1.3 Unit cell : ordering of Li^{+} and Al^{3+}

The unit cell of lithiophorite was recalculated from the indexed powder pattern of a stoichiometric preparation (Table 5). Several reflection could not be indexed using Wadsley's value for b_0. As these reflections were consistent in all preparations and also consistent with additional reflections in the electron diffractions, they have to be considered as superlattice reflections. Using b_0 three times that of Wadsley's resulted in a satisfactory indexing. On the other hand about 4 reflections (listed in

TABLE 5. — *X-ray powder pattern of synthetic stoichiometric lithiophorite.*

Reflection No.	Intensity (visual 1-10	d (Å)		hkl
		Measured	Calculated	
1	8	9,52	9,46	001
2	1	8,11		
3	2	6,99	impurity	
4	1	6,13		
5	10	4,74	4,73	002
6	3	4,36	4,35	020
7	2	4,32	4,20	$\bar{1}11$
8	1	4,17	4,16	012
9	1	4,10	4,10	101
10	3	3,16	3,15	003
11	3	2,534	2,527	$\bar{2}01$
12	1	2,513	2,506	130
			2,481	$\bar{1}31$
			2,491	200
13	2	2,437	2,427	$\bar{2}11$
14	2	2,418	2,425	$\bar{1}23$
15	9	2,377	2,395	$\bar{2}02$
			2,368	131
16	2	2,307	2,306	$\bar{1}32$
			2,305	201
17	2	2,165	2,160	$\bar{2}03$
18	2	2,120	2,133	132
19	1	2,059	2,058	$\bar{1}33$
			2,052	202
20	1	1,973	impurity	
21	7	1,887	1,892	005
			1,878	133
22	3	1,583	1,583	$\bar{1}35$

Table 5 as Nos. 2, 3, 4 and 20) cannot be lithiophorite reflections, as they vary in intensity or may even be absent in some preparations. We thus attribute these reflections to traces of admixtures; e.g. No. 4 obviously is the most intensive reflection (020) of γ-AlOOH, with d = 6,11 Å.

The unit cell satisfying the values of Table 5 is only slightly different from Wadsley's cell (31), except that the b_0 is three times that of Wadsley's. The powder data are consistent with the electron diffractions of single crystals. These, however, differ from single crystal X-ray data by superstructure reflections. Such additional reflections have also been observed on natural material with electron diffraction by Wilson et al. (32). Table 6 lists the dimensions of the unit cell.

TABLE 6. — *Unit cell dimensions of synthetic stoichiometric lithiophorite.*

	This paper	Wadsley (31)
a_0	5,06 Å ± 0,01	5,06 Å ± 0,01
b_0	8,70 Å ± 0,01	2,91 Å ± 0,01
c_0	9,61 Å ± 0,01	9,55 Å ± 0,01
β	100°7′ ± 20′	100°30′ ± 20′

While Wadsley (31) had to leave unanswered the question as to whether or not the Li^+ and Al^{3+} ions were ordered, our electron diffraction indicate unambiguously that the b_0 of Wadsley's unit cell must be multiplied by three; the Li^+ and Al^{3+} ions, thus, are ordered.

1.4 Analysis

The analytical results, listed in Table 7, confirm the formula

$$[Mn^{4+}_{\frac{7}{3}}Mn^{2+}_{\frac{2}{3}}O_{12}]^- \cdot [Al_4Li_2(OH)_{12}]^+$$

which is more appropriate than the often quoted $(Al,Li)MnO_2(OH)_2$ as it gives the correct ratio of cations and valence states and moreover indicates the two different layers stacked on each other (1).

The three products 1.4, 1.5 and 1.14 were analyzed; they were pure with respect to X-rays and electron microscopical investigation.

TABLE 7. — *Analysis of synthetic stoichiometric lithiophorite.*

Preparation No.	Molar ratio		
	Li	Mn	Al
1.4	14	30,3	20,0
1.5	12	29,7	21,0
1.14	8	30,3	20,2
Theor.	10,000	30,000	20,000