American Mineralogist, Volume 67, pages 817–821, 1982

The crystal structure of lithiophorite

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Abstract

Application of structural principles, especially the electroneutrality principle, to lithiophorite leads to the suggestion that it contains alternating layers $Al_{14}Li_6(OH)_{42}$, with one octahedron in 21 vacant, and $Mn_3^{2+}Mn_{18}^{4+}O_{42}$, repeating in six layers and with hexagonal symmetry, a_{hex} = 13.37Å and c_{hex} = 28.20Å, space group $P3_1$. This structure is a superstructure of the monoclinic structure reported by Wadsley in 1952.

A. D. Wadsley (1952) reported the results of his X-ray study of lithiophorite: monoclinic, $a = 5.06$Å, $b = 2.91$Å, $c = 9.55$Å, $\beta = 100.50°$. The ratio a/b, 1.731, is very close to $3^{1/2}$. The structure as described contains complete octahedral layers, with an MnO_2 layer alternating with a lithium-filled hydrargillite layer, $(Al, Li)(OH)_2$. Hydrogen bonds are formed between these octahedral layers, with every oxygen atom involved.

The formula given by Wadsley, as determined by DeVilliers and Van der Walt (1945), is $Al_{0.68}Li_{0.32}Mn_{0.17}^{2+}Mn_{0.82}^{4+}O_3 \cdot 1.00H_2O$. There is accordingly the possibility of a superstructure involving ordering of Mn^{+2} and Mn^{+4} and also of Al and Li.

We believe that it is possible to derive some characteristics of the structure from rather simple arguments, based on principles discussed in the 1960 book by one of us (Pauling, 1960).

An important principle, upon which the arguments are to a considerable extent based, is the electroneutrality principle, which states that in stable structures atoms have a resultant charge close to zero. First we consider a hydrargillite layer, $Al(OH)_3$. In Wadsley's structure for lithiophorite each OH group of the hydrargillite layer is involved in formation of a hydrogen bond with an adjacent oxygen atom of the manganate layer. The O–H· · ·O distance is 2.76Å, as in ice. An equation connecting bond length and bond number that we have used a great deal can be applied to the longer O–H distance in the hydrogen bond to indicate that it has about 10% covalent character, with sufficient uncertainty that 5% or 15% might instead be assigned. Since this covalent character can be attributed to the transfer to the hydrogen atom of an electron from the oxygen atom of the manganate layer, there results a negative charge of magnitude 0.10 to 0.30 per $Al_{0.67}(OH)_2$ group in the hydrargillite layer. In this layer two-thirds of the octahedral positions are occupied by aluminum atoms. A lithium ion has the right size to occupy one of the other octahedral positions. If all of the vacant octahedral positions were occupied by lithium, the composition of the hydrargillite layer would be $Al_{0.67}Li_{0.33}(OH)_2$, and the resultant electric charge of the layer would be reduced.

The transfer of negative charge from the oxygen atoms of the MnO_2 layer through their formation of hydrogen bonds could be compensated for by reducing the oxidation number of some of the manganese atoms from +4 to +2, the number of Mn^{+2} being required to be half the number of Li^+ in the other layer to achieve electrical neutrality of the crystal. These changes in composition of the two layers result in a better approximation to the principle of electroneutrality, correcting for the deviation from electroneutrality of the ideal structure caused by hydrogen bonds, than in the ideal structure, and we suggest that it is the principle of electroneutrali-

0003–004X/82/0708–0817$02.00

ty that is responsible for the changes from the ideal composition $Al_2(OH)_6Mn_3O_6$.

We now consider what a reasonable structure is for a hydrargillite layer, $Al(OH)_3$ or $Al_2(OH)_6$. In such a layer two thirds of the octahedral sites are occupied by aluminum atoms. There is a simple way in which the aluminum atoms can be introduced into the octahedral cavities so as to make all of the hydroxyl groups equivalent by a symmetry operation of a hexagonal space group. This is the structure found in hydrargillite itself, a structure in which no vacant octahedron is adjacent to another vacant octahedron. It is likely that the aluminum atoms are distributed in this way in lithiophorite also.

The composition assigned to the crystal and the description given in the foregoing paragraphs suggest that about one-sixth of the manganese atoms are in the bipositive state. There is, however, no simple way of distributing these bipositive manganese atoms among the octahedral positions in the layer with the composition $Mn^{2+}Mn_5^{4+}$. The closest simple arrangement is one in which each octahedron occupied by a bipositive manganese atom is surrounded by a hexagon of six octahedra occupied by quadripositive manganese atoms. These groups of seven octahedra are then condensed together into a layer with hexagonal symmetry. The composition of the layer with this structure is $Mn_{0.14}^{2+}Mn_{0.86}^{4+}O_2$. We suggest that this is the actual composition of the manganate layers in lithiophorite, rather than the reported $Mn_{0.17}^{2+}Mn_{0.82}^{4+}O_2$.

Octahedral layers with six of the seven octahedra occupied by quadripositive manganese and with composition Mn_6O_{14} have been found in chalcophanite, $ZnMn_3O_7{\cdot}3H_2O$ (Wadsley, 1955). In this crystal six filled octahedra surround each empty one. The lattice constant $a = 7.54$Å ($7^{1/2}$ times the mean lateral octahedron edge 2.85Å) differs by only 2% from the corresponding value in lithiophorite, $7^{1/2} \times 2.91 = 7.70$Å.

If this structure is accepted for the $Mn_7O_{14}^{2+}$ layer, the electrical neutrality of the crystal requires that $\frac{6}{7}$ of the vacant octahedra in the hydrargillite layer be occupied by lithium ions, giving this layer the composition $[Al_{14}Li_6(OH)_{42}]$, with one octahedron vacant. This composition can be achieved in the way shown in Figure 1. With this distribution each empty octahedron is surrounded by six Al octahedra and, in the next circle, six Li octahedra, and each Li octahedron has only one empty octahedron in its second circle. The hexagonal unit in the layer has edge $7^{1/2}\,a = 13.39$Å or $21^{1/2}\,b = 13.34$Å, average 13.37Å.

The sequence of triangular close-packed layers of atoms along an axis normal to the layers is as follows:

$\cdots$ O(A)Mn(B)O(C) $\cdots$ H–O(C)Al(A)O (B)–H $\cdots$ O(B)Mn(C)O(A) $\cdots$ H–O(A) (Al(B)O(C)–H $\cdots$ O(C)Mn(A)O(B) $\cdots$ H–O(B) Al(C)O(A)–H $\cdots$ O(A)Mn(B)O(C) $\cdots$

In this representation, A refers to sites in a particular triangular close-packed layer—for example, the Al/Li layers—while B and C refer to sites in layers in the two positions that can be close-stacked over or under layer A. Referred to the hexagonal subcell shown with dashed lines in Figure 1, atoms in these layers have coordinates as follows: A: 0, 0, z; B: ⅓, ⅔, z; C: ⅔, ⅓, z, where z assumes a succession of values from 0 to 1, for the successive layers. It is seen that, viewed as a hexagonal crystal, the structure repeats along the hexagonal axis after six octahedral layers. It is similar to the $CrHO_2$ structure (Douglass, 1957), which has similar hydrogen bonding and repeats after three layers, with the sequence:

$\cdot\cdot$ H $\cdot\cdot$ O(A)Cr(B)O(C) $\cdot\cdot$H$\cdot\cdot$ O(C)Cr(A)O(B) $\cdot\cdot$H $\cdot\cdot$ O(C)Cr(A)O(B) $\cdot\cdot$H$\cdot\cdot$ O(A)Cr(B)O(C) $\cdot\cdot$

The value of c_{hex} for $CrHO_2$ is 13.40Å.

There seems to be little reason, from the above discussion, for lithiophorite not to be hexagonal. Wadsley has pointed out that the ratio a/b is close to $3^{1/2}$ and that the value of β is only 0.35° from a value that permits a vertical c axis between the first and third layers to be chosen. An ordered structure based on the arrangement shown in Figure 1 and the stacking sequence indicated above has a hexagonal unit cell with $a = 13.37$Å, $c = 28.20$Å, which contains 3 formula units of composition. $Al_{14}Li_6(OH)_{42}Mn_3^{2+}Mn_{18}^{4+}O_{42}$. The structure is in space group $P3_1$ or $P3_2$. Figure 1 shows the location of the 3_1 axes of this structure in relation to the atomic arrangement of the $Al_{14}Li_6$ layer and adjacent Mn layers.

There are sound structural reasons, as discussed above, for essentially complete ordering in the individual octahedral layers. As can be seen from Figure 1, if the manganese atoms of two octahedral layers were directly above and below the metal ions of the Al, Li octahedral layer, as in the sequence

$\cdots$ O (A)Mn(B)O(C)HO(C)Al(B)O(A)HO(A)Mn (B)O(C) $\cdots$,

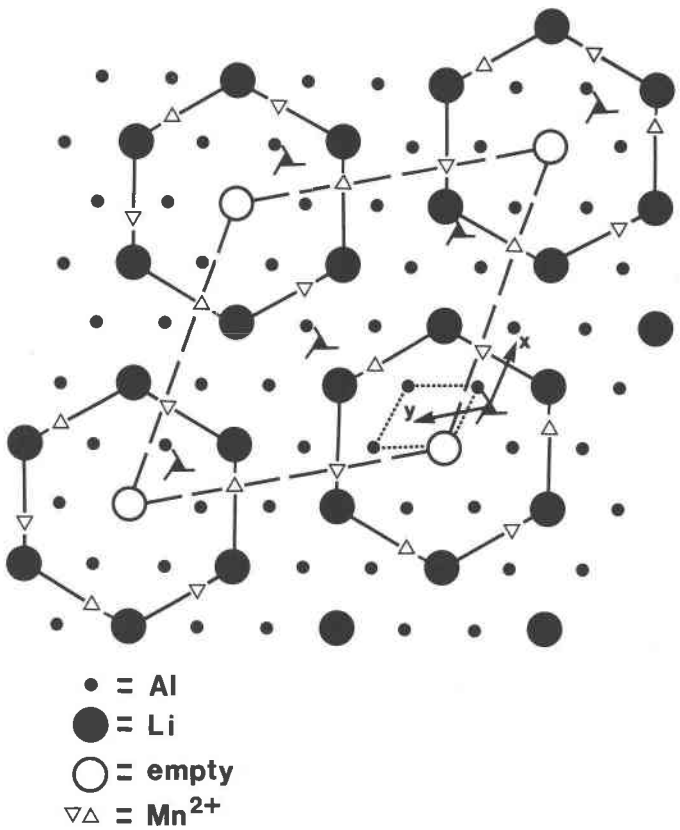

Fig. 1. The base of the proposed hexagonal unit of structure of lithiophorite is shown by dashed lines, with the center of the vacant octahedron in the $Al_{14}Li_6(OH)_{42}$ layer shown as a large open circle, the six Li atoms as large full circles, and the fourteen Al atoms as small circles. The Mn^{2+} atoms in the $Mn_3^{2+}Mn_{18}^{4+}O_{42}$ layer below are shown as upward-pointing triangles and those in the layer above as downward-pointing triangles. The complete structure is generated from this arrangement by stacking layers with operation of 3_1 axes at the locations shown. The small dashed rhombus is the hexagonal subcell. The x, y coordinate system, with origin at the 3_1 axis, is used for the atomic coordinates in Table 1.

the cations of adjacent layers would be closer to one another than for other sequences, leading to instability. It is for this reason that lithiophorite and $CrHO_2$ are based on a sort of cubic closest packing sequence of the oxygen–hydroxide double layers rather than the hexagonal sequence.

The most stable way of superimposing the layers would be that in which the Mn^{2+} atoms and the vacancies are as far apart as possible; that is, the vacancies are as close to the Mn^{4+} atoms as possible. This can be achieved in the way shown in Figure 1 by triangles for Mn^{2+} in both the layer below and the layer above the $Al_{14}Li_6$ layer. Atomic coordinates of the metal atoms in the structure described above are given in Table 1. Coordinates of the oxygen atoms can be generated from the coordinates given for the Mn atoms in Table 1 as follows. There are four groups of oxygen atoms, in four separate layers:

$$(i = 1, 21)\ x_{O(i)} = x_{Mn(i)},\ y_{O(i)} = y_{Mn(i)},\ z_{O(i)} = 0.034$$

$$(i = 22, 42)\ x_{O(i)} = x_{Mn(i-21)},\ y_{O(i)} = y_{Mn(i-21)},\ z_{O(i)} = 0.132$$

$$(i = 43, 63)\ x_{O(i)} = x_{Mn(i-24)} - 0.048,\ y_{O(i)} = y_{Mn(i-42)} + 0.095,\ z_{O(i)} = -0.034$$

$$(i = 64, 84)\ x_{O(i)} = x_{Mn(i-63)} - 0.048,\ y_{O(i)} = y_{Mn(i-63)} + 0.095,\ z_{O(i)} = -0.132$$

Here the notation i = m, n means i running from

Table 1. Coordinates of metal atoms in the lithiophorite structure

Atom	x	y	z	Atom	x	y	z
	-0.111	0.111	0	Mn (1)	0.222	0.111	0.167
Li (1)	0.318	0.254	0	Mn (2)	-0.111	-0.444	0.167
Li (2)	0.175	0.540	0	Mn (3)	-0.444	-0.222	0.167
Li (3)	-0.254	0.397	0	Mn (4)	0.032	0.159	0.167
Li (4)	0.460	-0.032	0	Mn (5)	0.413	0.064	0.167
Li (5)	-0.397	-0.318	0	Mn (6)	0.603	0.006	0.167
Li (6)	0.032	-0.175	0	Mn (7)	-0.216	-0.031	0.167
Al (1)	0.079	0.063	0	Mn (8)	0.080	0.397	0.167
Al (2)	-0.063	0.349	0	Mn (9)	0.270	0.349	0.167
Al (3)	0.127	0.301	0	Mn (10)	0.461	0.302	0.167
Al (4)	-0.301	0.159	0	Mn (11)	-0.349	0.254	0.167
Al (5)	-0.349	-0.079	0	Mn (12)	-0.158	0.207	0.167
Al (6)	-0.159	-0.127	0	Mn (13)	0.127	0.635	0.167
Al (7)	0.508	0.206	0	Mn (14)	-0.318	0.588	0.167
Al (8)	0.556	0.444	0	Mn (15)	-0.508	0.540	0.167
Al (9)	0.365	0.492	0	Mn (16)	-0.301	0.492	0.167
Al (10)	0.413	-0.270	0	Mn (17)	-0.006	-0.079	0.167
Al (11)	0.222	-0.222	0	Mn (18)	0.175	-0.127	0.167
Al (12)	-0.006	0.587	0	Mn (19)	-0.365	-0.174	0.167
Al (13)	0.270	0.006	0	Mn (20)	-0.254	-0.270	0.167
Al (14)	-0.206	-0.365	0	Mn (21)	-0.063	-0.317	0.167

m to n in integral steps. The above coordinates place the oxygen atoms in triangular close packing, which ignores small shifts in position resulting from the shortening of edges shared between coordination polyhedra. The origin of coordinates is noted in Figure 1. The remaining atoms are generated from those given above by the symmetry operations of space group $P3_1$, with the 3_1 axis passing through the origin as indicated in Figure 1.

We have not succeeded in developing any structural argument to explain the monoclinic deformation reported by Wadsley (1952), and we suggest that the crystal may in fact be hexagonal. In 1950 on the basis of X-ray powder photographs Wadsley had reported the crystal to have a hexagonal unit of structure. His 1952 values of a and c are 5.06±0.01Å and 2.91±0.01Å, respectively. The values 5.052Å and 2.917Å, which lie within the reported ranges, are in the ratio $3^{1/2}$, and the value of the monoclinic angle β corresponding to the hexagonal unit, 110.32°, agrees to within the reported range with Wadsley's value, 110.50±0.33°. Also, the O and OH positions given by Wadsley's values of the parameters are within 0.03Å of those corresponding to the hexagonal structure.

Wadsley reported that he had prepared strongly exposed Weissenberg films taken about the a axis without obtaining any evidence that the unit cell is larger than the simple one with the dimensions given above. He stated that this proves that the lithium ions cannot occur systematically in sites corresponding to the holes of the hydrargillite layer, but are randomly distributed with the aluminum atoms over all the sites in the layer. The failure to observe X-ray reflections indicating a superstructure, may simply be the result of the fact that the X-ray reflections from the hexagonal superstructure would be weak. Moreover, there is the possibility that there is some disorder within the sheets or especially in their superposition such as to make these reflections still weaker. A Laue photograph taken with the X-ray beam along the hexagonal or pseudohexagonal axis might reveal the symmetry and the correct unit of structure.

A report on electron microscopy and X-ray diffraction studies of synthetic lithiophorite has been published by Giovanoli, Bühler, and Sokolowska (1973). Their electron-diffraction photographs showed trigonal symmetry, within the limits of experimental accuracy. They interpreted their X-ray powder pattern in terms of a unit with b three times as large as Wadsley's value: monoclinic, a = 5.06±0.01Å, b = 8.70±0.01Å, c = 9.61±0.01Å, β = 100.12°±0.33°. These dimensions are compatible with the superstructure shown in Figure 1 to within their assigned accuracy.

Acknowledgments

This study was supported in part by a grant from the National Science Foundation.

References

Douglas, R. M. (1957) The crystal structure of $HCrO_2$. Acta Crystallographica, 10, 423–427.

Giovanoli, R., H. Buhler, and K. Sokolowska (1973) Synthetic lithiophorite: electron microscopy and X-ray diffraction. Journal de Microscopie, 18, 271–284.

Pauling, L. (1980) The Nature of the Chemical Bond, 3rd Ed., Cornell University Press, Ithaca, New York.

Villiers, J. E. De, and van der Walt, C. F. J., (1945) Lithiophorite from the Postmasburg manganese deposits. American Mineralogist, 30, 629–634.

Wadsley, A. D. (1950) Synthesis of some hydrated manganese minerals. American Mineralogist, 35, 485–499.

Wadsley, A. D. (1952) The structure of lithiophorite, $(Al, Li)MnO_2(OH)_2$. Acta Crystallographica, 5, 676–680.

Wadsley, A. D. (1955) The crystal structure of chalcophanite, $ZnMn_3O_7 \cdot 3H_2O$. Acta Crystallographica, 8, 165–172.

Manuscript received, April 6, 1981;
accepted for publication, February 15, 1982.