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Crystal structure refinement of lithiophorite

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ABSTRACT

A single-crystal X-ray diffraction study of lithiophorite [$(Al,Li)MnO_2(OH)_2$] revealed that the structure is trigonal ($R\bar{3}m$), not monoclinic as previously reported, and yielded unit-cell parameters $a = 2.9247(4)$, $c = 28.169(6)$ Å. The study confirmed that the structure consists of alternately stacked layers of Mn-O and (Al,Li)-OH octahedra. The refinement successfully revealed the H atom position. Structure energy calculations were used to assess the effects of various Al-Li ordering schemes on the H atom position. Precession photographs show weak superstructure reflections, corresponding to a primitive trigonal unit cell with $a = 5.056$ and $c = 56.34$ Å.

INTRODUCTION

Naturally occurring manganese oxides containing small amounts of Li have been known since the 1870s (Frenzel, 1870; Laspeyres, 1876) as lithiophorite (meaning Li bearer), but for many years they were grouped with a variety of undifferentiated manganese oxides, referred to collectively as "wad" or "psilomelane." In 1932, Ramsdell showed that lithiophorite is a distinct mineral, and today lithiophorite is recognized as occurring widely in soils, in ocean-floor Mn crusts, and in weathering zones of ore deposits. Typically lithiophorite is found as fine-grained masses; relatively large euhedral crystals (up to several centimeters in diameter) apparently are unique to the Mn deposits at Postmasburg, South Africa. The crystal structure of lithiophorite was determined by Wadsley (1952) using Weissenberg film data and a crystal from Postmasburg, South Africa, and was refined using difference-Fourier maps to a residual of 0.13. The structure consists of alternately stacked layers of Mn-O and (Al,Li)-OH octahedra, respectively (Fig. 1). Based upon the chemical analysis given by De Villiers and Van Der Walt (1945) for the Postmasburg lithiophorite, Wadsley proposed the ideal chemical formula: $(Al,Li)(Mn^{4+}_{0.82}Mn^{2+}_{0.17})O_2(OH)_2$. Wadsley assumed that the reduced valence Mn is Mn^{2+}, but, as is discussed below, Mn^{3+} is more likely. Published chemical analyses of lithiophorite samples from a variety of localities show that the Li content ranges from 0.2 to 3.3 oxide weight percent (Mitchell and Meintzer, 1967; Ostwald, 1988), with the Postmasburg material being the most Li rich. The lithiophorite structure can also accommodate significant substitution of transition elements such as Zn, Co, Cu, and Ni (Ostwald, 1988), although these elements were not observed for the material from Postmasburg.

Wadley determined the crystal structure of lithiophorite in space group $C2/m$ ($a = 5.06$, $b = 2.91$, $c = 9.55$ Å, $\beta = 100.5°$). Recently, however, Pauling and Kamb (1982) pointed out that Wadsley's unit-cell parameters transform almost exactly to a hexagonal cell, suggesting that the correct symmetry is trigonal. Using primarily electroneutrality arguments, Pauling and Kamb (1982) proposed a structure for lithiophorite in space group $P3_1$ that is a superstructure of Wadsley's monoclinic cell, with $a = 13.37$ and $c = 28.20$ Å. In the present study, we have carried out a detailed single-crystal X-ray diffraction study of lithiophorite in order to determine the correct space group and to obtain a precise and accurate structure refinement. We have also used structure energy calculations to investigate possible ordering schemes in lithiophorite and their effects on H atom positions.

EXPERIMENTAL DETAILS

A single crystal of lithiophorite was selected from a sample from Postmasburg, South Africa (NMNH no. 162391). The crystal is a platelet measuring approximately 0.04 × 0.30 × 0.40 mm. Precession and Laue photographs confirmed the suspicions of Pauling and Kamb (1982) that lithiophorite has trigonal symmetry, showing an R-centered cell in Laue class $\bar{3}m$ ($a = 2.9247$ and $c = 28.169$ Å), which indicates possible space groups $R\bar{3}m$, $R3m$, or $R32$. The threefold axis is normal to the platelet. Also visible on the precession photographs are weak superstructure reflections that are consistent with a primitive trigonal cell having $a = 5.056$ Å and c equal to twice that of the subcell (2 × 28.12 Å). These superstructure reflections are similar to those observed by Giovanoli et al. (1973) in electron diffraction patterns from synthetic lithiophorite crystals. The significance of the superstructure reflections will be discussed below. Intensity data were collected for the subcell with a Krisel-automated Picker four-circle diffractometer by the step-scan method, using graphite monochromated Mo$K\alpha$ radiation. The experimental parameters are summarized in Table 1. The reflections were examined graphically, and the background points adjusted as needed. Reflections with intensities $>3\sigma$ were tagged as observed. The data were corrected for absorption using the Gaussian integration method in the XTAL crystallographic computing

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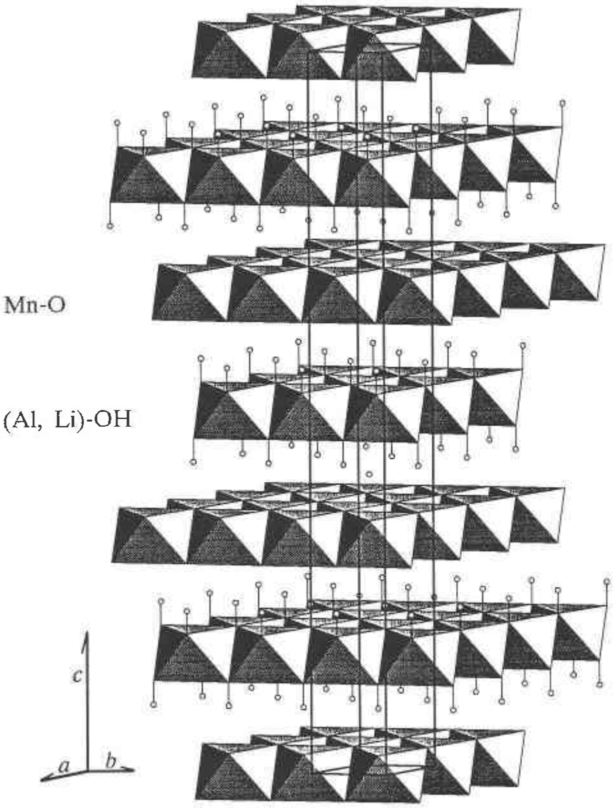

Fig. 1. Polyhedral representation of the lithiophorite crystal structure, showing the outline of the hexagonal unit cell.

package (Stewart and Hall, 1985) for $\mu = 45.6$ cm^{-1}. Refinement of the setting angles by the method of Hamilton (Ibers and Hamilton, 1974) for 20 reflections ($45° < 2\theta < 70°$) yielded the unit-cell parameters listed in Table 1. The structure refinements were performed using the XTAL computing package (Stewart and Hall, 1985). Statistical distribution of the normalized structure factors strongly indicated a centrosymmetric structure ($R\bar{3}m$). Ionic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). The initial atom positions were those transformed from Wadsley's (1952) monoclinic unit cell. The space group of the subcell requires that Al and Li are disordered over a single site. We, therefore, fixed the value of the Li occupancy factor to the value determined chemically (0.33) and refined the Al occupancy factor. Full matrix least-squares refinement with isotropic temperature factors yielded a residual of 0.038. Inclusion of anisotropic temperature factors lowered the residual to 0.028. At this point in the refinement, the largest feature on a difference-Fourier map was a diffuse electron density maximum (0.6 e/Å^3) at about ⅔,⅓,0.099) that was consistent with the expected H atom position. The H atom was included in the final cycles of refinement.

Table 1. Lithiophorite crystal and refinement data

Space group	$R\bar{3}m$
a (Å)	2.9247(4)
c (Å)	28.169(6)
2θ range (°)	3–60
Data collected	$\pm h, \pm k, \pm l$
Step-scan parameters	
Step size (°)	0.04
Time/step (s)	4.0
Time between standards (min)	120
Merging *R* factor for equivalent reflections	0.037
Unique reflections	158
Parameters refined	18
R factor	0.028

Observed and calculated structure factors are given in Table 2,[1] and atom positions and bond lengths are listed in Tables 3 and 4, respectively.

Discussion

The structure reported here is similar to that determined by Wadsley (1952), but it is in a trigonal, rather than monoclinic, space group and has slight differences in atom positions and bond lengths. The cation sites in the Mn-O octahedral sheet are fully occupied, unlike chalcophanite, which also has a layer structure but with one out of every seven Mn sites vacant (Wadsley, 1955; Post and Appleman, 1988). The Mn-O bond length of 1.945 Å is considerably longer than is typical for Mn^{4+}-O distances, e.g., the mean Mn-O distance in pyrolusite (MnO_2) is 1.887 Å (Baur, 1976). The larger Mn-O distance in lithiophorite reflects the presence of some lower valence Mn along with the Mn^{4+}. There has been some uncertainty as to whether Mn^{3+} or Mn^{2+} substitutes for Mn^{4+} in lithiophorite. De Villiers and Van Der Walt (1945) reported chemical formulae, based on wet-chemical analyses, for each of the two valence state possibilities. Wadsley (1952), apparently arbitrarily, adopted the formula with Mn^{2+}, as did Pauling and Kamb (1982). From a crystal chemical point of view, however, Mn^{3+} should be more easily accommodated into the lithiophorite structure than Mn^{2+}. With the ionic radii of Shannon (1976), a typical Mn^{3+}-O distance is about 2.01 Å (high spin), which is considerably closer to the observed Mn-O distance in lithiophorite than is the comparable value of 2.19 Å (high spin) for divalent Mn. Also, several other studies of predominantly tetravalent manganese oxide phases have concluded that Mn^{3+} rather than Mn^{2+} is the lower valence form of Mn (Yanchek, 1977; Post et al., 1982; Turner and Post, 1988; Post and Bish, 1988). With the assumption of trivalent Mn, the chemical analyses reported by De Villiers and Van Der Walt (1945) showed just the right amounts of the lower valence Mn to offset the positive charges of the Li cations, i.e., one-third of

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[1] A copy of the structure factors (Table 2) may be ordered as Document AM-94-548 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Lithiophorite atom positions and temperature factors

	x	*y*	*z*	Occ	U_{11}	U_{22}	U_{33}	U_{12}
Mn	0	0	0		131(3)	131(3)	158(4)	66(1)
Al	⅓	⅔	⅙	0.65(2)	73(6)*	73(6)	128(9)	36(3)
Li	⅓	⅔	⅙	0.33**	73(6)*	73(6)	128(9)	36(3)
O1	⅔	⅓	0.0343(1)		224(11)	224(11)	182(13)	112(5)
O2	⅔	⅓	0.1319(1)		217(10)	217(10)	129(11)	109(5)
H	⅔	⅓	0.099(2)		1200(300)†			

Note: temperature factors are in Å² × 10⁴; anisotropic temperature factors have the form $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})]$.

* The thermal parameters for Li and Al were constrained to be equivalent.

** The Li occupancy factor was fixed to the analytical value.

† Only $U_{\text{isotropic}}$ was refined for the H atom.

the Mn sites are occupied by Mn^{3+}. With the ionic radii of Shannon (1976), the average Mn-O distance, if one assumes ⅓Mn^{3+}, should be approximately 1.93 Å, which agrees closely with the observed value.

The structure refinement is consistent with the chemical analyses (De Villiers and Van Der Walt, 1945) in that two-thirds of the octahedral sites in the (Al,Li)-OH layer are occupied by Al and one-third by Li cations (Table 3). The observed (Al,Li)-OH distance of 1.952 Å compares well with the value of 1.95 Å calculated using tabulated ionic radii (Shannon, 1976). The close match between the cation to O distances for the two octahedral layers might at least in part account for the fact that the lithiophorite from Postmasburg occurs in large euhedral crystals. Perhaps the chemical composition and resulting degree of size coherency of the two types of octahedral layers is an important factor in determining the crystallinity of lithiophorite. This notion is supported by the observation that lithiophorite samples with compositions different from the Postmasburg material (generally with less Li and with minor amounts of Ni, Cu, Co, etc., presumably substituting into the Al layer) typically occur as fine-grained, poorly crystalline masses. As indicated above, the final difference-Fourier map revealed a diffuse electron-density maximum at about the expected position for the H atom in the (Al,Li)-OH layer. The O2-H distance is 0.93 Å, with an O2-H···O1 angle of 180° (by symmetry). The O1···O2 distance is 2.749 Å, and the H···O1 distance is 1.82 Å. The H bond, O1···H-O2, undoubtedly provides most of the interlayer cohesion.

STRUCTURE ENERGY CALCULATIONS

In order to understand the nature of the H atom position better and to explore the possibility of cation ordering in the octahedral layers, we undertook a series of structure energy calculations, using methods described by Post and Burnham (1986) and Abbot et al. (1989). The calculations were performed using the computer program WMIN (Busing, 1981), modified to use short-range energy parameters derived from modified electron gas (MEG) formulations (Post and Burnham, 1986). Because the MEG theory does not permit calculation of parameters for H^+, we used short-range parameters for O-H interactions derived by fitting to observed layer silicate structures containing OH^- anions (ρ = 0.25 Å and λ = 30000 kJ/mol: Abbott et al., 1989). We have shown previously that these empirical O-H parameters can successfully be used to model H positions in chalcophanite (Post and Appleman, 1988). For all of the structure energy calculations, the positions of octahedral cations and O atoms and the unit-cell parameters were held fixed to the values determined by our X-ray study. Only H atom positions varied during the minimization calculations, which were carried out assuming *P*1 symmetry for a variety of octahedral cation ordering schemes.

TABLE 4. Lithiophorite selected bond lengths (Å)

Mn-O1	1.945(1)	O1-O1	2.566(4)
(Al,Li)-O2	1.952(1)	-O1	2.9247(4)
Mn-Mn	2.9247(4)	-O2	2.749(4)
		-H	1.82(6)
		O2-O2	2.586(4)
		-O2	2.9247(4)
		-H	0.93(6)

The minimum energy H-atom positions are close to the nominal H atom site determined by the X-ray study. There is, however, a range in the calculated H atom positions, depending upon the particular ordering schemes of the octahedral cations. In particular, the possible Al-Li arrangements result in three distinct H atom positions (Fig. 2). The configurations of Mn^{4+} and Mn^{3+} in the adjacent layers have only a minor effect on the minimum energy H-atom position. The structure energies calculated for the various cation ordering schemes also indicate that although Al and Li and Mn^{4+} and Mn^{3+} almost certainly are ordered within the respective layers, there is little tendency for ordering between layers. These results are consistent with the X-ray diffraction study, showing, in general, no evidence for three-dimensional long-range ordering of the octahedral cations. As will be discussed below, however, the very weak superstructure reflections obviously indicate some type of additional ordering in the lithiophorite structure, but the nature of the ordering is not understood, and in any case it is apparently a relatively minor structural feature.

The results of our structure energy calculations, then, suggest that the refined structure determined from the

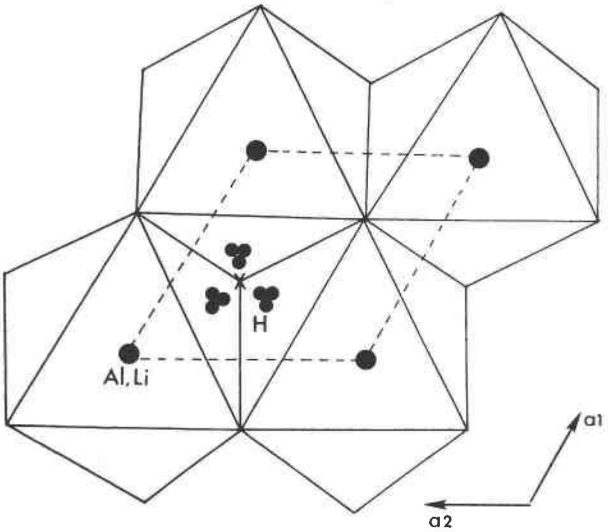

Fig. 2. Projection normal to the Al,Li-O octahedral layer. The possible minimum energy H-atom positions determined by structure energy calculations correspond to various Al-Li ordering schemes. The H atom position located by the X-ray study is indicated by the ×.

X-ray study is an average of several octahedral cation ordering schemes. This is consistent with the fact that the refined temperature factors, especially for Mn and O, are slightly larger than normally observed for well-ordered structures. (Table 3). The larger apparent thermal motions describe the positional disorder resulting from slightly different Mn and O positions, for example, depending upon whether a particular site is occupied by Mn^{4+} (Mn-O = 1.89 Å) or Mn^{3+} (Mn-O = 2.01 Å, which also gives rise to Jahn-Teller type distortions of the octahedron). Likewise the significant difference between the expected Al-OH and Li-OH distances (1.88 vs. 2.10 Å, respectively: Shannon, 1976) should give rise to positional disorder at the Al,Li and O2 sites.

Our model calculations suggest that the H atom occupies one of three slightly different sites, depending, primarily, upon the local Al-Li configuration. This positional disorder fits well with the diffuse nature of the electron density in this region of the difference-Fourier map. Also, if one assumes that the H atom is at the special position at the center of the electron density peak, then the O-H-O angle has the highly unlikely value of 180°. The comparable values for the three minimum energy H sites are 174.6°.

SUPERSTRUCTURE

As indicated above, long-exposure (48 h) precession photographs revealed weak superstructure reflections corresponding to a primitive, trigonal unit cell. Intensity data were collected for as many of these reflections as possible, using a Rigaku single-crystal diffractometer fitted with a high-intensity rotating-anode X-ray source. The resulting data were decomposed into the component Bragg reflections. The intensities for 31 reflections were scaled, converted to structure factors, and combined with the subcell data (for which the reflection indices had been transformed into the appropriate values for the supercell). Unfortunately, attempts to refine the complete supercell structure resulted in unrealistic cation to O bond lengths, almost certainly a consequence of superstructure reflections that were too few and too weak and high correlations during the least-squares refinement. Our refinement efforts do, however, suggest that the superstructure probably is not the result of three-dimensional ordering of the Al and Li cations, or at least that there is only a weak tendency for such ordering. The exact nature of the superstructure exhibited by this lithiophorite specimen is a subject of continuing study.

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REFERENCES CITED

Abbott, R.N., Jr., Post, J.E., and Burnham, C.W. (1989) Treatment of the hydroxyl in structure energy calculations. American Mineralogist, 74, 141–150.

Baur, W.H. (1976) Rutile-type compounds. V. Refinements of MnO_2 and MgF_2. Acta Crystallographica, B32, 2200–2204.

Busing, W.R. (1981) WMIN, a computer program to model molecules and crystals in terms of potential energy functions. U.S. National Technical Information Service, ORNL-5747.

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

Frenzel, A. (1870) Lithiophorit, ein lithiohältiges Manganerz. Journal praktische Chemie, 110, 203–206.

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

Ibers, J.A., and Hamilton, W.C., Eds. (1974) International tables for X-ray crystallography, vol. IV, 366 p. Kynoch, Birmingham, England.

Laspeyres, H. (1876) Der Lithion-Psilomelan von Salm-Chateau in Belgien und die chemische Constitution der Psilomelane. Journal praktische Chemie, 121, 1–28.

Mitchell, R.S., and Meintzer, R.E. (1967) Lithiophorite from Charlottesville, Virginia. American Mineralogist, 52, 1545–1549.

Ostwald, J. (1988) Mineralogy of the Groote Eylandt manganese oxides: A review. Ore Geology Reviews, 4, 3–45.

Pauling, L, and Kamb, B. (1982) The crystal structure of lithiophorite. American Mineralogist, 67, 817–821.

Post, J.E., and Appleman, D.E. (1988) Chalcophanite, $ZnMn_3O_7 \cdot 3H_2O$: New crystal structure determinations. American Mineralogist, 73, 1401–1404.

Post, J.E., and Bish, D.L. (1988) Rietveld refinement of the todorokite structure. American Mineralogist, 73, 861–869.

Post, J.E., and Burnham, C.W. (1986) Ionic modeling of mineral structures in the electron gas approximation: TiO_2 polymorphs, quartz, forsterite, diopside. American Mineralogist, 71, 142–150.

Post, J.E., Von Dreele, R.B., and Buseck, P.R. (1982) Symmetry and cation displacements in hollandites: Structure refinements of hollandite, cryptomelane, and priderite. Acta Crystallographica, B38, 1056–1065.

Ramsdell, L.S. (1932) An X-ray study of psilomelane and wad. American Mineralogist, 17, 143–149.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Stewart, J.M., and Hall, S.R. (1985) The XTAL system of crystallographic programs. University of Maryland, Computer Science Center, College Park, Maryland, Document TR-1364.1.

Turner, S., and Post, J.E. (1988) Refinement of the substructure and superstructure of romanechite. American Mineralogist, 73, 1155–1161.

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

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

Yanchek, E.A. (1977) Trivalent manganese in minerals. Lithology and Mineral Resources, 12, 733–737.

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