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The Structure of Lithiophorite, (Al, Li)$MnO_2(OH)_2$

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Lithiophorite crystallizes in the monoclinic system, space group $C2/m$, with the constants $a = 5{\cdot}06$, $b = 2{\cdot}91$, $c = 9{\cdot}55$ Å, $\beta = 100°\ 30'$. The unit cell contains 2(Al, Li)$MnO_2(OH)_2$. The mineral has a layer structure in which alternate sheets of MnO_6 and (Al, Li)$(OH)_6$ octahedra are stacked so that the O and (OH) ions of adjacent layers are placed one on top of the other, and held together by hydroxyl bonds. Each layer consists of an infinite two-dimensional sheet formed by octahedra sharing six edges with adjacent ones. The lithium and aluminium occupy similar sites in a layer which can be regarded as a modification of the grouping found in hydrargillite (= gibbsite).

Introduction

It has long been recognized that lithium and aluminium are often associated with manganese in 'wads', which are ill-defined hydrous manganese oxide minerals. In an examination of wads, Ramsdell (1932) established lithiophorite as a distinct species in which these elements were essential constituents. This was subsequently confirmed by a survey of the manganese minerals (Fleischer & Richmond, 1943) in which a complex empirical formula, subject to revision, was advanced. Since then a well-crystallized specimen from Postmasburg, South Africa, has been examined chemically and microscopically (de Villiers & van der Walt, 1945) and preliminary X-ray measurements on part of this specimen led to the adoption of a simplified formula (Li, Al)$MnO_3.H_2O$ (Wadsley, 1950). This formulation would suggest that the structure is based upon the grouping found in the isodimorphous oxy-hydroxides of the type RO(OH), where R may be the cations Fe, Al, or Mn. The latter ions are trivalent, whereas the manganese in lithiophorite is predominantly tetravalent. The only other compound closely related chemically to lithiophorite is the mineral quenselite, $PbMnO_2(OH)$, which, however, contains only one hydroxyl ion (Byström, 1945). Since lithiophorite appears to be a new structural type the crystal structure has been determined.

Experimental

The specimen from South Africa was coarse grained and black, possessing an extreme cleavage parallel to the (001) face. The crystals were soft and easily bent, and without terminal faces. The cell dimensions, taken from zero-level Weissenberg photographs on a camera of radius 2·865 cm., with unfiltered iron radiation, were

$$a=5{\cdot}06\pm0{\cdot}01,\ b=2{\cdot}91\pm0{\cdot}01,\ c=9{\cdot}55\pm0{\cdot}01\text{ Å},\ \beta=100°\ 30'\pm20'\ .$$

The systematic absences of reflexions indicated the choice of space groups $C2/m$, $C2$ or Cm. If the C centring is ignored, the symmetry of the mineral is close to hexagonal, and was erroneously reported as such by the writer in a survey of the hydrous manganese oxide minerals based on the powder method (Wadsley, 1950).

The unit cell contains two formula units $Al_{0.68}Li_{0.32}Mn^{2+}_{0{\cdot}17}Mn^{4+}_{0{\cdot}82}O_3.1{\cdot}00\,H_2O$, as derived from the chemical analysis in de Villiers & van der Walt (1945), giving a calculated density 3·33 g.cm.$^{-3}$, measured 3·37 g.cm.$^{-3}$.

Intensity series were recorded for the zero levels about the a and b axes using filtered molybdenum radiation. Two sets of four films were exposed, the time ratio being 20:1, and the films were interleaved with tin foil to increase absorption. The intensities were measured using a calibrated time scale. No correction for absorption in the crystal was made. Structure amplitudes were subsequently placed on an absolute scale by comparison with the calculated values, to which a temperature factor $B=1{\cdot}2\times10^{-16}$ cm.^{2} had been applied. This factor was obtained experimentally by plotting the mean values of F_o/F_c within limited ranges of $\sin\theta$ against $\sin\theta$, and obtaining the best fit to this curve with selected Debye–Waller values.

Structure determination

Although a piezoelectric test was negative, there was no other evidence to distinguish between the space groups given above. The structure determination is based on the assumption that the mineral has a centre of symmetry, i.e. the space group $C2/m$, and this appears to be largely justified by the agreement ultimately reached between the observed and calculated F's.

The manganese in lithiophorite is predominantly tetravalent, although a considerable fraction of it is

Table 1. *Observed and calculated F's for the h0l and 0kl reflexions of lithiophorite*

Mo $K\alpha$ radiation

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	10	13	4,0,10	8	8	801	< 3	2
002	23	35	409	3	3	800	4	3
003	11	12	408	5	5	$80\bar{1}$	< 3	2
004	5	6	407	4	4	$80\bar{2}$	4	2
005	9	9	406	6	5	$80\bar{3}$	< 3	3
006	9	8	405	5	6	$80\bar{4}$	5	5
007	8	7	404	15	13	$80\bar{5}$	< 3	3
008	19	17	403	6	6	$80\bar{6}$	6	7
009	4	5	402	23	21	$80\bar{7}$	< 3	2
0,0,10	20	16	401	6	6	$80\bar{8}$	5	5
0,0,11	4	4	400	20	18	$80\bar{9}$	< 3	2
0,0,12	9	8	$40\bar{1}$	6	5	$8,0,\overline{10}$	< 3	2
0,0,13	4	3	$40\bar{2}$	9	8	$8,0.\overline{11}$	< 3	2
0,0,14	4	3	$40\bar{3}$	6	6	$8,0,\overline{12}$	< 3	1
0,0,15	< 3	2	$40\bar{4}$	9	7			
0,0,16	< 3	2	$40\bar{5}$	5	7	10,0,1	< 3	2
0,0,17	< 3	2	$40\bar{6}$	16	15	10,0,0	4	4
0,0,18	5	4	$40\bar{7}$	5	5	$10,0,\bar{1}$	< 3	1
0,0,19	< 3	1	$40\bar{8}$	16	16	$10,0,\bar{2}$	4	3
0,0,20	5	3	$40\bar{9}$	3	4	$10,0,\bar{3}$	< 3	1
			$4,0,\overline{10}$	8	9	$10,0,\bar{4}$	< 3	1
2,0,17	< 3	2	$4,0,\overline{11}$	3	3	$10,0,\bar{5}$	< 3	1
2,0,16	7	5	$4,0,\overline{12}$	< 3	3	$10,0,\bar{6}$	< 3	1
2,0,15	< 3	4	$4,0,\overline{13}$	< 3	3			
2,0,14	8	6	$4,0,\overline{14}$	3	3	020	29	28
2,0,13	3	3	$4,0,\overline{15}$	< 3	3	021	10	11
2,0,12	4	4	$4,0,\overline{16}$	5	5	022	21	19
2,0,11	4	4	$4,0,\overline{17}$	< 3	2	023	9	11
2,0,10	3	4	$4,0,\overline{18}$	5	4	024	10	7
209	4	5	$4,0,\overline{19}$	< 3	1	025	7	10
208	11	12				026	10	7
207	4	6	6,0,10	4	4	027	7	7
206	24	23	609	< 3	3	028	12	12
205	8	7	608	7	7	029	5	6
204	23	23	607	3	3	0,2,10	12	12
203	10	8	606	8	7	0,2,11	3	5
202	9	8	605	3	3	0,2,12	7	6
201	11	11	604	5	4	0,2,13	3	4
200	7	7	603	3	3	0,2,14	3	2
$20\bar{1}$	10	12	602	5	4	0,2,15	3	3
$20\bar{2}$	35	29	601	3	5	0,2,16	3	2
$20\bar{3}$	10	11	600	10	9	0,2,17	< 2	2
$20\bar{4}$	37	36	$60\bar{1}$	3	5	0,2,18	3	3
$20\bar{5}$	9	7	$60\bar{2}$	14	13	040	12	10
$20\bar{6}$	17	19	$60\bar{3}$	3	4	041	3	5
$20\bar{7}$	5	6	$60\bar{4}$	12	10	042	10	7
$20\bar{8}$	4	6	$60\bar{5}$	3	3	043	3	4
$20\bar{9}$	4	5	$60\bar{6}$	5	4	044	6	3
$2,0,\overline{10}$	5	6	$60\bar{7}$	3	4	045	3	4
$2,0,\overline{11}$	3	5	$60\bar{8}$	4	4	046	6	3
$2,0,\overline{12}$	9	9	$60\bar{9}$	3	4	047	3	4
$2,0,\overline{13}$	3	3	$6,0,\overline{10}$	6	7	048	7	6
$2,0,\overline{14}$	9	8	$6,0,\overline{11}$	< 3	3	049	< 2	3
$2,0,\overline{15}$	< 3	2	$6,0,\overline{12}$	5	7	0,4,10	6	6
$2,0,\overline{16}$	4	4	$6,0,\overline{13}$	< 3	2	0,4,11	< 2	2
$2,0,\overline{17}$	< 3	2	$6,0,\overline{14}$	< 3	4	0,4,12	2	3
$2,0,\overline{18}$	< 3	1	$6,0,\overline{15}$	< 3	1	0,4,13	< 2	2
						060	3	4
4,0,15	< 3	2	806	4	3	061	< 2	1
4,0,14	4	3	805	< 3	2	062	2	2
4,0,13	< 3	2	804	5	6	063	< 2	1
4,0,12	7	7	803	< 3	2	064	< 2	1
4,0,11	< 3	3	802	5	5	065	< 2	1

also present as lower valency ions. It seems most probable that these two ionic states are crystallographically indistinguishable, this being a common feature of the higher manganese oxides. The lithium and aluminium may then be grouped together as forming another structural unit. Since there are only two Mn and two (Al, Li) groups in the unit cell, each must occupy a special position 2(*a*)–2(*d*) for the space group $C2/m$ listed in the *Internationale Tabellen*. The reflexions of high $\sin\theta$ value, which are virtually independent of the contributions of the oxygen atoms, show an apparent centring on the A face, as the only reflexions of appreciable intensity are those for which $h+l$ are even. This condition is satisfied if the Mn is chosen to be in $2(a)$ at (0, 0, 0) and the (Al, Li) in $2(d)$ at $(0, \frac{1}{2}, \frac{1}{2})$.

The other ions may be grouped either as six oxygen ions and two water molecules, or as four oxygen and four hydroxyl ions. For the first alternative, the water molecules and two oxygens would be required to fill special positions $2(b)$ and $2(c)$. Because the b axis is short, however, there is insufficient space available for them in these sites. For the second alternative, the oxygen and hydroxyl ions will occupy fourfold positions, and in order to satisfy the charge distribution the oxygen ions will be bonded to the manganese and the hydroxyl ions to the (Al, Li).

A one-dimensional Patterson synthesis using the $F^2(00l)$ terms showed a prominent peak at $z=\frac{1}{2}$, corresponding to the (Al, Li), and two lesser peaks at $z=0{\cdot}10$ and 0·40. Since the manganese is at the origin, these will be the actual z parameters of the oxygen and hydroxyl ions respectively, which will therefore be in the position $4(i)$ for the space group $C2/m$.

The distance between these latter ions projected on the c axis is approximately 2·86 Å, the normal O–O separation. It seemed most probable, therefore, that these ions were situated one directly on top of the other rather than in the more usual close-packed manner which would here involve an O–OH distance of 3·0–3·2 Å. Since these ions are in special positions on the b axis if the structure is centrosymmetric, the approximate x parameters will be 0·70 for oxygen and 0·80 for hydroxyl, assuming the normal Mn–O and Al–OH bond lengths. A set of structure factors based on this model was calculated, and it was immediately obvious that most of the phases would be positive because of the presence of the heaviest atom at the origin. A Fourier synthesis for the b-axis projection was computed with all the $(h0l)$ terms placed on an approximately absolute scale. The electron-density diagram is shown in Fig. 1, in which the oxygen and hydroxyl peaks as well as the metal atoms are clearly resolved.

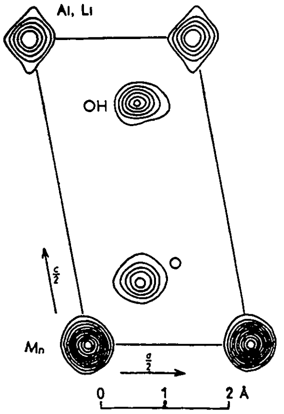

Fig. 1. Electron-density projection on the b axis. Contours are drawn at equal but arbitrary intervals.

Structure-factor calculations based on the parameters taken from Fig. 1 showed no changes of phase. Further slight refinements were made to the O and (OH) positions by computing an (F_o-F_c) synthesis in which the calculated metal-atom contributions were subtracted from the observed structure amplitudes. By this means the diffraction effects accompanying the heavier atoms which could alter the true positions of the lighter atoms were largely eliminated. A list of observed and calculated structure factors is given in Table 1, the discrepancy being 13%. Structure factors for the a-axis projection are also included in this table. Because they show good agreement with the measured values, it is reasonable to suppose that the choice of space group is correct.

Table 2. *Parameters of the ions in lithiophorite*

Space group: $C2/m$

2 Mn in $2(a)$ at (0, 0, 0)
2 (Al, Li) in $2(d)$ at $(0, \frac{1}{2}, \frac{1}{2})$
4 O in $4(i)$ at $(x_1, 0, z_1)$, where $x_1=0{\cdot}696$, $z_1=0{\cdot}103$
4 (OH) in $4(i)$ at $(x_2, 0, z_2)$, where $x_2=0{\cdot}794$, $z_2=0{\cdot}397$

Description of the structure

Lithiophorite has a layer structure with alternate sheets of MnO_6 and (Al, Li)$(OH)_6$ octahedra placed one on top of the other so that each of the upper oxygen ions of the manganese layer is directly below a hydroxyl ion from the next layer (Figs. 2 and 3). Each layer possesses hexagonal symmetry, but, because the aluminium ions are not directly above the manganese ions but are shifted $\frac{1}{2}b$ away, the layers of octahedra are displaced. In fact the monoclinic angle may be computed directly from the lengths of the cell edges, as Bragg (1937, p. 208) demonstrated for muscovite, a mica with a structure based upon alternating sheets of different composition in a fashion similar to that found in lithiophorite. Since the shift along the a axis from one layer to the next identical one is equal to one-third the a axis, the angle β is

Table 3. *Interatomic distances*

	Number per octahedron	Distance (Å)	
Al–OH	4	1·95	
–OH	2	1·93	
OH–OH	4	2·92	Unshared
	2	2·91	Unshared
	4	2·55	Shared
	2	2·59	Shared
Mn–O	4	1·93	
–O	2	1·97	
O–O	4	2·92	Unshared
	2	2·91	Unshared
	4	2·58	Shared
	2	2·53	Shared
O–OH	6	2·76	

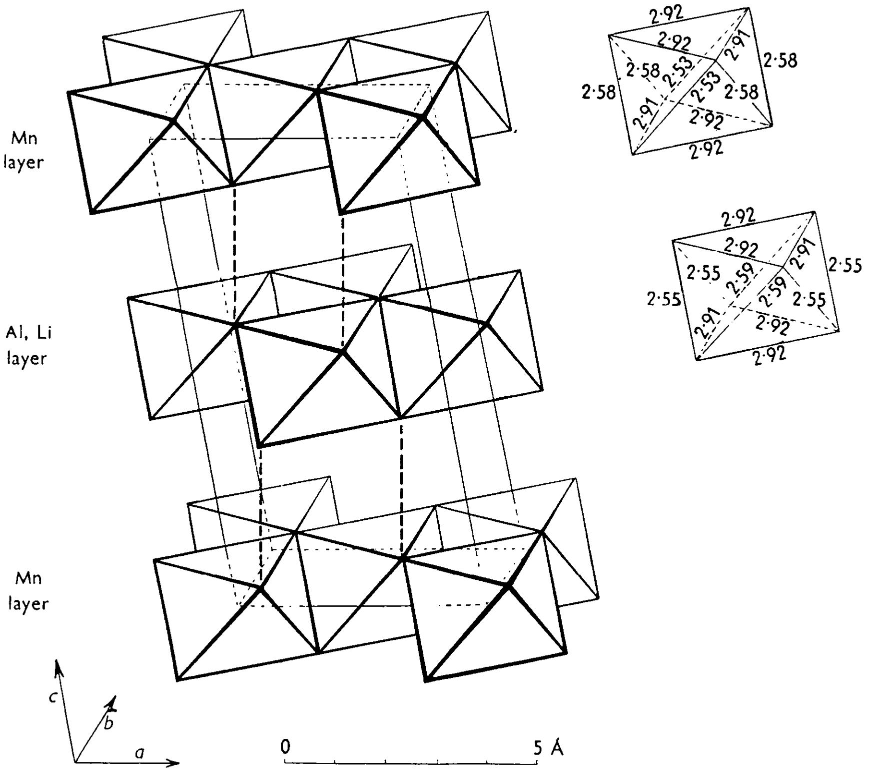

Fig. 2. The stacking of the layers in lithiophorite. The octahedra associated with one unit cell are shown. The thick broken lines normal to the a and b axes are hydroxyl bonds. The single octahedra are drawn to illustrate the shortening of the O–O and OH–OH pairs which are shared with their neighbours.

given by $\cos\beta = -\frac{1}{3}a/c = 100° 10'$, in good agreement with the measured value 100° 31′.

The aluminium–lithium–hydroxyl layer is identical with the manganese–oxygen layer, apart from small differences in the interionic distances (Table 3). Each (Al, Li) ion is octahedrally co-ordinated to six hydroxyl ions with four bonds of 1·95 Å and two of 1·93 Å, giving a mean value of 1·94 Å. This is in good agreement with the value 1·89 Å found for the mean Al–OH distance in hydrargillite by Megaw (1934), the slight and probably significant difference being due to the increase of the effective radius of the Al ion in lithiophorite by the Li ions which randomly occupy one-third of the sites. Each octahedron is bounded by six similar ones sharing the short edges (mean length 2·56 Å) with each other and with the central one. A layer therefore consists of the infinite two-dimensional sheet of closely bonded octahedra frequently found for the bivalent hydroxides of which brucite, $Mg(OH)_2$, is typical.

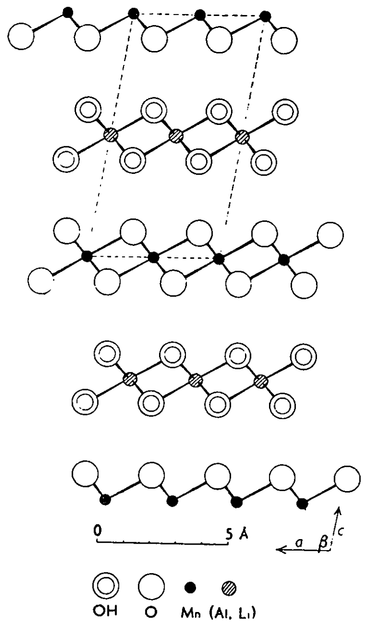

Fig. 3. The layers of lithiophorite projected on the b axis. The unit cell is shown by broken lines.

It may alternatively be represented as a modification of the hydrargillite structure. In this mineral, a single layer consists of a sheet of $Al(OH_6)$ octahedra arranged so that one-third of the aluminium sites are vacant, leaving a trigonal grouping of 'holes' (Megaw 1934). The presence of Li with Al in the ratio Li:Al = 1:2 modifies the mean valency of positive ions so that the stable structure for the $(Al, Li)(OH)_6$ layer in lithiophorite is similar to that found in brucite, in which no 'holes' occur.

It may perhaps be argued that lithium could fit between the trigonal prisms formed by the hydroxyl and oxygen ions of adjacent layers, and escape attention in the electron-density diagram because of its small scattering power. Were this the case, the aluminium layer would be a normal hydrargillite one, and, because of the systematic 'holes', the *b* axis would need to be $3\times2{\cdot}91 = 8{\cdot}73$ Å. Strongly exposed Weissenberg films taken about the *a* axis give, however, no evidence of a larger unit cell. The same argument proves that the lithium ions cannot occur systematically in sites corresponding to the holes of the hydrargillite layer, but are randomly distributed with the aluminiums over all the sites in a layer of the brucite type.

The manganese–oxygen layer is also composed of octahedra linked together in a closely bonded sheet. This is a most unusual grouping for a tetravalent oxide, and the octahedra, like those comprising the aluminium layer, are grossly distorted owing to the six short edges of each which are shared with its neighbours. The mean lengths of the shared edges, 2·56 Å for each layer, are in good agreement with values found for other compounds in which an O–O pair is shared by two cations of high valency (Pauling, 1940, p. 400).

The hydroxyl bond

An examination of the variations in the OH–OH distances of hydrargillite led Bernal & Megaw (1935) to define the role of hydrogen in intermolecular forces. The characteristic stacking of the $Al(OH)_6$ sheets in hydrargillite was due to the location of hydrogen atoms between the layers to form hydroxyl bonds. The hydrogen atoms themselves were closely associated with oxygen atoms to retain the identity of the (OH) groups.

It has been pointed out above that the stacking of the layers in lithiophorite resembles that of hydrargillite. The distance between adjacent O and (OH) ions is 2·76 Å, in good agreement with the length of the hydroxyl bond given by Bernal & Megaw as 2·7–2·8 Å. It appears, therefore, that the hydrogen atoms of the (Al, Li) layer are directed towards the oxygen ions beneath so as to form hydroxyl bonds, which may be readily disrupted to cause the prominent basal cleavage. The directions of the hydroxyl bonds are given as thick broken lines in Fig. 2.

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An Extension of the Use of Intensity Statistics

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The description, given by Taylor, of the optical basis of Wilson's statistical method for detecting centrosymmetry in a crystal suggests that there are certain conditions under which exceptions may arise. One of these exceptions—a structure with centrosymmetrical molecules arranged centrosymmetrically—gives a more extreme distribution of intensities than does an ordinary centrosymmetrical structure. It is proposed to call this distribution 'hypercentric', and its recognition may lead to useful preliminary information at the outset of a structure determination. The theory of the hypercentric distribution is discussed, and some examples of crystals in which it occurs are given.

1. The hypercentric distribution

The statistical analysis, introduced by Wilson (1949) and developed by Howells, Phillips & Rogers (1950), has provided an extremely powerful addition to the usual methods for determining space groups. As Wilson has pointed out, however, the success of the method