

The crystal structure of yeatmanite

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Abstract

The crystal structure of yeatmanite $[\text{Mn}_5\text{Sb}_2]^{VI}[\text{Zn}_5\text{Mn}_4(\text{Si}_{3.8}\text{Fe}_{0.2}^{3+})]^{IV}\text{O}_{28}$; PT , $a = 5.443(3)$, $b = 11.683(5)$, $c = 9.134(4)\text{\AA}$, $\alpha = 92.06(4)$, $\beta = 101.19(4)$, $\gamma = 76.34(4)^\circ$, $Z = 1$] from Franklin, New Jersey, has been refined to an $R = 0.100$ using 1881 reflections. The structure scheme proposed by Moore *et al.* [(1976); *Neues Jahrb. Abh.*, 127, 47-61] was proved to be correct. The octahedral sheet consisting of 5Mn and 2Sb is sandwiched by the upper and the lower tetrahedral sheets consisting of $\text{Zn}_3\text{Mn}_2\text{Si}_2$, respectively. Along the a -axis, there are two rows of Si tetrahedra, one of which is surrounded by 4ZnO_4 and 2MnO_4 , and the other by 3ZnO_4 and 3MnO_4 . A small portion of the latter is replaced by trivalent iron. The mean distances of M-O are as follows: $\text{Sb}^{VI}\text{-O}$ 2.00, $\text{Mn}(1)^{VI}\text{-O}$ 2.24, $\text{Mn}(2)^{VI}\text{-O}$ 2.19, $\text{Mn}(3)^{VI}\text{-O}$ 2.22, $\text{Mn}(4)^{VI}\text{-O}$ 2.12, $\text{Mn}(5)^{IV}\text{-O}$ 2.08, $\text{Zn}(1)^{IV}\text{-O}$ 2.03, $\text{Zn}(2)^{IV}\text{-O}$ 1.95, $\text{Zn}(3)^{IV}\text{-O}$ 1.99, $\text{Si}(1)^{IV}\text{-O}$ 1.64 and $\text{Si}(2)^{IV}\text{-O}$ 1.66\AA.

Introduction

Yeatmanite is a very rare manganese zinc antimonate silicate which is found only in the Franklin mineral deposit, New Jersey, U.S.A. This mineral was first described by Palache *et al.* (1938). They proposed the formula $(\text{Mn,Zn})_{16}\text{Si}_4\text{Sb}_2\text{O}_{29}$, noting that manganese and zinc were present in approximately equal amounts.

Moore (1966) studied catoptrite and found that catoptrite shows a close relationship in the unit cell dimensions with yeatmanite. He also suggested that the structure of catoptrite is built of the simple motif of pyrochroite-like octahedral sheet.

Moore *et al.* (1976) determined the crystal structure of catoptrite and revealed that $\text{Mn}_5^{2+}\text{Sb}_2^{5+}$ octahedral sheet is sandwiched by the upper and the lower $\text{Mn}_4^{2+}\text{Al}_2\text{Si}$ tetrahedral sheet parallel to (001), and gave the formula $[\text{Mn}_5^{2+}\text{Sb}_2^{5+}]^{VI}[\text{Mn}_8^{2+}\text{Al}_4\text{Si}_2]^{IV}\text{O}_{28}$. They also predicted that the yeatmanite structure would be very similar to that of catoptrite and estimated the ordering scheme of tetrahedral fraction and proposed the formula $[\text{Mn}_5^{2+}\text{Sb}_2^{5+}]^{VI}[\text{Mn}_2^{2+}\text{Zn}_8\text{Si}_4]^{IV}\text{O}_{28}$.

Recently, Dunn and Leavens (1980) re-examined the type specimens of yeatmanite and described their X-ray powder diffraction data and the results of chemical analyses of four samples. They noticed that the composition of yeatmanite varies slightly from sample to sample in the Mn:Zn ratio, and their data supported a Mn:Zn

ratio 8:7 instead of the ratio 7:8 in the formula proposed by Moore *et al.* (1976).

In the present study, the crystal structure of this very rare mineral has been refined, giving the conclusion that the structure scheme predicted by Moore *et al.* (1976) is correct. This paper describes the details of the results.

Sample description

Yeatmanite crystals were supplied by the courtesy of Dr. P. J. Dunn, Smithsonian Institution. The sample number is NMNH#C6290. This sample was described by Dunn and Leavens (1980). They determined cell dimensions by X-ray powder method and the chemical composition. Their results are given in Table 1. Note that the Mn:Zn ratio is 9:6 in this sample. They presumed iron to be divalent. However, this iron was judged to be trivalent on structure analysis. Dunn (private communication) also confirmed this fact by a chemical test. This will be discussed later.

Experimental

A platy crystal $0.30 \times 0.15 \times 0.15$ mm in size was selected for X-ray work. Cell dimensions were determined by using 25 reflections measured on a Philips PW-1100 single crystal diffractometer. Crystal data are given in Table 1. The obtained cell dimensions are comparable with those determined by Dunn and Leavens (1980). Intensity data were collected on the same computer-controlled diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069\text{\AA}$). The $\theta - 2\theta$ scan mode was applied. The scan range was $1^\circ < \theta < 30^\circ$. The reflections of $I > 3\sigma(I)$ were considered

TABLE 1. Crystal data

Formula*:	$[\text{Mn}_{4.8}\text{Fe}_{0.2}\text{Sb}_{2.0}]^{\text{VI}}[\text{Mn}_4\text{Zn}_6\text{Si}_4]^{\text{IV}}\text{O}_{28}$	
Unit cell dimensions:	This study	Dunn <i>et al.</i> (1980)
$a =$	5.544(3)\AA	5.604(2)\AA
$b =$	11.683(5)	11.602(7)
$c =$	9.134(4)	9.058(4)
$\alpha =$	92.06(4)°	92° 10(3)'
$\beta =$	101.19(4)°	100° 54(2)'
$\gamma =$	76.34(4)°	77° 18(5)'
Space group	P $\bar{1}$	
Z	1	

*Data by Dunn *et al.* (1980). Fe was judged as trivalent and assigned to one of to Si sites (see text).

to be observed. Absorption correction was made by using a program ACACA written by Prewitt (Wuensch and Prewitt, 1965). The number of independent reflections was 1881.

It was a very critical problem to judge whether the structure was centric or non-centric. The results of $N(Z)$ test was not conclusive. All cations and oxygens could be located from Patterson maps. Adopting the space group of $P1$ and choosing the origin at one of Sb atoms in the octahedral sheet, refinement was carried out with a block diagonal least-squares program, BDLS-60 in the UNICS-II system (Sakurai *et al.*, 1973). Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). At an early stage, it became clear that the structure scheme predicted by Moore *et al.* (1976) is correct. Repeated cycles of isotropic least-squares refinement, adopting the unit weight scheme for observed reflection, converged to give an $R = 0.093$ and $R_2 = 0.110$. Completing the refinement, it was found that the structure is nearly centro-symmetric if one of Mn atoms in the octahedral sheet was chosen as the origin. Thus, adopting the space group of $P\bar{1}$, the refinement was repeated. In this case, the final R and R_2 were 0.100 and 0.112, respectively. The obtained values of coordinates, temperature factors, and bond distances are more reasonable, so it was judged that the most probable space group of this yeatmanite crystal is $P\bar{1}$. In the course of the refinement adopting $P\bar{1}$, isotropic temperature factor of Si(2) became extraordinarily low, 0.10, so divalent iron in the original chemical analysis was judged to be trivalent and assigned to this site. (A similar effect was also observed in the refinement adopting $P1$.)

The final atomic parameters are given in Table 2. The interatomic distances and angles are presented in Table 3.

Discussion

Yeatmanite and catoptrite are based on the same structure principle of the densest sphere packing. Their structures are expressed as (2:1) structure if we follow the expression used in the field of clay mineralogy. That is, the octahedral sheet common to these two minerals is sandwiched by the upper and the lower tetrahedral sheets. The formulas are given as $7M^{VI}T_2O_4$ for the yeatmanite cell and $14M^{VI}T_2O_4$ for the catoptrite cell, respectively. Differences of the kinds of cations and their ordering scheme in these minerals result in different symmetry and different cell dimensions as follows:

yeatmanite; a 5.544, b 11.683, c 9.134Å, α 92.06, β 101.19°, γ 76.34°, $P\bar{1}$
 catoptrite; a 5.617, b 23.02, c 9.079Å, β 101°23', $C2/m$ (Moore *et al.*, 1976)

However, their cell dimensions are closely related as described by Moore (1966). An excellent fit is made by assuming that $a_{\text{yeatmanite}} = a_{\text{catoptrite}}$ and $b_{\text{yeatmanite}}$

TABLE 2. Atomic parameters

Atom	Number of coordination	x	y	z	B(Å ²)
Mn(1)	6	.0	.0	.0	0.49(8)
Mn(2)	6	.5710(8)	.8565(4)	-.0060(5)	0.50(6)
Mn(3)	6	.2952(8)	.4249(4)	.0007(5)	0.64(6)
Sb	6	.1415(4)	.7199(2)	-.0021(2)	0.35(2)
Mn(4)	4	.6403(7)	.2845(4)	.3590(4)	0.28(5)
Mn(5)	4	.9337(8)	.7081(4)	.3465(4)	0.41(5)
Zn(1)	4	.2068(7)	.1392(3)	.3489(4)	1.19(6)
Zn(2)	4	.4847(7)	.5716(3)	.3297(4)	0.81(5)
Zn(3)	4	.3436(6)	.8600(3)	.3382(4)	0.74(5)
Si(1)	4	.7651(14)	-.0060(6)	.3086(8)	0.39(10)
Si(2)*	4	.0561(13)	.4275(6)	.3172(7)	0.51(10)
O(1)		.6906(35)	-.0039(16)	.1280(20)	0.41(26)
O(2)		.1186(36)	.1540(17)	.1190(21)	0.52(27)
O(3)		.5959(37)	.2884(17)	.1244(22)	0.64(27)
O(4)		.9953(34)	.4108(16)	.1293(20)	0.33(25)
O(5)		.3832(42)	.5835(20)	.1080(24)	1.17(33)
O(6)		.8775(38)	.7112(18)	.1135(22)	0.79(29)
O(7)		.2718(36)	.8447(17)	.1135(21)	0.54(27)
O(8)		.9368(35)	.0027(16)	.6445(20)	0.43(26)
O(9)		.2936(39)	.1218(18)	.6185(23)	0.85(30)
O(10)		.6959(39)	.2880(18)	.5915(23)	0.87(30)
O(11)		.1472(40)	.4557(19)	.6479(23)	1.07(32)
O(12)		.6486(36)	.5615(17)	.6367(21)	0.59(27)
O(13)		.9761(38)	.6960(18)	.6084(22)	0.78(29)
O(14)		.4160(44)	.8855(21)	.6266(26)	1.43(36)

*Fe was assigned to this site.

= $(a + b)/2c_{\text{catoptrite}}$. The angle γ calculated by Moore (1966) from an ideal pyrochroite sheet is $76^{\circ}06'$, in excellent agreement with the observed data. As to β Moore *et al.* (1976) calculated the inclination of the c -axis from the normal of the sheet in terms of dense-packed scheme of anions. Ideally the inclination angle $\beta - 90^{\circ}$ has the relation $\tan(\beta - 90^{\circ}) = \frac{1}{4\sqrt{2}}$ or $\beta = 100^{\circ}01'$. The observed angles are 101.10° for catoptrite and 101.19° for yeatmanite. Also, each mineral has a perfect cleavage (001) due to the nature of the structure. The yeatmanite crystals are fragile and reflections are somewhat diffused. The rather high R value is due to these reasons. The relationship between the cells of yeatmanite and catoptrite is shown in Fig. 1.

The structure of yeatmanite can be decomposed into the upper tetrahedral, middle octahedral and the lower tetrahedral sheets as illustrated in Fig. 2. The ordering scheme of cation is compared with that of catoptrite in Fig. 3.

TABLE 3. Interatomic distances(Å) and angles(°)

<u>Mn(1) Octahedron</u>								
– O(1)	x2	2.27	O(1) – O(2)'	x2	3.01	O(1) – O(2)	x2	3.35
– O(2)	x2	2.23	O(1)' – O(7)	x2	3.00	O(1) – O(7)	x2	3.32
– O(7)	x2	2.21	O(2)' – O(7)	x2	2.72	O(2) – O(7)	x2	3.51
Mean		2.24	Mean (shared)		2.91	Mean (unshared)		3.39
						Mean	3.15	
<u>Mn(2) Octahedron</u>								
– O(1)		2.16	O(1) – O(1)'		2.82	O(1) – O(6)		3.25
– O(1)'		2.16	O(1) – O(2)'		3.01	O(1) – O(7)		3.22
– O(2)'		2.15	O(1)' – O(7)		3.00	O(1)' – O(2)'		3.26
– O(3)'		2.26	O(2)' – O(6)		2.70	O(1)' – O(3)'		3.33
– O(6)		2.24	O(3)' – O(6)		3.07	O(2)' – O(3)'		3.37
– O(7)		2.19	O(3)' – O(7)		2.74	O(6) – O(7)		3.35
Mean		2.19	Mean		2.89	Mean		3.30
						Mean	3.09	
<u>Mn(3) Octahedron</u>								
– O(3)		2.18	O(3) – O(5)'		2.68	O(3) – O(4)'		3.31
– O(4)		2.25	O(3) – O(6)'		3.06	O(3) – O(5)'		3.37
– O(4)'		2.38	O(4) – O(4)'		3.22	O(4) – O(5)'		3.31
– O(5)		2.18	O(4) – O(6)		2.71	O(4)' – O(6)'		3.42
– O(5)'		2.18	O(4)' – O(5)		2.70	O(4)' – O(5)'		3.49
– O(6)'		2.17	O(5) – O(5)'		2.98	O(5)' – O(6)'		3.40
Mean		2.22	Mean		2.89	Mean		3.38
						Mean	3.14	
<u>Sb Octahedron</u>								
– O(2)'		1.98	O(2)' – O(6)		2.70	O(2)' – O(3)'		2.96
– O(3)'		1.98	O(2)' – O(7)		2.72	O(2)' – O(4)'		2.92
– O(4)'		2.08	O(3)' – O(5)		2.68	O(3)' – O(4)'		2.90
– O(5)		1.98	O(3)' – O(7)		2.74	O(5) – O(6)		2.86
– O(6)		1.99	O(4)' – O(5)		2.70	O(5) – O(7)		2.87
– O(7)		1.96	O(4)' – O(6)		2.71	O(6) – O(7)		2.97
Mean		2.00	Mean		2.71	Mean		2.93
						Mean	2.82	

TABLE 3. (continued)

Mn(4) Tetrahedron							around cation	
–	O(3)	2.11	O(3)	–	O(12)'	3.07	93.8	
–	O(12)'	2.11		–	O(13)'	3.09	92.8	
–	O(13)'	2.15		–	O(14)'	3.12	96.0	
–	O(14)'	2.10	O(12)'	–	O(13)'	3.65	117.7	
Mean		2.12		–	O(14)'	3.70	123.0	
			O(13)'	–	O(14)'	3.64	117.8	
			Mean			3.38	106.9	
Mn(5) Tetrahedron								
–	O(7)	2.09	O(7)	–	O(9)'	3.22	99.3	
–	O(9)'	2.14		–	O(10)'	3.22	102.8	
–	O(10)'	2.03		–	O(11)'	3.02	93.0	
–	O(11)'	2.07	O(9)'	–	O(10)'	3.39	108.7	
Mean		2.08		–	O(11)'	3.80	129.3	
			O(10)'	–	O(11)'	3.48	116.0	
			Mean			3.36	108.2	
Zn(1) Tetrahedron								
–	O(2)	2.07	O(2)	–	O(11)'	2.99	94.3	
–	O(11)'	2.01		–	O(13)'	3.05	96.7	
–	O(13)'	2.02		–	O(14)'	3.08	97.6	
–	O(14)'	2.01	O(11)'	–	O(13)'	3.55	123.5	
Mean		2.03		–	O(14)'	3.45	118.2	
			O(13)'	–	O(14)'	3.39	114.7	
			Mean			3.25	107.5	
Zn(2) Tetrahedron								
–	O(5)	2.00	O(5)	–	O(10)'	3.14	107.1	
–	O(10)'	1.91		–	O(11)'	3.04	100.3	
–	O(11)'	1.96		–	O(12)'	2.99	99.1	
–	O(12)'	1.93	O(10)'	–	O(11)'	3.33	118.9	
Mean		1.95		–	O(12)'	3.16	111.1	
			O(11)'	–	O(12)'	3.32	117.0	
			Mean			3.16	108.9	
Zn(3) Tetrahedron								
–	O(7)	2.02	O(7)	–	O(8)'	3.02	98.1	
–	O(8)'	1.98		–	O(9)'	3.17	102.7	
–	O(9)'	2.03		–	O(10)'	3.11	103.4	
–	O(10)'	1.94	O(8)'	–	O(9)'	3.47	119.9	
Mean		1.99		–	O(10)'	3.30	114.7	
			O(9)'	–	O(10)'	3.33	113.9	
			Mean			3.23	108.8	

TABLE 3. (continued)

Si(1) Tetrahedron			
—	O(1)	1.62	
—	O(8)'	1.63	
—	O(9)'	1.65	
—	O(14)'	1.68	
Mean		1.64	

O(1)	—	O(8)'	2.63	108.0
	—	O(9)'	2.71	111.9
	—	O(14)'	2.68	108.4
O(8)'	—	O(9)'	2.72	111.7
	—	O(14)'	2.72	109.9
O(9)'	—	O(14)'	2.68	106.8
Mean			2.69	109.5

Si(2) Tetrahedron			
—	O(4)	1.70	
—	O(11)'	1.62	
—	O(12)'	1.65	
—	O(13)'	1.68	
Mean		1.66	

O(4)	—	O(11)'	2.65	106.1
	—	O(12)'	2.68	106.7
	—	O(13)'	2.70	106.3
O(11)'	—	O(12)'	2.73	113.8
	—	O(13)'	2.76	113.5
O(12)'	—	O(13)'	2.72	109.9
Mean			2.71	109.4

Standard deviations are 0.02Å for M—O and T—O, 0.02–0.03Å for O—O and 0.8–1.0° for O—T—O/means (–x, –y, –z).

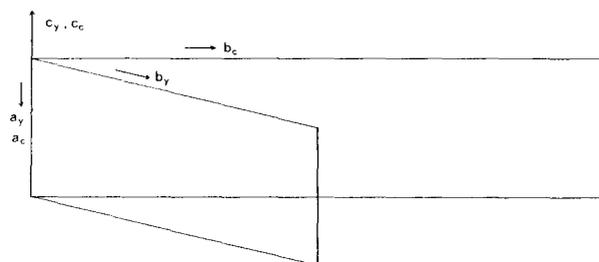


FIG. 1. The relationship between the cell of yeatmanite (y) and that of catoptrite (c).

The octahedral sheet of yeatmanite is identical with that of catoptrite, though the situation of symmetry is different. All the available octahedral voids in this sheet are occupied by 5Mn and 2Sb atoms. The oxygen atoms associated with this sheet are simultaneously the apices of tetrahedral sheets above and below the plane of the octahedral cations. Sb atoms in the octahedral sheet are so situated that each Sb octahedron is surrounded by 6Mn octahedra. The mean distance of M—O in 5Mn octahedra is 2.21Å and in agreement with the expected Mn—O 2.23Å average. The M—O mean distance in Sb octahedra is 2.00Å and comparable with the distance found in catoptrite 2.04Å. Owing to cation-cation repulsion, the short polyhedral edge distances appear in those between Sb⁵⁺ and Mn²⁺, and between Mn²⁺ and Mn²⁺ as shown in Table 3.

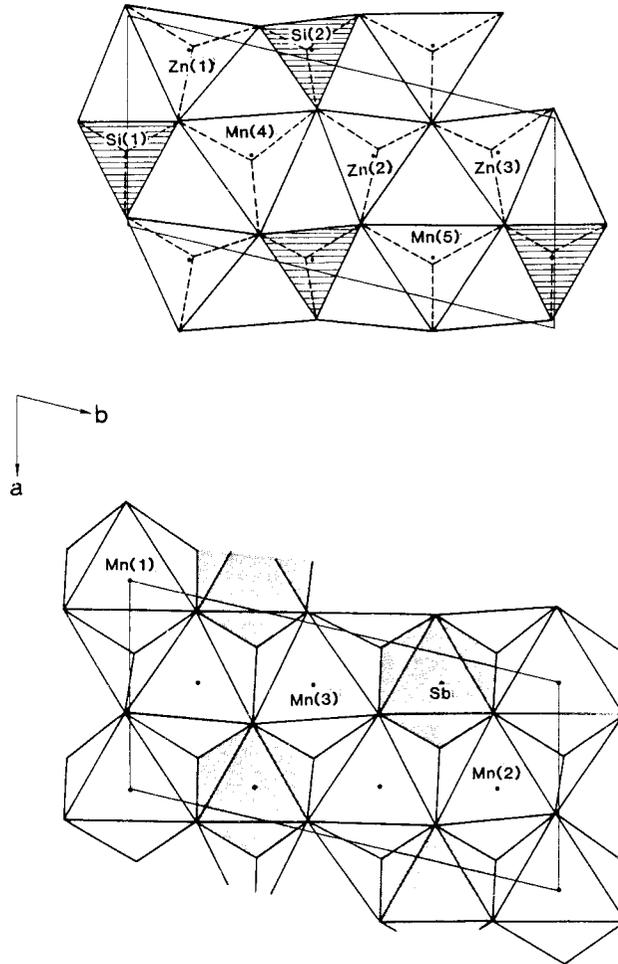


FIG. 2. Crystal structure of yeatmanite. The upper tetrahedral and the middle octahedral sheets are projected on the *ab* plane, respectively.

In the catoptrite structure, tetrahedral cations are composed of $\text{Mn}_4\text{Al}_2\text{Si}$. The AlO_4 tetrahedra link with each other to form simple chains which run parallel to the *a*-axis, and the MnO_4 tetrahedra define chains of six-membered rings which also run in this direction. The interior of these rings is linked to the SiO_4 tetrahedra, which are in this manner insulated from the AlO_4 tetrahedra.

Based on this ordering scheme in the catoptrite structure, Moore *et al.* (1976) proposed an ordering model of tetrahedral fraction in the yeatmanite structure,

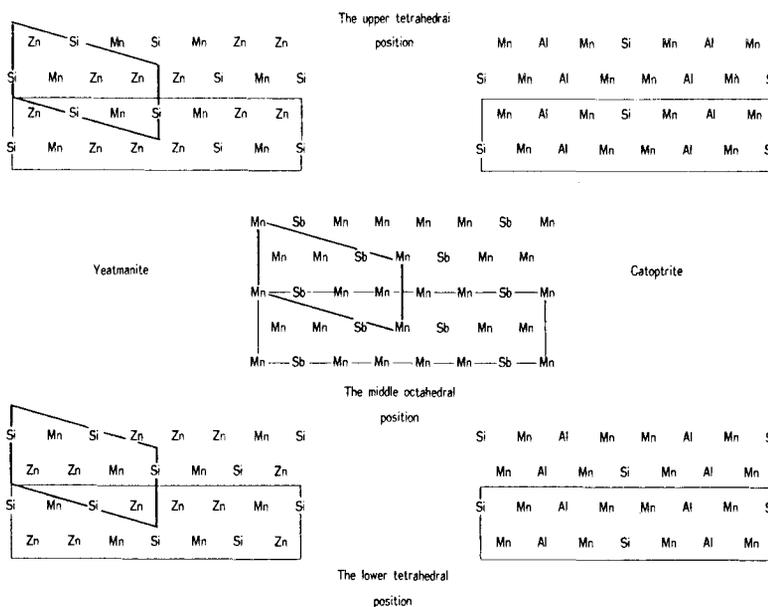


FIG. 3. Diagram shows the cation ordering in the yeatmanite and catoptrite structure.

presuming that tetrahedral positions were composed of Zn_4Si_2Mn . They selected the best fit model for electrostatic valence bond sums of cations about anions. In their scheme, the AlO_4 chains were replaced by SiO_4-ZnO_4 -chains. All of the MnO_4 were replaced by the ZnO_4 except one MnO_4 per unit cell. Their scheme was proved to be correct. However, one more MnO_4 is present instead of ZnO_4 expected by Moore *et al.* (1976), because they assumed that Zn:Mn ratio in the tetrahedral sheet was 4:1 instead of 3:2 in the examined specimen (NMNH#C6290).

The determined ordering of tetrahedral fraction in yeatmanite (NMNH#C6290) structure is expressed as follows:

(1) The arrangement of cations perpendicular to the a -axis is in the order of Si-Mn-Si-Mn-Zn-Zn-Zn-. Two lines (ranks) of such cation sequence form the tetrahedral cations. In the catoptrite structure, the corresponding cation sequence is Al-Mn-Si-Mn-Al-Mn-Mn-. Thus the existence of the ZnO_4 triplet is a unique feature.

(2) If we look along the a -axis, we can presume two rows of SiO_4 surrounded by six tetrahedra; one is $Si(1)O_4$ tetrahedra surrounded by $4ZnO_4$ and $2MnO_4$ and the other is $Si(2)O_4$ tetrahedra surrounded by $3ZnO_4$ and $3MnO_4$. Thus the situation of $Si(1)O_4$ and $Si(2)O_4$ tetrahedra are somewhat different from each other.

It is a very critical problem whether there exists limited solubility between Mn^{2+} and Zn^{2+} at the tetrahedral positions or not. A trial refinement was carried out with a full-matrix least-squares program, FLS-2, in the UNICS-II system (Sakurai *et al.*, 1973) to estimate these cation occupancies by varying the multiplicities. However, a definite conclusion could not be obtained. So, complete ordering of Mn and Zn was assumed.

In the tetrahedral sheet, there exist 3Zn, 2Mn and 2Si positions. The mean distances of M-O in the Zn(1), Zn(2) and Zn(3) tetrahedra are 2.03, 1.95 and 1.99Å, respectively. The described $\text{Zn}^{\text{IV}}\text{-O}$ distance is about 1.98Å (Zn₂SiO₄II 1.98Å by Marumo and Syono, 1971; hemimorphite 1.96Å by McDonald and Cruickshank, 1967; ZnSiO₃(M) 1.982Å by Morimoto *et al.*, 1975; wurtzite 1.977Å by Kihara and G. Donnay (personal communication); 2.00Å by Shannon and Prewitt's data (1967); 1.97Å by Pauling's tetrahedral covalent bond). Zn(2)-O and Zn(3)-O are comparable with these values. Zn(1)-O is somewhat larger than these value and might suggest a limited solution of Mn^{2+} in this site, and also larger value of isotropic temperature factor might support this hypothesis but it is not conclusive.

The mean distances of M-O in Mn(4) and Mn(5) tetrahedra are 2.21 and 2.08Å, respectively. The value of Mn(4)-O is somewhat larger, and that of Mn(5)-O is comparable with those observed in the catoptrite structure, 2.04-2.08Å.

There exists two Si sites. The value of isotropic temperature factor of Si(1) is normal. However, that of Si(2) became very small, 0.10, in the course of the refinement. Moore *et al.* (1976) suggested that the electrostatic valence bond sums (P_x) of O(4) bonded of Si(2) is 2.50 by the model proposed by them. Thus, it is reasonable to assume that iron judged to be divalent by Dunn and Leavens (1980) is really trivalent and replaces a portion of Si in this site to compensate p_x sums. Dunn (personal communication) examined and confirmed by a chemical test that iron in yeatmanite NMNH#C6290 is trivalent. The M-O mean distance in Si(2)O₄ tetrahedra is 1.66Å, and supports the expansion of Si(2)O₄ tetrahedra by the introduction of trivalent iron.

Orientation of oxygen sheet at $z = 3/8$ (basal oxygens of the upper tetrahedral sheet) and $z = 5/8$ (those of the lower tetrahedral sheet) are illustrated in Fig. 4. Distorted octahedral holes occur in between the sheets as described by Moore *et al.* (1976).

So far, the results of the structure analysis of NMNH#C6290 have been described. It has been proved positively that the structure of this crystal is centro-symmetric, $P\bar{1}$ as suggested by Moore *et al.* (1976). This is all right because the tetrahedral Zn:Mn ratio is 6:4 in this crystal. However, we cannot extend these results to other samples such as NMNH#R9371 and NMNH#22621, because the ratio is 7:3 in these samples. There are two possibilities in distribution of the tetrahedral cations. In the first model,

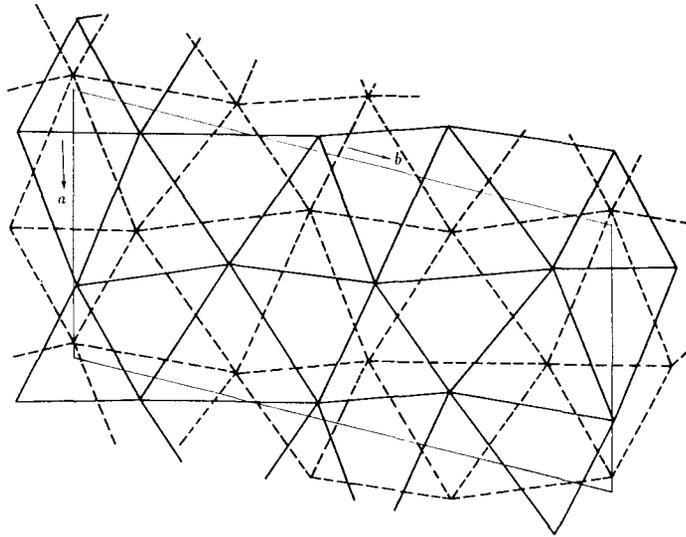


FIG. 4. The relation between the oxygen sheet at $z = 3/8$ (dashed lines, the basal oxygens of the upper tetrahedral sheet) and $Z = 5/8$ (solid lines, those of the lower tetrahedral sheet).

the symmetry still maintain $P\bar{1}$ owing to the disordering of extra Zn over two tetrahedral Mn positions. In the second, the symmetry degrades to noncentro-symmetric $P1$, by the nearly complete ordering of Zn and Mn. A definite conclusion must wait the structure analysis of these samples.

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