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NOTE

The Unexpected Lithium-Deficient Phase of Li_3Ga_7: Synthesis and X-Ray Crystal Structure of Li_3Ga_{14}

The first phase diagram of the system lithium–gallium was established by Thümmel and Klemm (*1*). These authors have reported the compounds $LiGa_2$, Li_3Ga_2, and LiGa, of which the crystal structures have been determined by Zintl and Brauer (*2*) and Müller and Stöhr (*3*). Recently, the hitherto unknown phase Li_5Ga_4 was found and its crystal structure was described by Stöhr and Schäfer (*4*). In the meantime the phase diagram had been revised by Yatsenko (*5*), who reported the two gallium-richer phases $LiGa_2$ and $LiGa_3$. The purpose of our work has been to verify the existence of such phases and eventually determine their crystal structure.

A 95 mole% gallium mixture was heated to 400°C in an evacuated Pyrex tube, then allowed to cool slowly (14°/hr) to 150°C. The product was immediately centrifuged and filtered through clean silica cotton within the same tube to separate the crystals from the unreacted gallium. The elemental analysis of single crystals is consistent with the stoichiometry $LiGa_{4.666}$ (Li_3Ga_{14}). The crystal is rhombohedral with a strong tendency to twin around [001] when too rapidly grown.

The space group is $R\bar{3}m$ with $a = b = 8.441(2)$, $c = 16.793(3)$ Å, $\gamma = 120°$ (hexagonal axes), $Z = 3$, and $Dm = 4.79$ g cm^{-1}. Intensity data were collected at room temperature by the $\omega - \frac{4}{3}\theta$ scan technique on a Nonius CAD 4 diffractometer in the range $4 \leq 2\theta \leq 60°$ using graphite-monochromated Mo$K\alpha$ radiation. Three hundred and twenty-five unique reflections were obtained with $I > 3\sigma(I)$. The data were corrected for background and Lorentz polarization effects and for the effect of absorption by Gaussian integration with a linear absorption coefficient $\mu = 282$ cm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares to a final R of 8.2% with anisotropic thermal parameters for gallium and both isotropic temperature factor and half-occupancy for lithium according to the precise chemical analysis.

The structure is shown in Fig. 1 and is characterized by a noncompact stacking of interconnected icosahedra of gallium. Each icosahedron conforms to the m point symmetry with Ga–Ga distances ranging from 2.613(4) to 2.733(3) Å and each is linked to six adjacent homologs through direct Ga(2)–Ga(2) bonds (2.492 Å). The third gallium atom achieves the linkage between icosahedra while leaving room for the lithium atom. The unit cell contains three icosahedra and eighteen equivalent cavities for nine disordered lithium atoms. If the structure were not lithium deficient, the formula would be Li_3Ga_7, which is close to $LiGa_2$, one of the new phases indicated by Yatsenko in his diagram (*5*).

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TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$) FOR ATOMS IN Li_3Ga_{14}

	N^a	x	y	z	U_{11}	$U_{22}{}^b$	U_{33}	U_{12}	U_{13}	U_{23}	$B_{eq}{}^c$ (Å^2)
Ga(1)	18(h)	1608(3)	−1608	−1354(2)	42(21)	42	231(14)	32(10)	7(11)	7	0.79
Ga(2)	18(h)	5611(3)	−5611	9485(1)	40(20)	40	186(16)	25(10)	11(11)	11	0.69
Ga(3)	6(c)	0	0	9224(3)	72(19)	72	219(22)	72	0	0	1.24
Li	18(h)	8229(86)	−8229	580(34)							2.3(8)

[a] N = Number of positions and Wyckoff notation.

[b] The thermal parameter expression is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[c] Equivalent temperature factor according to Willis and Pryor (*12*).

The compound Li_3Ga_{14} found in this work probably corresponds to Yatsenko's gallium-richest phase $LiGa_3$. In addition to chemical analysis, we performed differential thermal analysis using clean single crystals. The two peritectic transformations observed at 288.4 and 356.3°C with particularly large thermal effect for the lower transformation are consistent with the existence of two gallium-rich phases in this range of concentration and confirm that Li_3Ga_{14} is the gallium-richer phase. We believe the formula $LiGa_3$ given by Yatsenko to be inaccurate since it is not deduced by analysis of the Tammann thermal effect diagram. An example of such stoichiometric error is found in the Rb–Ga system, where the author indicates the existence of the compounds $RbGa_2$ and $RbGa_5$ which we demonstrated crystallographically to be, in fact, $RbGa_8$ (*6*) and $RbGa_7$ (*7*) (Table I).

In the Li–Ga system, Li_3Ga_{14} is the first compound with gallium atoms coordinated within icosahedra in a noncompact netting. Similar structures with trend to clustering for gallium have been encountered in compounds with the other alkali metals. $Na_{22}Ga_{39}$ (*8*) and $RbGa_7$ (*7*) contain icosahedra, K_3Ga_{13} (*9*) contains both icosahedra and 11 vertex polyhedra, while KGa_3 or $RbGa_3$ (*6*) are characterized by dodecahedra (Table II).

These structures where the alkali metals occupy vacant holes or channels may be considered as host structures similar to those observed with sodium–boron com-

TABLE II

INTERATOMIC DISTANCES LESS THAN 4.0 Å IN Li_3Ga_{14}

Ga(1)		Ga(2)		Ga(3)		Li	
Neighbor	Distance	Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
1 Ga(3)	2.543(3)	1 Ga(2)	2.492(4)	3 Ga(1)	2.543(3)	1 Ga(3)	2.61(6)
2 Ga(2)	2.613(3)	2 Ga(1)	2.613(3)	1 Ga(3)	2.607(9)	2 Ga(2)	2.73(4)
1 Ga(2)	2.645(3)	1 Ga(1)	2.645(3)	3 Li	2.61 (6)	2 Ga(1)	2.80(5)
2 Ga(1)	2.733(3)	2 Ga(2)	2.673(4)	3 Li	3.45 (6)	2 Ga(2)	2.95(4)
2 Li	2.80 (5)	2 Li	2.73 (4)			2 Li	3.24(6)
1 Li	3.26 (5)	2 Li	2.95 (4)			1 Ga(1)	3.26(5)
2 Li	3.30 (5)					2 Ga(1)	3.30(5)
						1 Ga(3)	3.45(6)

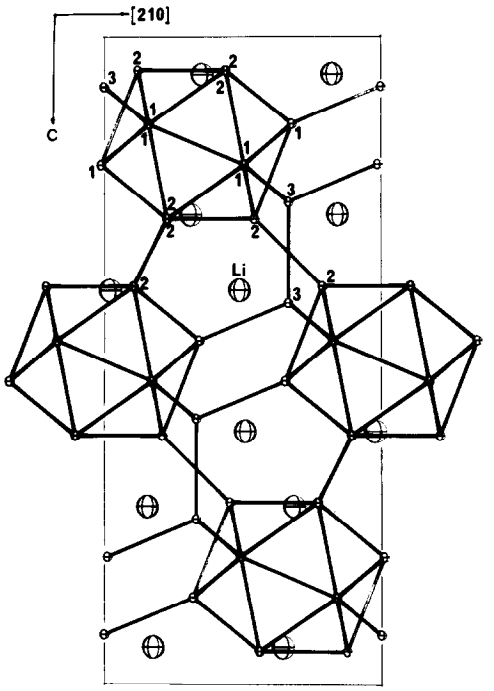

FIG. 1. Projection of crystal packing down the y axis. Locations of atoms: Ga(1), $x = 0.1608$, $y = -x$, $z = 0.1354$; Ga(2), $x = 0.5611$, $y = -x$, $z = 0.9483$; Ga(3), $x = y = 0$, $z = 0.9224$; Li, $x = 0.823$, $y = -x$, $z = 0.058$.

pounds (*10*) from which the sodium can be removed by smooth pyrolysis leading to nonstoichiometric phases.

On the other hand, K_3Ga_{13} (*9*) can accept extra lithium atoms which are thermally or electrochemically inserted (*11*).

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