Table 2 (cont.)

	Un-corrected	E.s.d.
O(2)–N	2·672	0·007
C(6)–H(1)	0·94	0·08
C(5)–H(2)	1·18	0·08
C(4)–H(3)	0·79	0·08
C(3)–H(4)	0·83	0·08
N——H(9)	0·97	0·07
O(1)–H(5)	0·74	0·08
C(8)–H(6)	1·11	0·08
C(8)–H(7)	1·09	0·09
C(8)–H(8)	1·07	0·08
O(2)–H(9)	2·02	0·07

Table 3. Equations of planes

(1) Benzene ring
$$0·2530x + 0·8410y + 0·4783z + 0·0419 = 0$$
(2) Carboxylic group
$$0·2651x + 0·8515y + 0·4526z - 0·0890 = 0$$
(3) Plane through C(2), N and C(8)
$$0·2330x + 0·8822y + 0·4092z - 0·2892 = 0$$

Angles between different planes

	(2)	(3)
(1)	1·3°	4·8°
(2)	–	3·4

Deviations of atoms from different planes (Å)

	Planes (1)	(2)	(3)
C(1)	0·016	−0·012	−0·072
C(2)	−0·016	—	0·000
C(3)	0·001	—	0·112
C(4)	0·015	—	—
C(5)	−0·014	—	—
C(6)	−0·001	—	—
C(7)	0·072	0·000	—
C(8)	−0·129	—	0·000
O(1)	0·085	0·000	—
O(2)	0·096	0·000	—
N	−0·025	—	0·000
H(1)	−0·03	—	—
H(2)	−0·06	—	—
H(3)	0·08	—	—
H(4)	0·04	—	—
H(5)	−0·12	−0·22	—
H(6)	0·61	—	0·79
H(7)	−1·20	—	−1·05
H(8)	−0·06	—	0·04
H(9)	−0·12	—	−0·15

Å (uncorrected; Brown & Marsh, 1963) and in p-nitro-aniline, 1·371±0·007 Å (uncorrected value, 1·353 Å; Trueblood, Goldish & Donohue, 1961); it is a little longer in the two crystallographically independent molecules of p-aminobenzoic acid, 1·378±0·006 and 1·382±0·006 Å (uncorrected; Lai & Marsh, 1967), and in the molecule of p-methyl-m-nitro-N-methylaniline, 1·377±0·006 Å (uncorrected; Chiaroni, 1971). In the structure of anthranilic acid (Brown, 1968), there are two crystallographically independent molecules; one of them is neutral while the other is a zwitterion. The C–N distance in the zwitterion is as expected much longer, 1·501±0·006 Å (uncorrected) but its value in the neutral molecule, 1·371±0·006 Å (uncorrected) is close to that in N-methylanthranilic acid. The nitrogen atom in N-methylanthranilic acid departs slightly but probably significantly from the plane containing the attached carbon and hydrogen atoms.

The hydrogen atom H(9) attached to the nitrogen atom is involved in an intramolecular NH···O hydrogen bond in which the N–O distance is 2·672 Å; the corresponding distances in other similar structures are: 2·706 Å in 2-amino-3-methylbenzoic acid, 2·685 Å in neutral anthranilic acid and 2·613 Å in the zwitterion, and 2·679 Å in 3·5 dichloroanthranilic acid (Arora & Pant, 1969; the value is not quoted in the paper). The O(2)–H(9) distance, 2·02±0·08 Å agrees with the corresponding distance in 2-amino-3-methylbenzoic acid, 2·05 Å.

The arrangement of molecules in the unit cell is shown in Fig. 2, in which the principal intermolecular distances (< 4·0 Å) are also given.

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The crystal structure of lillianite. By JUNKOU TAKAGI and YOSHIO TAKÉUCHI, Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo

The crystal structure of lillianite, $3PbS.Bi_2S_3$, has been reinvestigated by the symbolic addition method. The result has fully confirmed the structural scheme proposed by Otto & Strunz (Neues Jb. Miner. Abh. (1968). 108, 1). Refinement to an $R = 0·10$ has revealed the mode of distortions characteristic of the structure.

Of the crystalline phases in the system $PbS-Bi_2S_3$, the lead-rich members have structures consisting of fragments of the galena-type structure. The dimensions of the fragments and the way of joining the fragments to form a structure vary according to the Bi_2S_3 to PbS ratio. Takéuchi & Sadanaga (1969) have suggested that the variations would be explainable in terms of the difference in distortions of the fragments due to replacement by Bi of Pb atoms.

However, none of the structures of these phases so far reported have the required accuracy to substantiate their view. Therefore, a series of reinvestigations of the structures has been undertaken. The present paper is to report, as one of the results of this work, the crystal structure of lillianite.

A previous study of the structure of lillianite has been reported by Otto & Strunz (1968) using synthetic crystals. They proposed the structure based upon Weissenberg data and from considerations of the cell dimensions and the space group.

The specimens used are from Tsubakihara mine, Gifu Prefecture, Japan. Preliminary investigations carried out by Kato (1968) using precession and powder methods showed that the crystallographic data of the specimens agree with those of lillianite given by Kupčik, Franc & Makovický (1969), and with those of the synthetic material $Pb_3Bi_2S_6$ (Klyakhin & Dmitrieva, 1968; Otto & Strunz, 1968; Salanci & Moh, 1969). Salanci & Moh denoted this synthetic phase in the $PbS-Bi_2S_3$ system by 'phase III', and they have shown that it has the compositional range
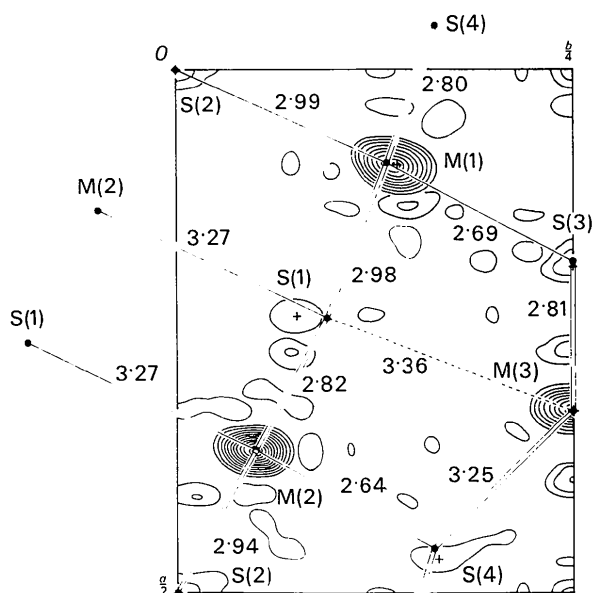

Fig. 1. A composite three-dimensional E map of lillianite projected along the c axis. The initial atomic coordinates as deduced from the E map and corresponding final coordinates are respectively indicated by crosses and dots. Bond lengths are indicated in Å.

from $Pb_3Bi_2S_6$ to $Pb_{2.4}Bi_{2.4}S_6$. A microprobe analysis made on the present specimens showed that they contain a small amount of Ag. The lattice constants were obtained by least-squares based upon 68 reflexions selected in the zero-level Weissenberg photographs. The d spacings of the reflexions were calibrated with reference to silicon powder lines which were simultaneously recorded in the Weissenberg photographs. The lattice constants thus determined are: $a = 13.535 \pm 0.003$, $b = 20.451 \pm 0.005$, $c = 4.104 \pm 0.001$ Å. The unit cell contains four formula units. The $N(z)$ test (Howells, Phillips & Rogers, 1950) confirmed the structure to be centric. The space group is $Bbmm$.

A piece of crystal whose external form is approximately that of a parallelepiped with dimensions $0.11 \times 0.11 \times 0.07$ mm was used to obtain diffraction intensity data. The linear absorption coefficient of this crystal was calculated to be 866 cm^{-1} for Mo $K\alpha$. Using the multiple-film technique, intensities of reflexions were visually estimated. After corrections for Lorentz–polarization, transmission and spot size, a set of 518 independent structure factors was derived.

Instead of starting with the atomic coordinates given by Otto & Strunz (1968), we decided to redetermine the structure by the use of symbolic addition methods (Karle & Karle, 1966), mainly because of our interest to see the power of this method when it is applied to this sort of compound. The initial set of reflexions used for this statistical method is as follows:

hkl	$\|E\|$	Sign allotted
250	1·86	+
181	2·74	−
951	2·85	+

The program written by Ashida (1967) was used to calculate the E values and to obtain a listing of all possible combinations E_h, E_k, E_{h+k} with $|E| \geq 1.5$. After five cycles of hand calculations with the Σ_2 equation, 51 signs were determined, with the probability level higher than 0·98, out of 81 reflexions with $|E| \geq 1.5$. The procedure was then extended to 192 reflexions with $|E| \geq 1.0$ and, without introducing any symbols for unknown signs, a total of 118 signs were determined with the probability level higher than 0·96. A three-dimensional E map based upon these signs revealed the locations of the heavy atoms. The probable locations of the sulphur atoms were readily determined in the map by taking account of the bond lengths between the heavy atoms and the sulphur atoms (Fig. 1). Structure factor calculations using this initial set of atomic coordinates gave a residual $R = 0.25$. The atomic coordinates were

Table 1. *Atomic parameters of lillianite*

Errors in those of sulphur and metal atoms are respectively given by $\sigma(S)$ and $\sigma(M)$. The magnitudes of the shifts of atomic coordinates from those of the ideal structure (Otto & Strunz, 1968) are denoted by $\delta(x)$, $\delta(y)$ and $\delta(z)$.

	x	$\delta(x)$	y	$\delta(y)$	z	$\delta(z)$	B
S(1)	0·2386	0·012	0·0956	0·011	0	0·0	2·02
S(2)	0	0·0	0	0·0	$\frac{1}{4}$	0·0	2·16
S(3)	0·1822	0·0	$\frac{1}{4}$	0·0	$\frac{1}{4}$	0·0	1·62
S(4)	0·4561	0·001	0·1630	−0·008	$\frac{1}{4}$	0·0	1·42
M(1)	0·0896	−0·001	0·1338	0·006	$\frac{1}{4}$	0·0	1·58
M(2)	0·3635	0·0	0·0495	0·007	$\frac{1}{4}$	0·0	1·19
M(3)	0·3239	−0·016	$\frac{1}{4}$	0·0	0	0·0	3·02
$\sigma(S)$	0·0023		0·0013		0		0·56
$\sigma(M)$	0·0004		0·0002		0		0·11

immediately refined with the modified Busing–Martin–Levy least-squares program. Corrections for anomalous scattering were made for all atoms. The final atomic parameters gave $R = 0.14$ for all data and 0.10 if unobserved and very weak structure factors were excluded. The atomic parameters are listed in Table 1.

The salient feature of the crystal structure is that it is made up of a slab of the galena structure; the boundary planes of the slab are parallel to the (311) plane of the galena structure. In the structure of lillianite, the slabs are so juxtaposed that each is related to the adjacent slabs by operations of mirrors parallel to (010) (Fig. 2). The structure may therefore be described as a polysynthetic twinning of the galena structure. This structural scheme is essentially the same as that proposed by Otto & Strunz (1968) based upon the ideal galena lattice. However, our results have now brought out the distortions of the galena lattice characteristic of the slabs. The distortions are indicated in Table 1 in terms of the magnitudes of shifts of atomic coordinates from those given by Otto & Strunz (1968). A calculation shows that the maximum shift of atoms amounts to 0.28 Å.

As will be observed in Fig. 1, there are, in the slabs, two independent metal sites M(1) and M(2) which are octahedrally coordinated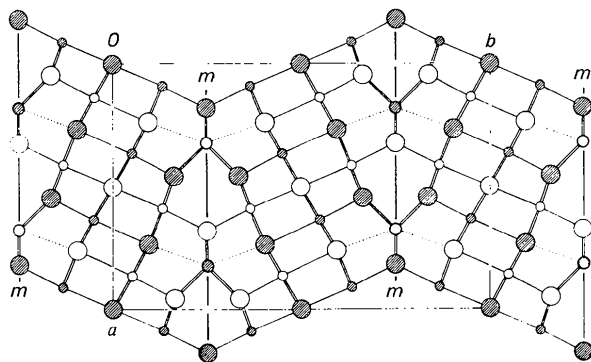 to six sulphur atoms. The differences in bond lengths between M(1)–S and M(2)–S are not significant, suggesting that Pb and Bi atoms are distributed over the two sites at random. On the other hand, the M(3) site in the boundary of the slabs has a trigonal prismatical coordination of sulphur atoms. The M(3)–S bond distances vary from 2.81 Å to 3.25 Å, giving a mean of 3.10 Å. The site is coordinated to two more sulphur atoms at a greater distance of 3.36 Å. The coordination and the distances suggest that the M(3) site is occupied by a Pb atom. The relatively higher temperature factor of the Pb atom in the M(3) site would seem to indicate a possible distribution of vacancies around this site.

In addition to the structure of lillianite, we have reinvestigated, by the symbolic addition procedure, the crystal structure of heyrovskýite, $6PbS.Bi_2S_3$, and confirmed the structure which has been proposed, also by Otto & Strunz (1968). At the present stage, refined atomic coordinates yield an R value of 0.09. Comparison of the refined structures of the crystalline phases under consideration will be given at a later date.

Fig. 2. The c-axis projection of the crystal structure of lillianite, showing that it consists of a polysynthetic twinning of the galena type slabs. Large circles represent sulphur atoms, medium circles Pb atoms and small circles Pb, Bi atoms. Shaded and open circles respectively indicate atoms at $z = \frac{1}{2}$ and $z = 0$.

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Structure cristalline de méthoniums. I. Dibromure de tétraméthonium dihydraté.

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In the cholinergic series of methoniums $[(CH_3)_3N-(CH_2)_n-N(CH_3)_3]^{2+}$, $2A^-$, tetramethonium ($n = 4$) manifests a low activity. The crystals of the dibromide are monoclinic, space group $C2/m$ with $Z = 2$. At room temperature, each molecule which has the symmetry $2/m$ is dihydrated and the water molecules are disordered. The structure is of the layer type. The methyl groups of the cationic head are related to several surrounding anions, the shortest distances $C \cdots Br^-$ corresponding to angles $N-C \cdots Br^-$ over $155°$.

Les structures cristallines de plusieurs composés à groupements ammonium quaternaire substitué ont été étudiées dans les séries des méthoniums et de la carbamoylcholine, en particulier du point de vue des relations des têtes cationiques avec leur environnement (Barrans, 1971). Plusieurs de ces substances agissent sur la transmission de l'influx nerveux