

### 1.5 Valence of manganese

We initially have planned an attempt to determine the manganese valence (indicated by the formal oxidation degree) as a function of Mn excess or deficiency. As, however, any distinctive departure from stoichiometry produced phase mixtures, this would be meaningless. It was determined, though, for the pure sample 1.15 and also for preparation 1.9 with an initial Mn deficiency of 20 Mol-%. Since in No. 1.9 the additional phase was  $\gamma$ -AlOOH, all Mn was in the lithiophorite phase, and the valence ratio can thus be given (cf. Table 8).

The considerable excess of  $\text{Li}^+$  in Nos. 1.4 and 1.5 must be put down as a consequence of insufficient washing. No. 1.14 has been washed thoroughly while Nos. 1.4 and 1.5 have been washed distinctly less. The variations in  $\text{Al}^{3+}$  content reflect that already under stoichiometric starting conditions part of the initial  $\text{Al}(\text{OH})_3$  may segregate as  $\gamma$ -AlOOH and does then no longer take part in the reaction. X-ray patterns often show very faintly the (020) reflection of this phase. This will be yet more pronounced in series 2 and 3.

TABLE 8. — Formal oxidation degree of Mn in synthetic lithiophorite.

Preparation No.	Starting composition	By-product	Oxidation degree
1.15	Stoichiometric	—	1,81
1.9	20 % Mn deficiency	$\gamma$ -AlOOH	1,86
Theoretical	Stoichiometric, calc.	—	1,83

The variations of the formal oxidation degree being within an expected statistical range of  $\pm 0,03$ , we conclude that the Mn valence is unaffected by variations of the initial material.

## 2. Na-substituted lithiophorite

### 2.1 X-ray diffraction and morphology

Figures *a* and *b* of Plate IV show the X-ray powder patterns of the preparations in this series. There appear some minor differences, originating in the Mn compound used as starting material. These were not followed further.

The overall result is that additional reflections turn up when  $\text{Na}^+$  ions are introduced. Lithiophorite does not form at all, when  $\text{Li}^+$  is entirely replaced by  $\text{Na}^+$ .  $\text{Li}^+$  ions, hence, are *essential* constituents of that structure that can not be substituted.

Figure *b* of Plate II shows a fairly representative sample (preparation No. 2.9). A needle shaped phase turned up, e.g., in preparation No. 2.8 (Pl. II, figs. *c* and *d*). Its morphology and X-ray pattern have some resemblance to those of the cryptomelane-hollandite group.

Several preparations, e.g. No. 2.22, contained rafts of needles (Pl. III, figs. *e* and *f*).

Some of the more predominant X-ray lines which do not belong to lithiophorite could be attributed again to  $\gamma$ -AlOOH (mineral name: boehmite). In one case, i.e. preparation No. 2.5, we isolated the  $\gamma$ -AlOOH by dissolving the sample in hot HCl (38 %). The white residue was filtered off after dilution with H<sub>2</sub>O, thoroughly washed with deionized water, dried, and investigated by X-rays and electron microscopy. Its powder pattern is shown in fig. a, Pl. III.

## 2.2 Electron diffraction

The lithiophorite platelets could be identified by selected area electron diffractions similar to those mentioned before. Typical spacing were 4,32 Å (=  $d_{020}$ ) and 2,52 Å (=  $d_{200}$ ) (cf. Table 4). The rafts of needles already mentioned (Pl. III, figs. e and f), which presumably take up the Na<sup>+</sup> ions, show a distinctive electron diffraction with characteristic streaking perpendicular to the needle axis (Pl. III, fig. d). The d spacings found were  $2,82 \pm 0,07$  Å (direction of needle axis) and  $2,29 \pm 0,04$  Å (perpendicular to needle axis) (average of 14 and 10 measurements, respectively). The first of these two spacings obviously represents an octahedral Mn-Mn distance. Both Mn<sup>3+</sup> and Mn<sup>4+</sup> compounds have a preference for distances in this range, as is shown in Table 9.

TABLE 9. — Distances of octahedrally coordinated Mn<sup>4+</sup> and Mn<sup>3+</sup> ions.

Phase	Mineral name	Distance	Spacing (Å)
Ba <sub>2-x</sub> Mn <sub>8</sub> O <sub>16</sub>	Hollandite	$\frac{b_0}{2}$ (monoclinic) or $c_0$ (tetragonal)	2,88
Mn <sub>7</sub> O <sub>13</sub> .5H <sub>2</sub> O	Birnessite	$a_0$ (pseudo-hexag.)	2,845
ZnMn <sub>3</sub> O <sub>7</sub> .3H <sub>2</sub> O	Chalcophanite	$a_0$ (pseudo-hexag.)	2,84
Na <sub>4</sub> Mn <sub>14</sub> O <sub>27</sub> .9H <sub>2</sub> O	Na-Birnessite	$\frac{a_0}{3}$	2,847
$\gamma$ -MnOOH	Manganite	$\frac{c_0}{2}$	2,85
Mn <sub>5</sub> O <sub>8</sub>	—	$\frac{b_0}{2}$	2,86
$\alpha$ -MnOOH	Groutite	$c_0$	2,852
$\gamma$ -MnO <sub>2</sub>	Nsutite	$c_0$	2,849
$\beta$ -MnO <sub>2</sub>	Pyrolusite	$c_0$	2,87

$\gamma$ -AlOOH has usually been too thick to be penetrated by 100 keV electrons. Some selected area diffractions could, however, be obtained. An example is shown in fig. c, Pl. III. The spacings found were  $a_0 = 3,71 \pm 0,03$  Å (Literature: 3,700 Å (24)) and  $c_0 = 2,86 \pm 0,02$  Å (Literature: 2,868 Å (24)). It is interesting to note in this connection, that the  $c_0$  dimension of the