THE AMERICAN MINERALOGIST, VOL. 52, NOVEMBER-DECEMBER, 1967

CRYSTAL CHEMISTRY OF THE BASIC MANGANESE ARSENATE MINERALS 1. THE CRYSTAL STRUCTURES OF FLINKITE, $Mn_2^{2+}Mn^{3+}(OH)_4(AsO_4)$ AND RETZIAN, $Mn_2^{2+}Y^{3+}(OH)_4(AsO_4)$

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ABSTRACT

The crystal structure of flinkite, $Mn_2^{2+}Mn^{3+}(OH)_4(AsO_4)$, is derived from pyrochroite-like sheets by removing some of the octahedra and substituting AsO_4^{3-} tetradentate tetrahedra between the sheets. The Mn^{3+}-centered oxygen octahedra are elongate square bipyramids, consistent with Jahn-Teller tetragonal distortions in an octahedral crystal field.

The retzian, $Mn_2^{2+}Y^{3+}(OH)_4(AsO_4)$, structure consists of sheets built of Mn^{2+}-centered oxygen octahedra and Y^{3+}-centered oxygen square antiprisms. As in flinkite, the AsO_4^{3-} tetrahedra are situated between the sheets.

INTRODUCTION

The basic arsenates of manganese are a small group of very rare minerals which are quantized members of the general series $Mn_n^{2+}(OH)^-_{2n-3z}(AsO_4)_z^{-3}$. To date, no crystal structures of these peculiar species have been revealed and, consequently, their crystal chemistry is poorly understood.

In an earlier paper (Moore, 1965), the basic phosphates of manganese and iron were briefly reviewed in a structural classification based on linkages of octahedra. To add other anisodesmic oxysalts, such as the arsenates, to this classification may lead to a unified crystallochemical classification of large groups of minerals which eventually could assist in understanding their interrelationships.

The basic arsenates of manganese usually have manganese:oxygen ratios between 1:2 and 1:3, distinct from the phosphates which usually have lower ratios due to their rather open structures. High ratios in the arsenates suggest incompleted sheets of oxygen octahedra which is entirely substantiated by the two structures presented in this paper. These structures, though not strict members of the quantized series, are nevertheless closely related.

Flinkite, $Mn_2^{2+}Mn^{3+}(OH)_4(AsO_4)$, was named by Hamberg (1889) after the great Swedish mineralogist Gustav Flink. It occurs as extremely rare deep greenish-brown feathery aggregates of crystals implanted upon caryopilite, barite, and other arsenates at the Harstigen Mine, Pajsberg (near Filipstad), Värmland, Sweden. Owing to its great rarity, its analysis was open to question until structure cell studies by Culver and Berry (1963) were shown to support it. I used their structure cell data

(Table 1) though the space group is *Pnma*, not *Pnna*. The present structure analysis was based on the composition given earlier.

Flinkite is distinct in containing both the divalent and trivalent states of manganese which adds interest to its structure analysis. Very few examples of anisodesmic oxysalt structures containing trivalent manganese are known. In fact, of the wealth of minerals containing essential manganese, structures are known for only relatively few.

Retzian, $Mn_2^{2+}Y^{3+}(OH)_4(AsO_4)$ was named by Sjögren (1897) after the Swedish naturalist Anders Jahan Retzius. Like flinkite, just a few specimens are preserved from its only locality at the Moss Mine, Nordmarks Odalfält, Värmland, Sweden. Its analysis was not understood until detailed structure cell studies were undertaken by Moore (1967). The combination of Gladstone-Dale and cell molecular weight calculations indicated that CaO and RE oxides reported by Mauzelius in Sjögren (1897) were primarily yttrium. The structure analysis of retzian was based on the formula ratios given above and the cell data given in Table 1.

TABLE 1. FLINKITE AND RETZIAN. STRUCTURE CELL DATA

	Flinkite	Retzian
a	9.55 Å	5.670±0.004 Å
b	13.11	12.03 ±0.01
c	5.25	4.863±0.004
Z	4	2
S.G.	*Pnma*	*Pban*
Ideal formula	$Mn_2^{2+}Mn^{3+}(OH)_4(AsO_4)$	$Mn_2^{2+}Y^{3+}(OH)_4(AsO_4)$
Reference	Culver and Berry (1963); this paper	This paper

Though both retzian and flinkite have formulae suggesting isotypy, their structures are not closely related.

EXPERIMENTAL DATA

Crystals of flinkite were kindly donated by Prof. L. G. Berry and Mr. Paul E. Desautels. Neither were suitable for structure analysis but after some effort a fragment was secured from the latter material. It measured 0.06×0.20×0.30 mm and consisted of two crystals in near-parallel growth. 171 independent intensities of the *hk*0 and *h*0*l* projections were gathered on five sets of Weissenberg films using Zr-filtered Mo radiation, employing a spot scale of 20 units obtained from the fragment. These data were then processed with the absorption correction program GNABS of C. W. Burnham.

For retzian, a broken fragment of a type crystal was used—nearly a cube in shape of 0.26 mm mean length. A total of 255 independent intensities were gathered of the *h*0*l*-*h*7*l* levels with a manual Weissenberg counter-diffractometer using Zr-filtered Mo radiation.

These data were not corrected for absorption effects due to uncertainties in the atomic absorption coefficient for yttrium.

SOLUTION OF THE STRUCTURES

The flinkite structure has four molecules of $Mn_2Mn(OH)_4(AsO_4)$ in a unit cell of space group *Pnma*. Thus, Mn^{3+} and As^{5+} must reside on special positions, the latter on a mirror plane at $y=1/4$ with two degrees of freedom due to the expected tetrahedral nature of the arsenate group. The trivalent manganese could either appear on the mirror plane with two degrees of freedom or at the origin of the cell with no degrees of freedom.

The structure was then solved by vector sets applied to the Patterson projections $P(uv)$ and $P(uw)$. The metals were located in this manner and the oxygen atoms were obtained from subsequent Fourier electron density syntheses. A final full-matrix least squares coordinate-isotropic temperature factor refinement led to $R_{hk0,h0l}=0.144$. The coordinates of the two manganese, one arsenic, and five oxygen atoms in an asymmetric unit of structure and their isotropic temperature factors are given in Table 2.

TABLE 2. FLINKITE AND RETZIAN. COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B	
		Flinkite			
Mn (1)	0	0	0	1.26±0.17	
Mn (2)	0.0205±0.0006	0.1319±0.0006	0.4875±0.0022	1.41± .15	
As	0.1542± .0007	3/4	0.0257± .0020	0.47± .12	
O (1)[a]	0.1398± .0032	0.0756±0.0026	0.1617± .0087	1.31± .56	
O (2)	−.0916± .0030	0.1474±0.0024	0.8361± .0079	0.96± .51	
O (3)[a]	−.0994± .0030	0.0059±0.0024	0.2974± .0066	1.06± .47	
O (4)	0.0988± .0054	3/4	0.7067± .0065	1.00± .62	
O (5)	0.1705± .0042	1/4	0.5438± .0131	0.98± .74	
		Retzian			
					M[b]
Y	1/4	1/4	0	0.06±0.09	1.18
As	3/4	1/4	1/2	0.44±0.14	1.00
Mn	1/4	0.5548±0.0008	0	0.81±0.16	1.80
O (1)	0.5769±0.0048	0.3198±0.0036	0.3045±0.0054	1.09±0.48	4.00
O (2)[a]	0.5783±0.0044	0.5770±0.0034	0.2010±0.0049	1.08±0.47	4.00

[a] Hydroxyl oxygens.

[b] Multipliers locked into final refinement.

TABLE 3. RETZIAN. CRYSTAL CHEMISTRY

	Analysis of Mauzelius	M.W. in cell	Moles in cell	Theoretical[a]
MgO	2.7	22.94	0.57	2.7
CaO	19.2	163.16	2.91	32.8 (as X_2O_3)
R. E. Oxides	10.3	87.53	—	
MnO	30.2	256.64	3.62	29.4
FeO	1.7	14.45	0.20 (Fe)	1.7 (Fe_2O_3)
PbO	0.2	1.70	0.01	—
As_2O_5	24.4	207.35	1.80 (As)	24.1
SiO_2	0.5	4.25	0.07	0.6
H_2O	8.4	71.38	7.92 (OH)	8.7
	97.6			100.0
+4.3% insol.	4.3			
	101.9			

	Specific refractive energy contributions
MgO	0.005
CaO	0.053 (as X_2O_3)[b]
R. E. Oxides	
MnO	0.056
Fe_2O_3	0.005
PbO	—
As_2O_5	0.041
SiO_2	0.001
H_2O	0.029
	0.190

[a] Composition based on structure cell formula.

[b] Calculated from $(\alpha+\beta+\gamma/3)$ and the contributions of the other oxides.

The structure of retzian was solved directly. First, a few words should be mentioned about its composition. Owing to its extreme rarity, the analysis of retzian by Mauzelius in Sjögren (1897) was on 79.5 mg of material and its composition could not be established with certainty. The crystal chemistry was investigated by Moore (1967) and calculations mentioned earlier suggested an approximate composition $Mn^{2+}Y^{3+}(OH)_4(AsO_4)$. Limited substitutions apparently occur in retzian with (Mg, Fe)→Mn; Fe, Si→As; and RE→Y. The retzian crystal chemistry is summarized in Table 3. Since very little material was analyzed, errors in the analysis are largely unknown. Further, yttrium was deduced from calculations based on this analysis and on the specific refractive energies of the other known contributors. Since no great claims to truth are expressed in these deductions, the structure analysis of retzian is largely a study of a compound with an unknown composition. Results of this structure analysis are in general agreement with the formula suggested above.

Since the retzian cell contains two Y, two As, four Mn and sixteen (O,OH) atoms, the Y and As atoms must be confined to positions with point symmetry 222, having no degrees of freedom. Furthermore, this provides the orientation of the arsenate groups. The four Mn atoms were then placed in point positions 2 with one degree of freedom. The remaining eight (OH) atoms in the general positions with three degrees of freedom were approximately deduced from packing considerations. Thus, there are only five atoms in the asymmetric unit.

Refinement proceeded until $R=0.124$ for all reflections. When 67 zero intensities and 68 weak intensities ($F^2hkl<0.03F^2$ largest intensity) were excluded, $R=0.062$. It was also necessary to vary the atom multiplicities for Mn and Y. The multiplicities decreased the scattering density for Mn by 10 percent and increased Y by 19 percent. The decrease in Mn density is evidently due to Mg substitution for Mn, as suggested by the chemical analysis. Since yttrium was deduced by crude calculations, some of it is apparently replaced by members of the much denser lanthanide series. The over-all R-factor, higher than expected for scintillation counter data reflects the uncertainties in the shapes of the scattering curves for (Mn, Mg) and (Y, R.E.), the absence of transmission factor corrections for a dense crystal, and a high background due to fluorescing yttrium along with a large fraction of low intensity reflections. The coordinates, isotropic temperature factors, and multiplicities (obtained prior to final temperature factor refinement) are presented in Table 2. Table 5[1] lists the observed and final calculated structure factors of flinkite and retzian.

Discussion of the Structures

Though the compositions of flinkite and retzian suggest isotypy, the great differences in crystal radii between Mn^{3+} and Y^{3+} result in structures which are only remotely related. Both structures are built of sheets of $Mn^{2+}-Mn^{3+}(Y^{3+})$-oxygen polyhedra held together by arsenate tetrahedra (Fig. 1–2).

The flinkite structure has infinite chains of distorted edge-linked

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[1] Table 5 has been deposited as Document No. 9659 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. 20540. Copies may be secured by citing the document number, and remitting in advance $1.25 for photoprints or $1.25 for 35 mm microfilm.

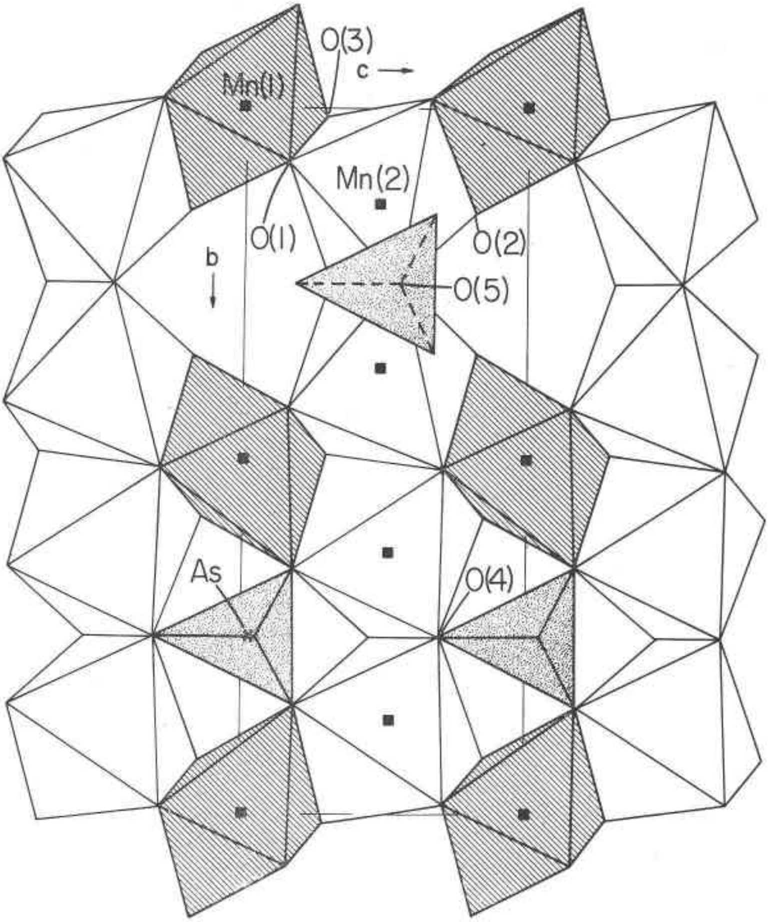

FIG. 1. The crystal structure of flinkite in the *bc* plane. One sheet of octahedra is shown and only a few of the arsenate tetrahedra between the sheets are drawn in. The Mn^{3+} octahedra are ruled.

$Mn^{2+}-O$ octahedra having mean distance of 2.19 Å and $Mn^{3+}-O$ square bipyramids which link these chains together forming an open sheet. The flinkite crystal structure offers us one of the very few examples of the presence of both Mn^{2+} and Mn^{3+} cations making up a fairly densely packed coordination complex. For the following well-known discussion flinkite is taken to be a transition metal coordination complex with OH^- and tetradentate AsO_4^{3-} tetrahedra as the participating ligands.

The electronic configuration of Mn^{3+} is [Ar] $3d^4$ where [Ar] is the closed argon core. The Mn^{3+} electronic configuration in an octahedral field is further assumed to be that consistent with a weak crystal field, *i.e.*, a high spin arrangement. Using the conventional crystal field nomenclature, three electrons with parallel spins are placed in the t_{2g} orbitals and one in the e_g orbital, either in the d_{z^2} or $d_{x^2-y^2}$ suborbitals. The electron density of the $d_{x^2-y^2}$ suborbital is situated in a square plane, the nodes pointing toward the octahedral vertices. The d_{z^2} electron density is normal to this plane, pointing toward the two remaining vertices of the octahedron. If the $d_{x^2-y^2}$ suborbital is energetically lower than the d_{z^2} suborbital, the e_g electron is placed here. Consequent repulsion by the negatively charged ligands results in a compressed octahedron—a flattened square bipyramid. For the electron in the d_{z^2} suborbital, an elongated square bipyramid results, the arrangement most frequently observed. These arguments properly refer to a cubic crystal but they seem to explain the observations on the Mn^{3+} octahedral sites of point symmetry $\bar{1}$ in flinkite. These strong Jahn-Teller distortions occur in weak crystal fields for d^4 or d^9 complexes— that is, for Mn^{3+} or Cu^{2+} complexes. There are abundant structural data confirming Jahn-Teller distortions for Cu^{2+} complexes. Typical distances are summarized in International Tables, Vol. 3(1962), where four $Cu^{2+}-O$ distances average 1.97 Å and two average 2.46 Å. Very few examples for $Mn^{3+}-O$ complexes are known. The best example is MnF_3 (Hepworth, Jack, and Nyholm, 1957) where there are two $Mn^{3+}-F$ distances ~1.79 Å, two $Mn^{3+}-F$ distances ~1.91 Å, and two $Mn^{3+}-F$ distances ~2.09 Å, the last being unusually long bond lengths. This is compared with two $Mn^{3+}-O(3)$ ~1.80 Å, two

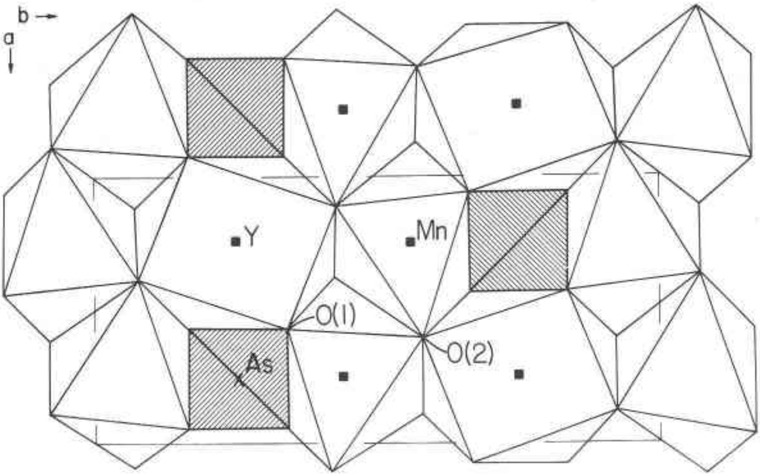

FIG. 2. One sheet of the crystal structure of retzian. Note that the ruled arsenate tetrahedra reside between sheets.

$Mn^{3+}-O(1)\sim1.91$ Å, and two $Mn^{3+}-O(2)\sim2.29$ Å for flinkite, the standard deviations being ±0.05 Å. This distortion accounts for a difference of ~0.4 Å between the distances *in* the square plane and the two apical distances *normal* to it.

For Mn^{2+}, the configuration is d^5 and in a weak field a high-spin complex results. Since repulsions are nearly uniformly directed along the planar and apical axes of the octahedron, the greatest differences in distances should be significantly less than those for the Mn^{3+} complex. In flinkite, this difference is ~0.12 Å, corresponding to a mildly distorted octahedron.

TABLE 4. FLINKITE AND RETZIAN. SOME INTERATOMIC DISTANCES

Flinkite[a]				Retzian[b]			
Octahedral Distances		Tetrahedral Distances		Octahedral Distances		Square Antiprism Distances	
(2) Mn(1)-O(1)	1.91 Å	(2)As-O(2)	1.64 Å	(2)Mn-O(1)	2.33 Å	(4) Y-O(1)	2.52 Å
(2) Mn(1)-O(3)	1.80	(1)As-O(4)	1.76	(2)Mn-O(2)	2.10	(4) Y-O(2)	2.50
aver.	1.86 Å	(1)As-O(5)	1.66	(2)Mn-O(1′)	2.12	aver.	2.51 Å
(2) Mn(1)-O(2)	2.29 Å	aver.	1.68 Å	aver.	2.18 Å		
		O-O Distances for Tetrahedron				Tetrahedral Distances	
(1) Mn(2)-O(2)	2.13 Å	(1)O(2)-O(2′)	2.69 Å			(4) As-O(1)	1.60 Å
(1) Mn(2)-O(3)	2.24	(1)O(4)-O(5)	2.83				
(1) Mn(2)-O(3′)	2.26	(2)O(2)-O(4)	2.75				
(1) Mn(2)-O(1)	2.18	(2)O(2)-O(5)	2.71			O-O Distances for Tetrahedron	
(1) Mn(2)-O(5)	2.14	aver.	2.74 Å			(2)O(1)-O(1′)	2.58 Å
(1) Mn(2)-O(4)	2.21					(4)O(1)-O(1″)	2.54
aver.	2.19 Å						2.55 Å

[a] Errors: Mn-O ± 0.05 Å, As-O ± 0.05 Å, O-O ± 0.08 Å.
[b] Errors: Mn-O ± 0.06 Å, Y-O ± 0.06 Å, As-O ± 0.06 Å, O-O ± 0.09 Å.

Remaining are the arsenate groups which, for flinkite, are distorted tetrahedra (Table 4). The distances deviate considerably from regularity, with ranges from 1.64 Å to 1.76 Å (all ± 0.05 Å), the average being 1.68 Å. The crystal structure of clinoclase, $Cu_3(OH)_3(AsO_4)$ by Ghose *et al.*, (1965) gave As—O distances ranging from 1.68 Å to 1.75 Å. Deviations from regularity appear to be typical for arsenate tetrahedra.

The crystal structure of retzian is an interesting sheet structure. Ribbons of $Mn^{2+}-O$ edge-linked octahedra are held together in a plane by $Y^{3+}-O$ square antiprisms. Figure 1 shows that this combination conserves space very well, leaving small cavities with square cross-section where tetrahedrally coordinated arsenic atoms are fitted between the sheets. The result is a stable structure in three-dimensions.

The $Mn^{2+}-O$ octahedra deviate considerably from regularity (Table 4), the mean $Mn^{2+}-O$ distance being 2.18 Å. The $Y^{3+}-O$ square antiprism has mean distance of 2.51 Å and is only slightly distorted. The hydroxyl and oxide ions obey Pauling's rule with $\xi O(2)=1.04$ and $\xi O(1)=1.96$.

The $As^{+5}-O$ tetrahedron is nearly regular, constrained by symmetry requirements. Its As—O distance is short: 1.60 ± 0.06 Å. Since the error associated with the As—O distance is quite high, this value may not be representative of the actual distance. The O—O distances associated with this tetrahedron are also quite short, the average being 2.55 Å, but the errors are ± 0.09 Å. Consequently, Si→As substitution might be expected, evidenced in the chemical analysis of Mauzelius, though this is apparently very limited. The substitution of silicon for arsenic in arsenate tetrahedra is a potentially important one as arsenates from Långban-type ore deposits often show the presence of minor to major amounts of silicon

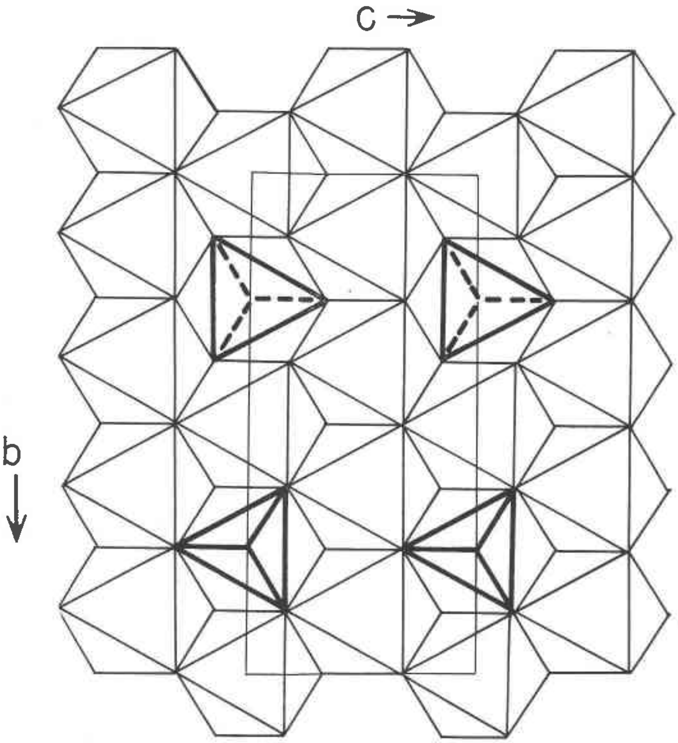

FIG. 3. The flinkite cell in the *bc* plane superimposed on a regular pyrochroite sheet.

in the analysis. The extent of such substitution cannot be presently assessed as no examples of possible extensive substitutions have been structurally analyzed.

FLINKITE: A PYROCHROITE-DERIVATIVE STRUCTURE

The crystal structure of pyrochroite, $Mn(OH)_2$, is of the brucite type—a sheet of hexagonally close-packed oxygen octahedra. Quite analogous is the structure of flinkite. In Figure 1, it is seen that along *b*, the Mn^{3+}-O octahedra alternate with hole-O octahedra. These dilated and distorted octahedral holes permit between-the-sheet linkage by the arsenate tetrahedra. If the flinkite structure is allowed to topologically deform into a regular pyrochroite-like sheet, the ideal arrangement in Figure 3 is the limit. This process of topological deformation may apply to other basic manganese arsenates as well, which could assist in their classification.

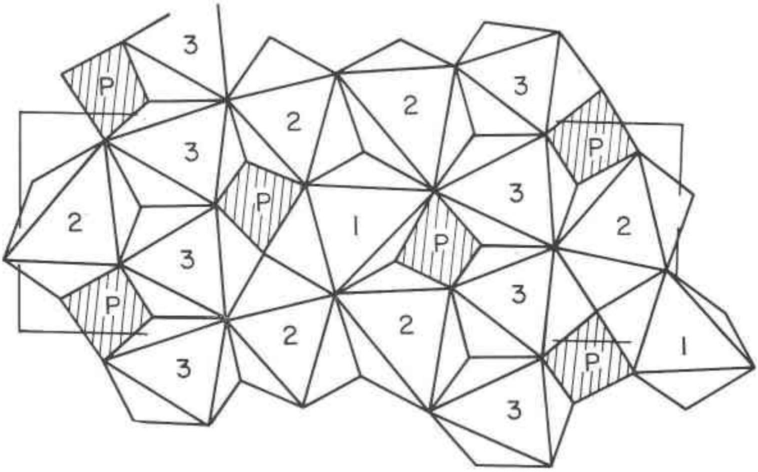

FIG. 4. Polyhedral diagram of pseudomalachite, $Cu_5(OH)_4(PO_4)_2$, structure, showing one octahedral sheet. The PO_4^{3-} tetrahedra are in the hatched areas between the sheets. Numbers on octahedra refer to the different non-equivalent atoms. The coordinates are from Ghose (1963).

A curious example of topological deformation of distorted octahedral sheets which *does not* lead to a pyrochroite sheet is offered by pseudomalachite, $Cu_5(OH)_4(PO_4)_2$. The octahedra are so severely distorted that a pyrochroite sheet—including octahedral holes—cannot be obtained without breaking some bonds and rejoining the polyhedra. The pseudomalachite structure was solved by Ghose (1963), and I used his coordinates to draw the polyhedral diagram of one sheet of octahedra in Figure 4. The orthophosphate tetradentate tetrahedra, as in flinkite, are situated between the sheets. It is seen that three octahedra (1,2, and 3 in the drawing) *and* an open space coordinate at one point; consequently, pseudomalachite is not a pyrochroite derivative structure. In this light, the structure of arsenoclasite, $Mn_5(OH)_4(AsO_4)_2$ would be illuminating and it is presently being studied.

ACKNOWLEDGEMENTS

This work was made possible by NSF Grant GA-572 awarded to Professor J. V. Smith as principal investigator.

REFERENCES

CULVER, K. B. AND L. G. BERRY (1963) Flinkite and atelestite. *Can. Mineral.*, **7:3,** 547–553.

GHOSE, S. (1963) The crystal structure of pseudomalachite, $Cu_5(PO_4)_4(OH)_4$. *Acta Crystallogr.* **16,** 124–128.

———, M. FEHLMANN AND M. SUNDARALINGAM (1965) The crystal structure of clinoclase. *Acta Crystallogr.* **18,** 777–787.

HAMBERG, A. (1889) Ueber Flinkit, ein wasserhaltiges Manganarseniat aus der Grube Harstigen bei Pajsberg in Vermland. *Geol. Fören. Förhandl.* **11,** 212.

HEPWORTH, M. A., K. H. JACK AND R. S. NYHOLM (1957) Interatomic bonding in manganese trifluoride. *Nature* **179,** 211.

International Tables for X-ray Crystallography, Vol. 3(1962) Physical and chemical tables. Kynoch Press, Birmingham, England, 268.

MOORE, P. B. (1965) A structural classification of Fe-Mn orthophosphate hydrates. *Amer. Mineral.* **50,** 2052–2062.

——— (1967) Contributions to Swedish mineralogy. 1. Studies on the basic arsenates of manganese: retzian, hemafibrite, synadelphite, arsenoclasite, arseniopleite, and akrochordite. *Ark. Min. Geol.*, in press.

SJÖGREN, HJ. (1897) Retzian och dess sammansättning. *Geol. Fören. Förhandl.* **19,** 106–112.

Manuscript received, April 10, 1967; accepted for publication, September 20, 1967.