. The ionic contribution of the alkali metals in the $\text{Li}_3\text{Ga}_{14}$, $\text{Na}_{22}\text{Ga}_{39}$, K_3Ga_{13} , RbGa_3 , and RbGa_7 phases has been established in a recent work (14) and experimentally verified for $\text{Li}_3\text{Ga}_{14}$ and the present compound by Li^7 NMR measurements. The Wade (15) electron-counting procedure proved successful in interpreting the structures of the above intermetallic phases of gallium containing Ga clusters.

The interpretation of the structure of $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ according to Wade's procedure appears more difficult due to the nonstoichiometry of the compound. The hypothetical $\text{K}_6\text{Li}_{17}\text{Ga}_{64}$ stoichiometric phase would contain full icosahedra of types (A), (B), and (C) and partial 11-vertex polyhedra fused to icosahedra (B) (Fig. 2); capping of the pentagonal face (20, 4, 6, 6, 4) of these polyhedra would give, by association to (B), the 21-vertex polyhedra (consisting of two icosahedra sharing a triangular face) and lead to the formula $\text{K}_6\text{Li}_{17}\text{Ga}_{66}$. In a first approximation, the skeletal electron counting for the icosahedra can be carried out according to the procedure used for borane anions. In fact, in the structure, the gallium

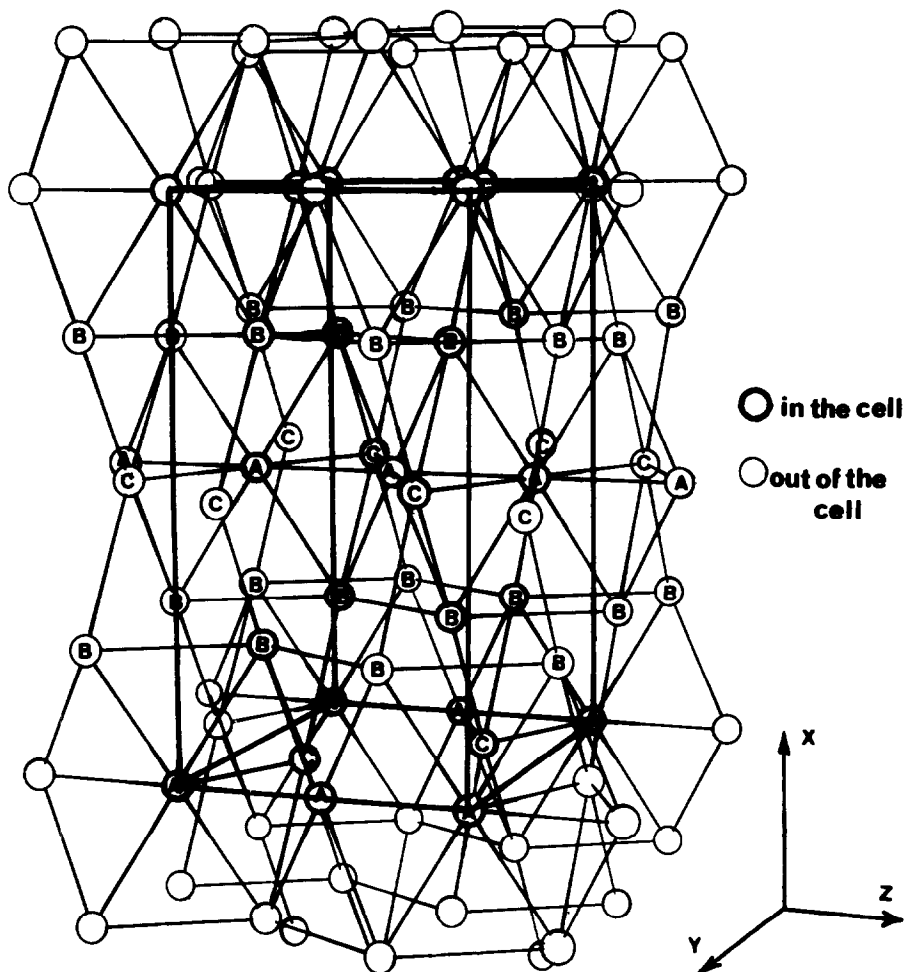


FIG. 3. Schematic representation of the packing of icosahedra inside the unit cell of $K_3Li_9Ga_{28.83}$.

icosahedra are, as shown above, partially dismantled into some "nido," "arachno," or even "hypho" polyhedra; however, we could consider that the stabilization of such polyhedra should need at least as many skeletal bonding electrons as are required for full icosahedra and this is particularly clear for partial icosahedron (A) where interatomic distances inside the polyhedron are considerably shortened by its higher electron concentration.

One can consider that a gallium icosahedron is stabilized with 26 skeletal bonding electrons. A skeletal bonding charge of 42

electrons may be estimated for the composite fused polyhedron (B).

On the other hand, bonding electrons are required for intericosahedral direct bonds; these are short compared to intraicosahedral ones and thus must be rather considered as two-center, two-electron bonds. Ga atoms except Ga(13) in icosahedra (C), are involved in such bonds, thus their electronic contribution to the bonding would be $12 \times 4 = 48e^-$ for icosahedra (A), $20 \times 8 = 160e^-$ for composite polyhedron (B), and $10 \times 4 = 40e^-$ for icosahedra (C); moreover, $2 \times 8 = 16e^-$ must be taken in account for the

Ga(13) outer lone pairs. The framework of gallium would be stabilized with 808 bonding electrons: 544 skeletal bonding electrons on polyhedra and 264 electrons on external bonds and lone pairs.

In the hypothetical stoichiometric compound $K_6Li_{17}Ga_{66}$, 884 valence electrons would be provided by lithium and gallium atoms; this is many more than are required for the stabilization of the structure and makes improbable the existence of such a stoichiometry.

In the actual nonstoichiometric phase $K_6Li_{18}Ga_{57.66}$, we will consider that the gallium framework is still stabilized with 808 bonding electrons and this better agrees with the 788 valence electrons furnished by all atoms. This means that the stoichiometric phase would be much too concentrated in alkaline elements for the whole content of gallium; from a geometrical point of view, the structure of the nonstoichiometric phase is stabilized by almost the same content of alkaline atoms, with their cations filling all the cavities between icosahedra; in compensation, the electronic balance has been adjusted by the removal of some icosahedra vertices leading to the formation of "opened" polyhedra.

On the other hand, the presence of two kinds of alkaline cations of different size to fit the cavities helps a little more to the stabilization of the structure.

In conclusion, the interpretation of this difficult structure according to Wade's rules does not work perfectly as, for example, in the case of K_3Ga_{13} (6) but this, combined with steric considerations, represents a good approach to the comprehension of this new nonstoichiometric Zintl phase

where the alkali metals give their valence electrons to the gallium atoms to build a three-dimensional anionic lattice containing interconnected clusters of gallium.

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