in boiling conc. HCl (38 %) that was diluted to 1 L. — Al had to be separated from this solution by the acetate method (7) and was then determined gravimetrically. — In the filtrate of this procedure Mn could be titrated with EDTA at pH 10 after reduction with $NH_2OH.HCl$. — The valence of Mn was determined by a modified iodometric-EDTA method (10). The result is given as the "formal oxidation degree" ranging from 1 to 2: divalent Mn gives 1, trivalent Mn yields $\frac{3}{2}$, and tetravalent Mn gives 2. Mixed valence Mn compounds will yield values in between. The formal oxidation degree actually is the ratio:

$$\frac{\text{Total number of positive charges}}{\text{Twice total Mn ions}}$$

Zn was not determined quantitatively for reasons to be discussed in section IV.

### 3. *X-ray diffraction*

Starting materials as well as products were finely ground and prepared on a sample holder using a Scotch tape and Bedacryl I.C.I. They were X-rayed with $FeK_{1,2}$ radiation using a Guinier camera with focusing quartz monochromator. The exposure time was approximately 8 to 16 h (mostly 10 h). For precise d spacings an internal standard was used: KCl proved unsatisfactory because of too few reflections in the higher d range, while $KAl(SO_4)_2.12H_2O$ gives too many coincidences. After some trials TlCl was used but later replaced by $\alpha$-$SiO_2$.

### 4. *Electron microscopy*

For the investigation of our samples in a Hitachi HU-11 and a Siemens Elmiskop I microscope, specimens were prepared according to current techniques, mainly directly in suspension on a carbon substrate. Surface replicas were also used, with Cr shadowing at 45° incident angle. Selected area electron diffraction (using evaporated TlCl as reference) served to identify single crystals.

## III. RESULTS

### 1. *Synthetic unsubstituted lithiophorite*

#### 1.1. X-ray diffraction and morpology

The only pure products (pure with respect to X-ray diffraction and electron microscopic morphology) were those of stoichiometric starting composition, as shown by Pl. I, fig. *a*. A run with 20 % Mn excess happened to yield almost pure lithiophorite (No. 1.8), out was not reproducible. On the other hand, some preparations with identical stoichiometric starting composition did not yield pure lithiophorite. Figures *b* and *c*, Pl. I, show electron micrographs of typical lithiophorite crystals.

Whenever the starting composition departed significantly from stoichiometry, additional phases turned up. Al excess led to the appearance of γ-AlOOH, whereas other contaminations could not be identified and were not traced any further. Synthetic Lithiophorite consists of plate shaped crystals, of about 500-2,000 Å thickness and of about 10,000 Å diameter.

### 1.2 Electron diffraction

Though most of the samples consisted of characteristically twinned crystals, thus making the evaluation tedious, 38 diffraction patterns of untwinned crystals could be photographed and evaluated. A typical example is shown in fig. *a*, Plate II. All diffractions, regardless of their history, gave *essentially identical spacings* and trigonal symmetry, at least within the limits of experimental accuracy.

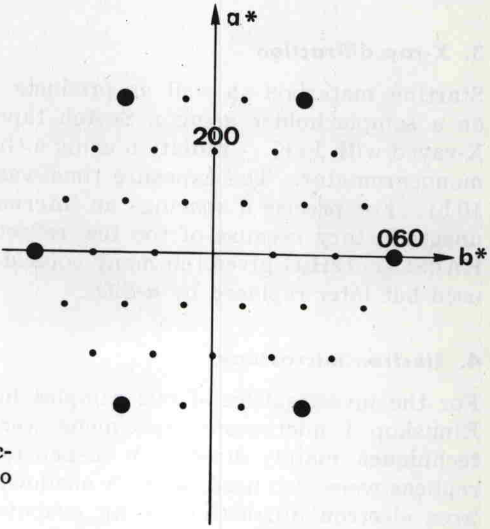

FIGURE 1. Indexed electron diffraction of lithiophorite, corresponding to fig. *a* on Pl. II.

Figure 1 represents an idealized version of such a pattern and illustrates the d spacings as listed in Table 4. The coordinates used in Figure 1 are orthogonal notwithstanding the trigonal (pseudo)-symmetry; the true unit cell actually is monoclinic as will be mentioned later.

TABLE 4. — *Spacings of electron diffractions of synthetic lithiophorite.*

| Spacing | Measured | Literature (32) |
|---|---|---|
| $d_{020}$ | $4{,}3_4$ Å | $4{,}4_1$ Å |
| $d_{200}$ | $2{,}5_3$ Å | $2{,}5_0$ Å |