Acta Cryst. (1969). B**25**, 2392

Crystal Structure of Li_2Sn_5*

By D. A. Hansen and L. J. Chang

Department of Mechanical Engineering, University of North Dakota, Grand Forks, North Dakota 58201, *U.S.A.*

(*Received* 6 *January* 1969)

Li_2Sn_5 (previously reported as '$LiSn_2$') crystallizes in the tetragonal system with $a_0 = 10{\cdot}274 \pm 0{\cdot}001$, $c_0 = 3{\cdot}125 \pm 0{\cdot}005$ Å and space group $P4/mbm$. The structure has been refined by least-squares techniques employing diffractometer data of 172 independent $hk0$ reflections ($R = 0{\cdot}081$). Li_2Sn_5 is isostructural with Mn_2Hg_5; the basic building unit of the structural motif is a pentagonal prism with two atoms at the extended poles.

Introduction

In an attempt to obtain crystals of LiSn, several crystalline fragments were isolated which exhibited unit cells much too small to account for the complex structure anticipated for LiSn (Hansen, 1966). Electron microprobe analysis of one of the fragments indicated its composition to be '$LiSn_2$', the structure of which was unknown (Foster, Crouthamel & Wood, 1966). The present work was undertaken in the hope that the coordination polyhedra found in this phase would yield some insight into the structure of LiSn. The structure determination indicates the composition to be Li_2Sn_5 rather than LiSn, as previously reported.

Experimental

An alloy containing crystals of Li_2Sn_5 was prepared from lithium supplied by the Lithium Corporation of America and from 99·999% tin supplied by the United Mineral and Chemical Corporation. The supplier's analysis of the lithium indicated a nominal purity $> 99{\cdot}8\%$ with sodium as the major impurity ($< 0{\cdot}05\%$). The bulk lithium was cut into small pieces and cleaned in a mixture of dry ice and absolute ethanol. All handling operations were conducted in an atmosphere of dry argon. The heterogeneous mixture of Li and Sn of nominal composition 95·2 wt.% Sn was sealed in a stainless steel crucible, homogenized at 600 °C for four hours and annealed four days at 350 °C. After removal from the crucible, the alloy was fragmented in a diamond mortar. Although the sample tended to deform plastically rather than shatter under the blow on the mortar, several fragments exhibiting bright metallic surfaces separated from the billet. Some of these were isolated and mounted in a manner previously described (Hansen, 1968). Fragments deliberately exposed to air were observed to decompose slowly.

Two different crystals were found to exhibit the Laue symmetry $4/mmm$. For convenience, a crystal having its fourfold axis parallel to the axis of rotation was used for the data collection. Precession photographs (hkl, $k = 0$ through 4, and hhl) did not contain any reflection of the kind $0kl$ with $k \neq 2n$. Hence, the probable space group is $P\bar{4}b2$, $P4bm$ or $P4/mbm$.

The lattice a_0 constant was determined from $hk0$ data measured on a Weissenberg photograph taken with nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54051$ Å for α_1). Twenty data points in the angular range $72° < 2\theta < 157°$, obtained at room temperature ($23° \pm 2$°C), were used for a linear least-squares fit (Williams, 1964) to the Nelson–Riley (1945) function to obtain $a_0 = 10{\cdot}274 \pm 0{\cdot}001$ Å. The length of the c axis, $c_0 = 3{\cdot}125 \pm 0{\cdot}005$ Å, was computed from $h0l$ precession data taken with palladium-filtered Ag $K\alpha$ radiation. The previously determined value of a_0 was used to calibrate the precession photograph.

Within experimental error, normal decline along the **c*** direction was observed in all of the precession data, indicating that the Sn atoms, at least, have the same z coordinates. Hence, only the $hk0$ intensities were measured. A Siemens diffractometer with a scintillation detector and zirconium-filtered Mo $K\alpha$ radiation were used. The crystal was an ungular cylinder approximately 0·43 mm long and 0·27 mm in diameter. Intensities were measured by the 2θ scan technique (scanning width 4° (2θ), scanning speed 2° (2θ) per minute). Background counts of one minute each were made at the beginning and end of each scan. Each intensity value used was the average of all symmetrically related reflections. For the purpose of absorption cor-

Table 1. *Atomic coordinates and temperature factors for* Li_2Sn_5

	Set	x	y	z	B
Sn(1)	8(i)	0·2954 (2)	0·4324 (2)	0	2·15 (4) Å^2
Sn(2)	2(d)	0	$\frac{1}{2}$	0	1·98 (6)
Li	4(h)	0·172 (3)	$x+\frac{1}{2}$	$\frac{1}{2}$	1·0 (7)

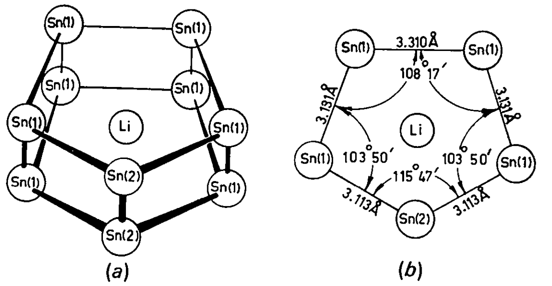
---

* This investigation was supported by the National Science Foundation under contract No. GK-2272.

rection, a right cylinder of equal volume (and hence with a radius of 0·094 mm) was assumed. The absorption function (Bond, 1959), plotted against the Bragg angle, was found to be approximated to within ±5% by the equation $A^*=11{\cdot}21-0{\cdot}09625\theta$, where A^* is the absorption correction factor and θ the Bragg angle. Lorentz and polarization corrections were applied in the usual manner. A total of 172 independent reflections were examined, of which 14 had zero intensity.

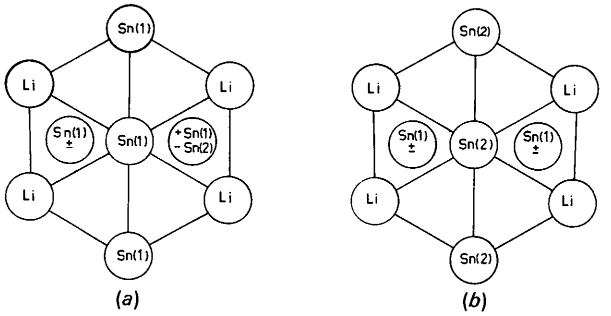
Determination and refinement of the structure

A $P(u,v)$ Patterson projection indicated that the tin atoms occupy special positions in the centric space group, *i.e.* Sn(1) in $8(i)(x,y,0;$ *etc.*) and Sn(2) in $2(d)(0,\frac{1}{2},0;\ \frac{1}{2},0,0)$ in the space group $P4/mbm$. The least-squares program of Busing, Martin & Levy (1962) was employed to confirm the initial trial structure of tin atoms only. An unweighted discrepancy index of 0·096 was obtained after refinement of the two variable coordinates and isotropic temperature factors. The lithium atoms were then assumed to occupy the centers of the polyhedra formed by the tin atoms. These sites correspond to the point set $4(h)(x,x+\frac{1}{2},\frac{1}{2};$ *etc.*) The three positional parameters and three isotropic temperature factors were refined until each shift was less than one-tenth of its standard deviation.



(a) (b)

Fig. 1. (*a*) The coordination polyhedron around the Li atoms in Li_2Sn_5. Two more Li atoms are at the extended poles (not shown). (*b*) The same coordination polyhedron projected onto the *xy* plane.



(a) (b)

Fig. 2. (*a*) The coordination polyhedron around the Sn (1) atoms in Li_2Sn_5. (*b*) The coordination polyhedron around the Sn(2) atoms in Li_2Sn_5. (Sn in ± sites represent Sn atoms above and below the plane of the hexagonal polygon).

A final difference density projection contained no significant extrema. Hence, a structure consisting of two formula units of Li_2Sn_5 (rather than '$LiSn_2$') per unit cell is indicated. The final unweighted discrepancy index is 0·081 for the structural parameters shown in Table 1. The observed and calculated structure factors are shown in Table 2, in which the reflections of zero intensity are indicated with asterisks.

Table 2. *Observed and calculated hk*0 *structure factors for* Li_2Sn_5

To be on an absolute scale (*i.e.* electrons per unit cell), each structure factor should be divided by 2·3128. Reflections of zero intensity are indicated by asterisks.

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
0	2	130	123	2	15	14	-16	5	7	203	-191	8	11	73	77
0	4	269	270	2	16	15	-12	5	8	95	104	8	12	78	79
0	6	40	-36	2	17	11	12	5	9	237	-219	8	13	10	19
0	8	217	-235	2	18	7	3	5	10	47	-50	8	14	20	-31
0	10	133	153	2	19	23	26	5	11	55	-61	8	15	11	0
0	12	*	0	2	20	39	33	5	12	27	-31	8	16	10	4
0	14	141	152	3	3	331	-336	5	13	38	33	8	17	17	-16
0	16	60	62	3	4	73	67	5	14	46	38	8	18	6	17
0	18	13	13	3	5	58	58	5	15	9	-0	9	9	125	-131
0	20	13	15	3	6	329	-326	5	16	26	-34	9	10	68	73
1	1	*	0	3	7	*	-4	5	17	19	16	9	11	24	-36
1	2	207	192	3	8	178	169	5	18	30	25	9	12	33	57
1	3	424	-415	3	9	25	28	5	19	30	-26	9	13	18	13
1	4	451	470	3	10	40	43	6	6	62	63	9	14	*	-8
1	5	76	71	3	11	42	-53	6	7	28	-9	9	15	17	-28
1	6	34	31	3	12	31	33	6	8	123	133	9	16	8	5
1	7	368	-383	3	13	102	-102	6	9	23	-20	9	17	9	13
1	8	11	7	3	14	60	64	6	10	41	-38	9	18	19	-27
1	9	43	-38	3	15	68	-61	6	11	155	-149	10	10	14	-21
1	10	160	-137	3	16	61	-59	6	12	111	117	10	11	24	39
1	11	68	-69	3	17	56	-46	6	13	19	-13	10	12	73	70
1	12	117	-107	3	18	*	7	6	14	*	5	10	13	40	-45
1	13	64	-72	3	19	16	-4	6	15	4	-6	10	14	48	45
1	14	9	-2	3	20	21	-19	6	16	31	31	10	15	14	13
1	15	38	34	4	4	110	116	6	17	19	22	10	16	38	39
1	16	*	5	4	5	235	-228	6	18	21	25	10	17	9	8
1	17	53	-52	4	6	27	29	6	19	23	27	11	11	45	-31
1	18	51	40	4	7	133	-123	7	7	196	193	11	12	31	-29
1	19	*	1	4	8	31	37	7	8	*	-2	11	13	22	-21
1	20	15	10	4	9	231	218	7	9	33	-40	11	14	34	-35
2	2	231	-234	4	10	31	28	7	10	25	-37	11	15	19	-16
2	3	359	366	4	11	4	-5	7	11	46	-44	11	16	37	33
2	4	303	297	4	12	89	74	7	12	37	-33	11	17	16	-11
2	5	97	95	4	13	125	110	7	13	41	-42	12	12	12	-4
2	6	349	334	4	14	61	57	7	14	*	-2	12	13	35	-32
2	7	39	-41	4	15	19	-25	7	15	104	-102	12	14	12	-3
2	8	184	181	4	16	47	41	7	16	*	3	12	15	7	9
2	9	37	47	4	17	35	-30	7	17	5	-4	12	16	7	-6
2	10	223	221	4	18	19	20	7	18	12	12	13	13	38	-40
2	11	168	-161	4	19	6	-6	7	19	24	-21	13	14	12	-6
2	12	41	-45	4	20	*	4	8	8	223	217	13	15	16	-9
2	13	22	26	5	5	356	-371	8	9	32	26	14	14	48	39
2	14	*	14	5	6	170	-159	8	10	9	-8	14	15	*	0

Additional least-squares calculations were carried out with lithium atoms placed according to the point sets $2(b)$ $(0,0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $4(h)$ $(x,x+\frac{1}{2},\frac{1}{2};$ *etc.* $x\simeq 0{\cdot}381)$. These sites describe the centers of the interstitial holes discussed in the following section. In all cases, including trial structures with either of the two interstices being occupied or both being occupied at the same time, the temperature factors for lithium in these sites diverged rapidly in the positive direction. This behavior was interpreted to indicate that, indeed, these interstitial sites are unoccupied, as indicated in the prototype structure of Mn_2Hg_5. In addition, refinement of trial structures in which the interstitial sites were allowed to be partially occupied yielded negligible occupancy (<5%).

The atomic form factors for lithium and tin were taken from the work of Cromer & Waber (1956). The weights were calculated according to the finite difference formula of Williams & Rundle (1964), *i.e.* $(F+\Delta F)^2=(I+\Delta I)A^*/(\mathrm{Lp})$, where ΔF is the standard deviation of the structure factor F, ΔI is the standard deviation of the integrated intensity I, A^* is the absorption correction factor and Lp is the Lorentz-polarization correction factor. ΔI is taken to be

$$(\Delta I)^2 = C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2 ,$$

where K_T is the time-dependent uncertainty in the total counts, C_T, and K_B is the time-dependent uncertainty in the background counts, C_B. In the course of measuring the integrated intensities, it was determined that $K_T \simeq K_B \simeq 0·08$. Unobserved reflections were arbitrarily assigned a weight of 10^{-4} in order to insure their negligible contribution to the refinements.

Discussion

The nature of the motif of the prototype structure, Mn_2Hg_5 (De Wett, 1961), has been well established. Hence, for Li_2Sn_5, it is sufficient to state that (1) the structure is built up of slightly irregular pentagonal prisms of tin in an array normal to the **c** direction; (2) contiguous prisms share a common corner, *i.e.* tin atom; (3) the center of each prism is occupied by a lithium atom, resulting in linear chains of contiguous lithium atoms lying parallel to the *c* axis; (4) the basic building unit of this structure is, therefore, a pentagonal prism with two atoms at the extended poles (see Fig. 1).

The coordination polyhedra around the tin atoms are shown in Fig. 2. Although these polyhedra are somewhat irregular and exhibit poor packing efficiency (coordination number (CN) 10 rather than the more common CN 12), the arrangement is notably similar to the coordination shells in the closest-packed hexagonal elemental structures.

The pentagonal prisms are nearly regular (see Fig. 1 & Table 3). If one assumes regularity and, further that the atoms pack as hard spheres, then the atom occupying the center of the pentagonal prism has a diameter ~3% smaller than the corner atoms. Hence one would expect this type of structure to be stable only in the case where the constituent occupying the center is slightly smaller than the constituent occupying the vertices of the prism. This conclusion is consistent with the observation of its occurence in Mn_2Hg_5 and Li_2Sn_5.

Each unit cell contains four pentagonal prisms. Although the packing efficiency within a (regular) prism is 73·6%, the packing efficiency of the unit cell is only 66%. This low value represents the effect of the inefficient packing of polyhedra having pseudo-fivefold axes. An examination of the manner in which these polyhedra are packed (see Fig. 3) reveals that the structure contains two types of large interstices. One of these is at an elevation of $c/2$ at the origin (point set $2(b)$: $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and is at the center of an almost regular cube. The center-to-vertex distance in this cube is 2·71 Å, *i.e.* a distance nearly the same as the shortest Li–Sn distance in Table 3. The second large interstice is at the center of an irregular trigonal prism and is also at an elevation of $c/2$. This site is in the point set $4(h)$ ($x,x+\frac{1}{2},\frac{1}{2}$; *etc.* $x=0·381$). The center-to-vertex distance in this polyhedron is ~2·40 Å. As indicated in the preceding section, there seems to be no scattering matter in either of the large interstices of Li_2Sn_5.

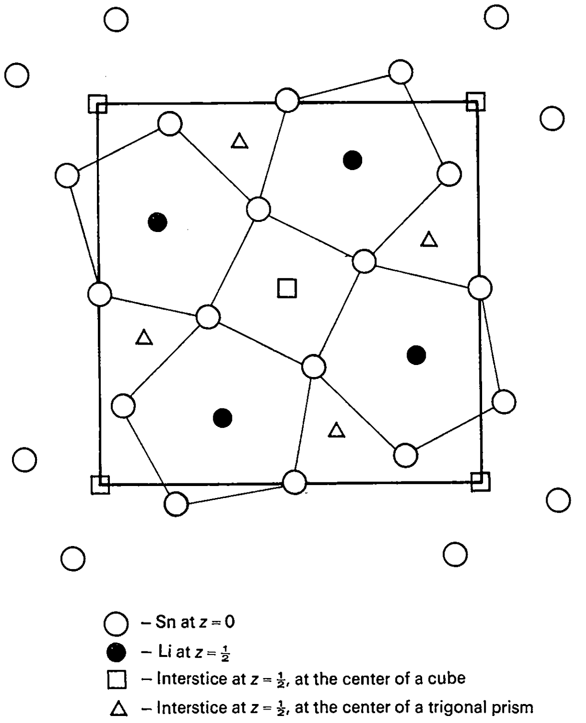


Fig. 3. Projection of the Li_2Sn_5 structure on the *xy* plane.

Table 3. *Interatomic distances in* Li_2Sn_5*

Neighbor	distance	Neighbor	distance	Neighbor	distance
Sn(1)		Sn(2)		Li	
2 Sn(1)	3·125 Å	4 Sn(1)	3·113 Å	4 Sn(1)	3·14 Å
2 Sn(1)	3·131	2 Sn(2)	3·125	4 Sn(1)	3·17
1 Sn(1)	3·310	4 Li	2·92	2 Sn(2)	2·92
1 Sn(2)	3·113			2 Li	3·125
2 Li	3·14				
2 Li	3·17				

*Distance	Standard deviation
Sn–Sn	0·005 Å
Li–Sn	0·04
Li–Li	0·005

The low packing efficiency exhibited by this structure, as well as its lack of directions of close-packing in the plane of the pentagonal polygons, indicates that strong, anisotropic local bonding is important in the stabilization of this structure. It is reasonable to anticipate the presence of similar bonding effects in LiSn, the structure of which is currently under investigation.

The authors acknowledge gratefully the assistance of Dr H. L. Haight in obtaining the microprobe analysis. The authors also thank Dr Sten Samson for his comments during the preparation of this manuscript.

References

BOND, W. L. (1959). *International Tables for X-ray Crystallography* Vol. II, p. 295. Birmingham: Kynoch Press.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). USAEC Report No. ORNL-TM-305.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst*, **18**, 104.

DE WETT, J. F. (1961). *Acta Cryst.* **14**, 733.

FOSTER, M. S., CROUTHAMEL, C. E. & WOOD, S. E. (1966). *J. Phys. Chem.* **70**, 3042.

HANSEN, D. A. (1966). Ph. D. Thesis, p. 56. Iowa State University.

HANSEN, D. A. (1968). *Norelco Reporter,* **15**, 30.

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. Lond.* **57**, 160.

WILLIAMS, D. E. (1964). USAEC Report No. IS-1052.

Acta Cryst. (1969). **B25**, 2395

The Crystal Structure of the 1:2 Potassium Iodide–Diacetamide Complex

BY J. P. ROUX[*] AND J. C. A. BOEYENS

Chemical Physics Group of the National Physical and Chemical Research Laboratories,
Council for Scientific and Industrial Research, Pretoria, South Africa

(*Received* 27 *January* 1969)

The crystal structure of the complex KI.2($C_4H_7NO_2$) has been determined by three-dimensional X-ray methods and the discrepancy R for all reflexions reduced to 10·8% by least-squares refinement. A layered arrangement corresponding to the NaBr. 2(diacetamide) structure was found. The two structures are compared and a mechanism for the complex formation is proposed.

Experimental

The complex was prepared as described by Gentile & Shankoff (1965) by dissolving the KI in molten diacetamide at 217 °C. After cooling the saturated solution, the white complex was washed with ether to remove the excess diacetamide and then recrystallized from absolute ethanol. The cylindrically shaped crystals were triclinic and were all found to be twinned. The crystals disintegrated on exposure to the atmosphere.

Great difficulty was experienced in cutting a cubically shaped crystal suitable for mounting on the Hilger and Watts automatic diffractometer from a large twinned crystal; the layer-like nature of the crystals very easily introduced shifts in the layers relative to one another during the cutting process. The very small crystal used was hermetically sealed into a Lindemann capillary and had dimensions of approximately 0·05 mm.

Cell dimensions were measured from oscillation, Weissenberg and precession photographs and refined on the automatic diffractometer. The unit cell that was chosen for convenience of data collection and structure refinement had the following dimensions: triclinic with

$$a = 9{\cdot}304 \pm 0{\cdot}005, \quad b = 7{\cdot}490 \pm 0{\cdot}005,$$
$$c = 10{\cdot}215 \pm 0{\cdot}005\ \text{Å}; \quad \alpha = 91{\cdot}05° \pm 0{\cdot}01°$$
$$\beta = 85{\cdot}03° \pm 0{\cdot}01°, \quad \gamma = 90{\cdot}89° \pm 0{\cdot}01°.$$

This, however, is not a reduced crystallographic cell. The reduced cell was related to the above unit cell by the matrix [100/0$\bar{1}\bar{1}$/010] and had dimensions of a = 9·304, b = 12·560, c = 7·490 Å; α = 125·55°, β = 90·89°, γ = 93·50°. The measured density was 1·79 g.cm^{-3}. The calculated density for two molecules per unit cell was 1·73 g.cm^{-3}. The structure was successfully solved by use of the space group $P\bar{1}$.

1330 intensities were measured on the automatic diffractometer by use of an ω–2θ scan with molybdenum radiation and Zr as β-filter.

Large discrepancies in background count on the two sides of the peaks were partially compensated by giving more weight to the lower background count. Since no attempt was made to refine the structure beyond the clarification of the chemical picture, this procedure was acceptable. No corrections for absorption were applied and the intensities were corrected for the Lorentz and polarization factors. A count of 10 after subtraction of the background was considered as the lowest reliable count after inspection of all the data. The 133 reflexions measured below this level were there-

---

[*] Present address: Department of Physics, University College, Western Cape, Bellville, South Africa.