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The crystal structure of $\text{Li}_{15}\text{Ge}_4$ * By Q. JOHNSON, GORDON S. SMITH and D. WOOD, *Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.*

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An investigation of the Li-Ge system in the region of Li_4Ge was undertaken to determine if a compound isomorphous with $\text{Li}_{22}\text{Pb}_5$ (Zalkin & Ramsey, 1958) exists.

'Reactor grade' lithium weighing 4.82 ± 0.02 g and believed to be 99.9% pure, together with 12.60 ± 0.02 g spectroscopically pure germanium, was placed in a clean tantalum crucible. The lithium was handled only in a dry box filled with argon and was clean and bright without any visible oxide. The lid of the crucible, which contained a thermocouple well, was welded in place in the dry box before the crucible was removed to a DTA furnace. The furnace could be rocked to stir the melt.

From a maximum temperature of 946 °C, cooling was accomplished without detection of thermal effects until 690 ± 2 °C. A subsequent strong heat effect was recorded at 667 ± 2 °C. Two weaker heat effects were observed at about 655 and 567 °C. The cooling was interrupted in the range 616–654 °C where it was held for 18 hours. Final cooling (from 654 °C) took place over a period of two hours. Owing to supercooling and the small amount

of material used, the nature of the heat effect could not be determined from the shape of the cooling curve.

X-ray powder diffraction studies with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) indicated the presence of two phases. Not only the sought for face-centered cubic phase with $a = 18.87$ Å, isomorphous with $\text{Li}_{22}\text{Pb}_5$, but also a body-centered cubic phase with $a = 10.72 \pm 0.05$ Å was observed. At this point we were not aware of the powder work by Gladyshevskii & Kripyakevich (1960) who had also observed this body-centered cubic phase with a cell constant of 10.783 ± 0.002 Å and had established this phase to be $\text{Li}_{15}\text{Ge}_4$; therefore single-crystal studies were undertaken in order to determine its composition and structure.

A single crystal of the latter compound was ground to a spherical shape in a dry box, sealed in a 0.2 mm capillary and examined by both Weissenberg and precession methods. In addition to the body centering extinctions, systematic extinctions were observed for hkl when $2h+l \neq 4n$. These extinctions are unique to space group $I43d$. Pseudo-extinctions were observed when $h, k = 2n$ and $h+k+l \neq 4n$. These conditions are met if germanium is located in the 16(c) position (*International Tables for X-ray Crystallography*, 1952). This suggests

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Table 1. *Observed and calculated structure factors for $\text{Li}_{15}\text{Ge}_4$*

<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	α	$\sigma(F_o)$	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	α	$\sigma(F_o)$
0	0	4	174	174	0.00	1.5	1	4	5	131	137	153.87	1.0
0	0	8	106	104	180.00	1.1	1	4	7	105	106	208.94	1.1
0	1	3	172	171	270.00	2.0	1	4	9	90	84	147.84	1.5
0	1	5	196	192	270.00	1.4	1	5	6	142	150	181.66	1.0
0	1	7	135	127	270.00	2.9	1	5	8	75	82	24.77	2.0
0	1	9	89	87	270.00	1.5	1	6	7	101	110	181.69	1.2
0	2	2	301	312	0.00	4.5	2	2	4	179	175	30.30	1.3
0	2	4	12	5	180.00	4.0	2	2	8	123	122	144.52	1.0
0	2	6	0	2	0.00	1.0	2	3	3	221	226	235.81	2.3
0	2	8	17	8	180.00	4.0	2	3	5	64	64	300.22	1.8
0	2	10	153	150	180.00	1.0	2	3	7	61	62	233.55	2.2
0	3	5	130	130	270.00	1.0	2	3	9	108	108	300.83	1.2
0	3	7	111	111	270.00	1.0	2	4	6	98	106	90.93	1.1
0	3	9	0	1	90.00	1.0	2	4	8	18	13	148.43	4.0
0	4	4	75	74	0.00	1.3	2	5	5	63	61	251.27	2.0
0	4	6	25	20	0.00	4.0	2	5	7	60	60	304.53	2.3
0	4	8	54	50	180.00	2.8	2	6	8	74	81	90.12	2.1
0	5	7	17	10	270.00	4.0	2	7	7	51	54	57.19	3.1
0	5	9	74	77	270.00	2.2	3	3	6	129	123	180.26	1.0
0	6	6	12	2	180.00	4.0	3	4	5	121	121	209.86	1.0
0	6	8	9	5	0.00	1.0	3	4	7	117	114	144.31	1.1
1	1	2	117	113	240.03	1.1	3	4	9	0	1	225.87	1.0
1	1	6	69	71	186.73	1.5	3	5	6	61	57	187.77	2.2
1	1	10	45	37	113.82	3.0	3	5	8	83	82	151.31	1.7
1	2	3	82	85	122.44	1.0	3	6	7	44	48	181.69	3.0
1	2	5	168	167	243.61	1.1	4	4	4	205	197	77.77	1.1
1	2	7	139	138	120.43	1.0	4	4	8	144	136	105.68	1.0
1	2	9	58	56	247.68	2.6	4	5	7	13	11	237.12	1.0
1	3	4	146	150	210.89	1.0	4	6	6	193	198	88.88	1.0
1	3	6	71	67	355.79	1.5	5	5	6	50	56	168.91	2.2
1	3	8	121	118	147.41	1.0							

isomorphism with the $\text{Cu}_{15}\text{Si}_4\text{-D8}_6$ structure (Morrall & Westgren, 1934). Based on this stoichiometry the crystallographic density is 2.13 g.cm^{-3} .

The intensities of 61 reflections were measured with $\text{Mo K}\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$) on a G.E. XRD 5 diffractometer equipped with a single-crystal orienter. A spherical absorption correction was applied to the data ($\mu R=0.75$). The structure was refined by the full-matrix least-squares program ACA No. 317 (Gantzel, Sparks & Trueblood, unpublished) with the use of a weighting scheme designed to take counting statistics into account. The observed and calculated structure factors along with $\sigma(F_o)$ are shown in Table 1 for which a final reliability index of 4.1% including missing reflections was obtained. Further least-squares refinements result in no change in atomic parameters. The atomic parameters are:

16 Ge (c)	$x = 0.2084 \pm 0.0002$	$B = 1.48 \pm 0.10 \text{ \AA}^2$
12 Li(1) (a)		$B = 0.9 \pm 1.2$
48 Li(2) (e)	$x = 0.129 \pm 0.004$	$B = 2.9 \pm 0.6$
	$y = 0.154 \pm 0.003$	
	$z = -0.040 \pm 0.004$	

The interatomic distances less than 3.1 \AA are shown in Table 2. These have been computed with $a=10.783 \text{ \AA}$.

The compounds which have so far been found to have the D8_6 structure are given in Table 3.

Table 2. *Interatomic distances for $\text{Li}_{15}\text{Ge}_4$*

Ge-3 Li(1)	$2.912 \pm 0.001 \text{ \AA}$
-3 Li(2)	2.60 ± 0.04
-3 Li(2)	2.80 ± 0.04
-3 Li(2)	2.87 ± 0.04
Li(1)-4 Ge	2.912 ± 0.001
-4 Li(2)	2.75 ± 0.04
-4 Li(2)	2.81 ± 0.04
Li(2)-Ge	2.60 ± 0.04
-Ge	2.80 ± 0.04
-Ge	2.87 ± 0.04
-Li(1)	2.75 ± 0.04
-Li(1)	2.81 ± 0.04
-Li(2)	2.75 ± 0.08
-2 Li(2)	2.78 ± 0.07
-2 Li(2)	3.07 ± 0.06

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Crystal data for the double salt, lithium ammonium hexafluorosilicate. By REUBEN RUDMAN, *Polytechnic Institute of Brooklyn, Brooklyn 1, N. Y., U.S.A.* and JOHN A. SKARULIS, *Department of Chemistry, St. Johns University, Jamaica 32, N. Y., U.S.A.*

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The hitherto unreported double salt, lithium ammonium hexafluorosilicate, $\text{LiNH}_4\text{SiF}_6$, was discovered during a systematic study of the dissociation pressures and solubilities of the $\text{Li}_2\text{SiF}_6\text{-(NH}_4)_2\text{SiF}_6\text{-H}_2\text{O}$ system at 25°C . Single crystals of $\text{LiNH}_4\text{SiF}_6$ were prepared by slow precipitation from aqueous solution by addition of ethanol. The results of these studies as well as the experimental details of the growth of single crystals of this compound are described elsewhere. (Skarulis, Darnowski, Kilroy & Milazzo, 1964.)

Table 3. *Compounds with the D8_6 structure*

Compound	Cell constant	r_a/r_b	
$\text{Cu}_{15}\text{Si}_4$	9.71 \AA	0.97	Morrall & Westgren (1934)
$\text{Na}_{15}\text{Pb}_4$	13.32	1.09	Zintl & Harder (1936)
$\text{Li}_{15}\text{Ge}_4$	10.783	1.14	Gladyshevskii & Kripyakevich (1960); this work

The radius ratios have been computed with values from the compilation of Teatum, Gschneidner & Waber (1959). In addition to the above compounds, Pearson (1958) suggests that the compound ' Cu_3As ' studied by Steenberg (1936-1938) is also of the D8_6 type. The radius ratio of 0.92 for this compound is similar to the above ratios.

Although the evidence appears to favor an isomorphous $\text{Li}_{15}\text{Sn}_4$ ($r_a/r_b=1.01$), we have not observed such a compound in preparations near this composition. $\text{Na}_{15}\text{Sn}_4$ ($r_a/r_b=1.24$) is not isomorphous (Zintl & Harder, 1936). This appears to establish an upper limit to the radius ratio for this structure type.

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Chemical analysis of the crystals confirmed the existence of $\text{LiNH}_4\text{SiF}_6$. The density was determined by the use of a pycnometer with benzene as the displacing liquid. Rotation and Weissenberg photographs were obtained with Ni-filtered Cu K radiation and precession photographs were obtained with Zr-filtered Mo K radiation. $\text{LiNH}_4\text{SiF}_6$ was found to be pseudo-orthorhombic, actually monoclinic. All of the crystals which were examined (by optical means as well as by X-ray diffraction) were twinned, a tendency of crystals pos-