

CRYSTAL CHEMISTRY OF THE BASIC
MANGANESE ARSENATES:
V. MIXED MANGANESE COORDINATION IN THE
ATOMIC ARRANGEMENT OF ARSENOCLASITE

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ABSTRACT

Arsenoclasite, $Mn_4(OH)_6(AsO_4)_2$, a 18.29 (2), b 5.75 (1), c 9.31 (2) Å, $Z=4$, space group $P 2_12_12_1$, is based on "double" hexagonal close-packed ($\cdots ch \cdots$) oxygen anions whose layers are normal to the c -axis. Its structure was deciphered from direct methods, and $R(hkl)=0.07$ for 1800 independent reflections.

The cationic occupancies are very complicated. Three non-equivalent octahedra, Mn(2)-O, Mn(3)-O and Mn(4)-O, link by edge-sharing to form walls alternately one- and two-octahedra wide which run parallel to the b -axis. Also running parallel to this axis are chains of corner-sharing Mn(1)-O trigonal bipyramids which further link by corner-sharing to As(2)-O tetrahedra forming three-membered rings; and chains of corner-linked As(1)-O and Mn(5)-O tetrahedra.

The interatomic Me-O averages are Mn(1)^V-O 2.19, Mn(2)^{VI}-O 2.25, Mn(3)^{VI}-O 2.22, Mn(4)^{VI}-O 2.19, Mn(5)^{IV}-O 2.13, As(1)^{IV}-O 1.67 and As(2)^{IV}-O 1.69 Å. Although the Mn(5)^{IV}-O polyhedron is of distorted tetrahedral shape, the Mn(5) cation resides nearly in the plane of the base and the polyhedron is more properly a trigonal pyramid.

INTRODUCTION

Systematic structural investigations on members of the series $Mn^{2+n}(OH)_{2n-3z}(AsO_4)^{3-z}$ by Moore (1967a, 1967b, 1968a, 1968b, 1970a) shall lead to novel insights concerning the interaction between crystal-chemical homology and paragenesis. We report studies on the atomic arrangement of yet another member, arsenoclasite.

Arsenoclasite, $Mn_5(OH_4)(AsO_4)_2$, was first described by Aminoff (1931) as a new species from the famous Långban mines, in the province of Värmland, Sweden. It occurs in the paragenesis adelite-sarkinite-arsenoclasite in calcite-filled fissures cutting hausmannite impregnated dolomitic marble from the "Irland" drift. Both arsenoclasite and sarkinite crystallized later than adelite but it is difficult to decipher the relative positions in time for the first two species. Flink (1924) discussed the occurrences of sarkinite at Långban and noted some specimens with the characteristic flesh-red color of sarkinite but with one perfect cleavage. As shown by Aminoff, "sarkinites" with perfect cleavage proved to be arsenoclasite. Moore (1967b) re-investigated type arsenoclasite, confirmed the crystal cell data of Aminoff, and established the uniquely determined space group $P 2_12_12_1$. This present investigation was performed on the same crystal used in that study.

EXPERIMENTAL

Crystal cell parameters are presented in Table 1, citing the paper of Moore (1967b) which also includes indexed powder data. A crystal of 0.0003 mm³ volume was selected for three-dimensional structure analysis utilizing a PAILRED diffractometer and graphite "monochromatized" MoK_α radiation. With *c* as the rotation axis, 4800 reflections including the symmetry equivalent pairs *I*(*hkl*) and *I*($\bar{h}kl$) from the *l*=0- to 12-levels were obtained using a 2.2° half-angle scan and a background counting time on both sides of each peak of 20 seconds.

At first, the individual reflections were processed to obtain raw *F*(*obs*) data. Since $\mu = 137$ cm⁻¹, polyhedral transmission correction was applied using a local version of the GNABS program (Burnham, 1963) and symmetry equivalent reflections were averaged. Remaining were 1800 independent reflections above background error and 620 independent reflections of "zero" intensity. Only the non-zero data were used in the following study.

SOLUTION OF THE STRUCTURE

Solution of the arsenoclasite atomic arrangement was a miserable problem. At first, attempts were made to decipher the structure on the basis of a structural relationship with pseudomalachite but several trials of heavy atom refinement failed. One key to the solution of the structure was the subsequent assumption that arsenoclasite is based on oxygen close-packing, a typical feature among the known basic manganese arsenate structures. Accordingly, the assumed structural relationship

TABLE 1. CRYSTAL CELL DATA FOR ARSENOCLASITE,
CORNWALLITE AND PSEUDOMALACHITE.

| | Arsenoclasite | Cornwallite | Pseudomalachite |
|--|--|--|---|
| <u>a</u> (Å) | 18.29 (2) | 17.61 | 17.06 |
| <u>b</u> (Å) | 5.75 (1) | 5.81 | 5.76 |
| <u>c</u> (Å) | 9.31 (2) | 4.60 | 4.49 |
| β | 90° | 92°15' | 91°02' |
| space group | P2 ₁ 2 ₁ 2 ₁ | P2 ₁ /a | P2 ₁ /a |
| Z | 4 | 2 | 2 |
| formula | Mn ₅ (OH) ₄ (AsO ₄) ₂ | Cu ₅ (OH) ₄ (AsO ₄) ₂ | Cu ₅ (OH) ₄ (PO ₄) ₂ |
| ρ <u>obs</u> | 4.16 ¹ | | 4.30-4.35 |
| ρ <u>calc</u> (gm/cm ³) | 4.21 | 4.68 | 4.34 |
| reference | Moore (1967b) | Berry (1951) | Berry (1950) |

¹Aminoff (1931)

with pseudomalachite had to be abandoned. The relationship $a/6 \sim b/\sqrt{3} \sim 3.2 \text{ \AA}$ suggested that the a -axis is the sum of six $\text{Mn}^{2+}\text{-O}$ octahedral edges, and the relationship with b automatically defines the orientation of the octahedral voids. Furthermore, $c/4 \sim 2.3 \text{ \AA}$, the typical oxide layer separation in close-packed structures. Tests of several electrostatically plausible heavy atom models were undertaken, but all failed.

It was then decided to attempt solution by direct methods using a tangent routine adapted for non-centrosymmetric crystals, as described by Dewar (1970). Normalized structure factors were calculated from the observed structure magnitudes applying a scale factor and an overall isotropic temperature factor obtained by the method of Wilson (1942). The four two-dimensional reflections initially chosen to select the origin and the enantiomorph led to a meaningless solution. On the second attempt, the reflections (160), (041), (671), (144), and (511) were assigned the values $\pi/2$, 0, x , y , and z respectively. Symbolic addition applied to these reflections with the program MAGIC (Dewar, 1970) yielded 118 additional phases with a variance ≤ 0.65 and indicated that $y = -\pi/2$, $x - z = \pi/2$, and $x = -\pi/4$ or $3\pi/4$. Setting $x = 3\pi/4$ and $z = \pi/4$ satisfied the criterion for origin and enantiomorph selection. The 123 phases from MAGIC were submitted to tangent formula refinement. After two cycles, a total of 263 reflections were determined with $E > 1.3$ and the phase shifts indicated reasonable convergence. An E -map calculated from these reflections appears in Figure 1 with location of the final heavy metal positions superimposed.

It is apparent that the E -map contained the sufficient heavy atom information for successful atomic parameter location and convergence through Fourier synthesis. The correct ascription of the initial atomic positions and species was facilitated by the previous assumption of oxygen close-packing. Approximate metal-metal distances which were compatible with sensible crystal chemistry expected for a basic manganese arsenate combined with relative peak heights led to peaks A, B, C, D, E, F = As(1), As(2), Mn(5), Mn(4), Mn(2) and Mn(3) respectively (Fig. 1). The reliability index,

$$R(hkl) = \frac{\sum || F(obs) | - | F(calc) ||}{\sum | F(obs) |} = 0.39$$

for this arrangement. A Fourier synthesis of the phases calculated revealed the Mn(1) atom which corresponds to the feeble peak labelled "G" in Figure 1. Further Fourier syntheses followed by parameter refinement for the metals led to $R(hkl) = 0.20$. At this stage, eight non-equivalent oxygen atoms were located on the Fourier map and a double

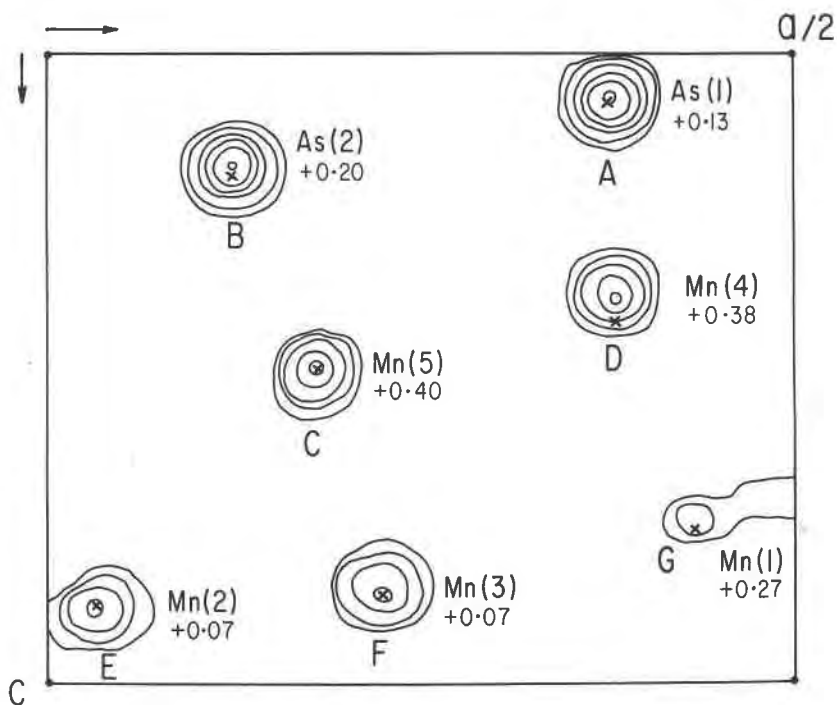


FIG. 1. Projection of the three-dimensional E -map down the b -axis resulting from the direct determination of 263 symmetry independent phase angles. The approximate y coordinates obtained from the three-dimensional map as well as the final heavy metals and their positions refined by least-squares are included.

hexagonal close-packed motif became apparent. The remaining four atoms were approximately located by interatomic distance calculations. Typical for a close-packed structure, some of the light atoms had to be "coaxed" along even at the stage of the relatively low reliability index mentioned above.

REFINEMENT

The arsenoclasite asymmetric formula unit constitutes one molecular unit of $H_4Mn_5As_2O_{12}$. Atomic coordinates of the five manganese, two arsenic and twelve oxygen atoms were refined using a local version of the familiar ORFLS least-squares program of Busing, Martin and Levy (1962) for the IBM 7094 computer. Finally, scale factor, atomic coordinate and isotropic thermal vibration parameters were refined on the basis of full-matrix inversion until the parameter shifts were within their limits of error. The final reliability index was $R(hkl) = 0.070$ for 1800

TABLE 2. ARSENOCLASITE: ATOMIC COORDINATES, CATION COORDINATION NUMBERS AND ISOTROPIC THERMAL VIBRATION PARAMETERS.
(Estimated standard errors in parentheses).

| | x | y | z | B (\AA^2) |
|--------------------------|------------|-------------|-------------|----------------------|
| Mn(1) V | 0.4323 (1) | 0.2697 (5) | 0.7522 (3) | 0.65 (3) |
| Mn(2) VI | .0303 (1) | .0544 (5) | .8886 (3) | .61 (3) |
| Mn(3) VI | .2214 (1) | .0712 (5) | .8582 (3) | .59 (3) |
| Mn(4) VI | .1241 (2) | .5587 (5) | .8796 (3) | .76 (3) |
| Mn(5) IV | .3164 (2) | .5804 (5) | .0009 (3) | .71 (3) |
| As(1) IV | .3744 (1) | .1117 (3) | .0719 (2) | .08 (2) |
| As(2) IV | .1243 (1) | .1928 (3) | .1838 (2) | .01 (2) |
| O(1) = (OH) ⁻ | .0519 (7) | .7350 (26) | .0215 (16) | .98 (21) |
| O(2) = (OH) ⁻ | .2025 (7) | .3844 (26) | .7397 (16) | .96 (18) |
| O(3) = (OH) ⁻ | .0412 (7) | .3676 (25) | .7569 (16) | .90 (17) |
| O(4) = (OH) ⁻ | .2171 (7) | .7461 (25) | -.0282 (15) | .90 (17) |
| O(5) | .1461 (6) | .4441 (23) | .2643 (15) | .62 (16) |
| O(6) | .1279 (9) | .2324 (24) | .0012 (17) | 1.04 (18) |
| O(7) | .1762 (7) | -.0277 (24) | .2332 (16) | .87 (16) |
| O(8) | .0380 (7) | .0980 (26) | .2282 (16) | 1.00 (19) |
| O(9) | .3755 (8) | .1103 (23) | .2508 (15) | .95 (17) |
| O(10) | .2934 (7) | .2187 (24) | .0206 (15) | .69 (17) |
| O(11) | .4342 (7) | .3007 (24) | -.0004 (16) | .87 (19) |
| O(12) | .3916 (7) | .8448 (25) | .0155 (16) | 1.07 (17) |

reflections, constituting a data to variable parameter ratio of about 25:1.

Final atomic and isotropic thermal vibration parameters are listed in Table 2. The oxygen thermal vibration parameters range from 0.6 to 1.1 \AA^2 , typical values for oxygen close-packing. The Mn^{2+} parameters range from 0.6 to 0.8 and As^{5+} from 0.0 to 0.1 \AA^2 . The $|F(\text{obs})| - F(\text{calc})$ data appear in Table 3.¹

¹ To obtain a copy of Table 3, order NAPS Document No. 01521 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York, 10022; remitting \$3.00 for microfiche or \$5.00 for photocopies, payable in advance to CCMIC-NAPS.

DISCUSSION OF THE STRUCTURE

Arsenoclasite has been generally regarded as structurally related to pseudomalachite, $\text{Cu}_5(\text{OH})_4(\text{PO}_4)_2$ and cornwallite, $\text{Cu}_5(\text{OH})_4(\text{AsO}_4)_2$, and their crystal cell relationships are summarized in Table 1. Palache, Berman, and Frondel (1951) classify arsenoclasite with pseudomalachite and Strunz (1970) places all three compounds together and suggests that arsenoclasite may possibly be derived from the others on the basis of unit cell twinning.

Despite the marked similarity in compositions and crystal cells, arsenoclasite is not closely related structurally to the other compounds except for the presence of the same kind of octahedral wall revealed in the structure of pseudomalachite investigated by Ghose (1963). Pseudomalachite is based on sheets of distorted Cu^{2+} -O octahedra; arsenoclasite is based on walls and chains of three distinct coordination polyhedra: Mn^{VI} -O octahedra, Mn^{V} -O trigonal bipyramids and Mn^{IV} -O tetrahedra (trigonal pyramids).

Arsenoclasite is constructed of a "double" hexagonal close-packed array of oxygen atoms whose layers are stacked perpendicular to the *c*-axis. It shares this feature in common with flinkite, $\text{Mn}^{2+}_2\text{Mn}^{3+}(\text{OH})_4(\text{AsO}_4)$; allactite, $\text{Mn}_7(\text{OH})_8(\text{AsO}_4)_2$; and synadelphite, $\text{Mn}_9(\text{OH})_9(\text{H}_2\text{O})_2(\text{AsO}_3)(\text{AsO}_4)_2$ and we conclude that the oxygen stacking sequence ($\cdots \text{ch} \cdots$) is one of the more persistent underlying aspects of the basic manganese arsenate crystal chemistry. Figure 2 illustrates the population sequence along the *c*-axis. Oxygen atoms are situated at $z \sim 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$. The trigonal bipyramidally coordinated Mn(1) cations are located at $z \sim \frac{1}{4}$ and $\frac{3}{4}$. The octahedrally coordinated cations, Mn(2), Mn(3) and Mn(4) are distributed at $z \sim \frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$. The tetrahedrally coordinated cations As(1) and Mn(5), are located above and below $z \sim 0, \frac{1}{2}$ and tetrahedrally coordinated As(2) above and below $z \sim \frac{1}{4}, \frac{3}{4}$. The crystallochemical formula can be written $\text{Mn}_3^{\text{VI}}\text{Mn}^{\text{V}}\text{Mn}^{\text{IV}}(\text{OH})_4(\text{As}^{\text{IV}}\text{O}_4)_2$; thus, $\frac{1}{4}$ of the available octahedral voids are occupied. The trigonal bipyramid is constituted of two tetrahedral voids joined by face-sharing with Mn(1) at the center of the shared face. Consequently, $\frac{5}{24}$ of the available tetrahedral voids are utilized by cations.

It is instructive to examine the oxygen packing density in the arsenoclasite structure. All close-packed layers are fully occupied with respect to anions and the volume per oxygen atom is 20.4 \AA^3 . This value can be compared with cubic close-packed manganosite, MnO, which has a volume of 21.8 \AA^3 , the major oxygen volume difference between the two doubtlessly arising from the more tightly bound As^{5+} -O tetrahedra in arsenoclasite.

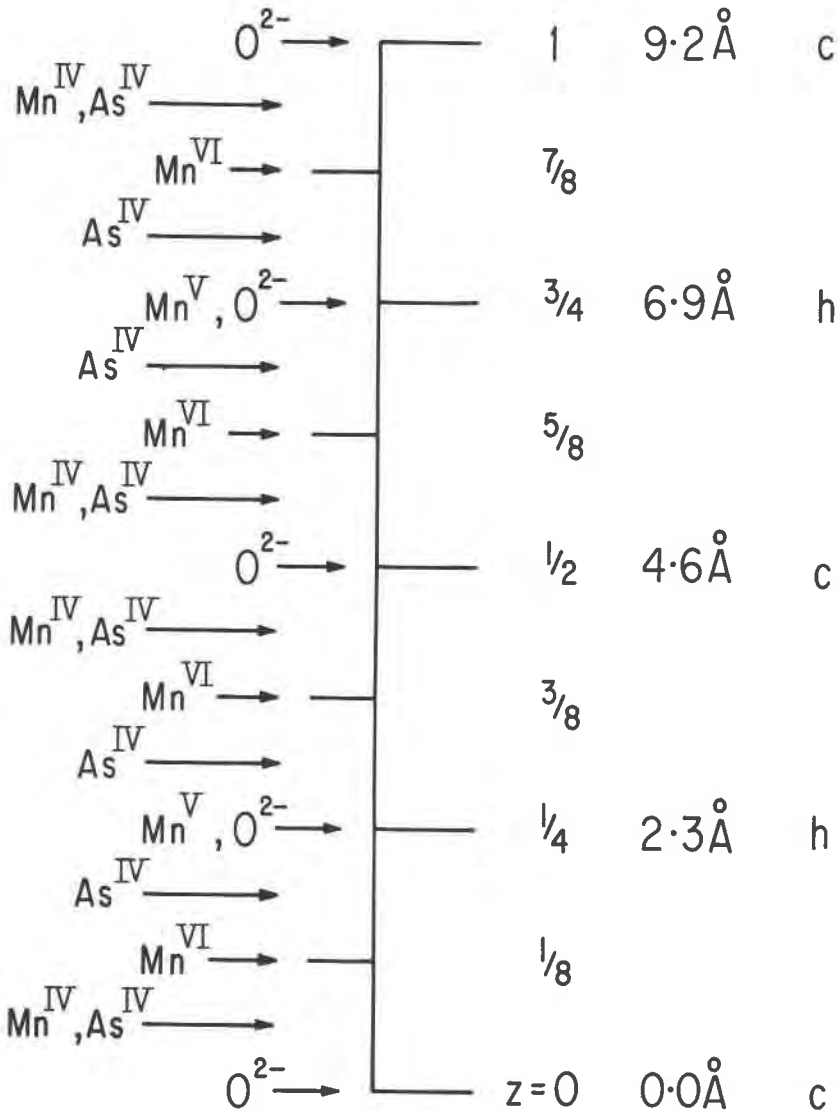


FIG. 2. Idealization of the population sequence of cations and their coordination numbers and anions along the z -direction in arsenoclasite. Heights are given as fractional and absolute coordinates with respect to the c -axis. The letters "c" and "h" refer to the centers of the cubic and hexagonal close-packed blocks respectively.

To describe thoroughly the very complex yet aesthetically pleasing arsenoclasite structure requires careful dissection. The Mn(2)-, Mn(3)- and Mn(4)-oxygen octahedra join by edge-sharing to form a wall of octahedra, alternately one- and two-octahedra wide which runs parallel to the b -axis and which is oriented parallel to $\{001\}$. This wall defines the $b = 5.75 \text{ \AA}$ repeat and is the component also common to the pseudomalachite structure. It is featured in Figure 3a. Ghose (1964) has commented on the occurrence of this wall in other first transition series oxysalt structures as well, including its presence in hydrozincite, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, and lindgrenite, $\text{Cu}_3(\text{OH})_2(\text{MoO}_4)_2$, the latter structure determined by Calvert and Barnes (1957). It is also the component in the kotoite, $\text{Mg}_3(\text{BO}_3)_2$, crystal structure, as discussed by Moore (1970b). Projected down the b -axis, the walls are stacked like brickwork as a result of the two-fold screw operations (Fig. 4) and possess no obvious stacking relationship to pseudomalachite.

The Mn(1)-O trigonal bipyramids link along two corners to form infinite chains which also run parallel to the b -axis. One of these corners also joins to the As(2)-O tetrahedron forming chains of Mn(1)-As(2)-Mn(1) three-membered rings (Figure 3b). This composite chain links through vertices at a common level along z by corner-sharing to the octahedral wall.

A third type of chain, also running parallel to the b -axis, is present in arsenoclasite and consists of corner-sharing Mn(5)-As(1) tetrahedra (Figure 3c). This chain links laterally to an octahedral wall on either side and through its apical oxygen atoms to another symmetry equivalent octahedral wall. The tetrahedral vertex, O(11), is also joined to vertices of the Mn(1)-O trigonal bipyramids.

Assembled, the arsenoclasite structure is shown idealized in Figure 5. It is remarkable in possessing three distinct Mn-O coordination polyhedra and it is gratifying that direct methods succeeded in unravelling an arrangement that would have been very difficult to decipher by other procedures. The solution of the arsenoclasite structure also adds confidence to the application of direct methods to noncentrosymmetric mineral structures.

The perfect cleavage parallel to $\{100\}$ is explicable in a relative sense since this plane is parallel to the axis of the chains (b) and the axis normal to the close-packed layers (c), the directions of strong Me-O-Me bonds bridging between the chains and the oxygen layers.

INTERATOMIC DISTANCES

The arsenoclasite analysis of Blix in Aminoff (1931) indicates that the compound is nearly pure stoichiometric $\text{Mn}_5(\text{OH})_4(\text{AsO}_4)_2$. The reason-

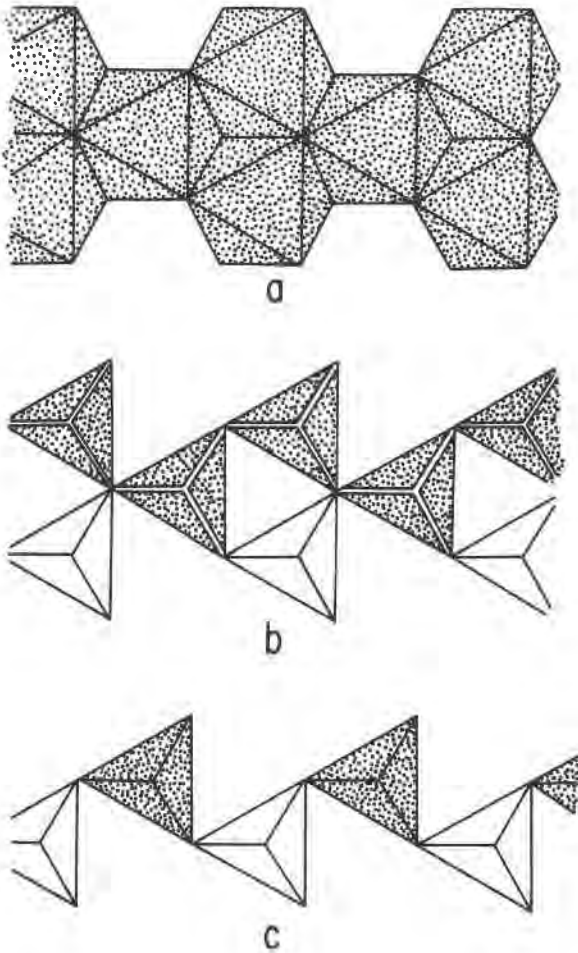


FIG. 3. Idealized polyhedral chains which are the components of the arsenoclasite structure projected down the c -axis. All chains run parallel to the b -axis.

- The wall of alternate one- and two-octahedra, comprised of the Mn(2)-, Mn(3)- and Mn(4)-oxygen octahedra.
- The corner-sharing chains of Mn(1)^V-O trigonal bipyramids (stippled) and As(2)-O tetrahedra. Note the presence of Mn(1)-Mn(1)-As(2) three-membered rings.
- The corner-sharing chain of alternate Mn(5)^{IV}-O trigonal pyramids (stippled) and As(1)-O tetrahedra.

able isotropic thermal vibration parameters for all ionic species attest to an ordered structure and the essential absence of substituting cations of different atomic number. We shall discuss the interatomic distances on the basis of an electrostatic model.

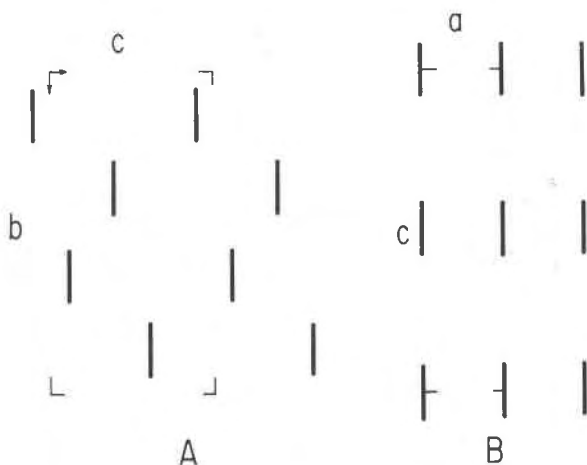


FIG. 4. Orientation of the geometrically equivalent octahedral walls in arsenoclasite (A) and pseudomalachite (B). The walls run perpendicular to the plane of the drawing and the connections between centers of the two-octahedra in the wall are drawn as bold lines.

According to such a model, effects on the Me-O distances should be noted if the anions are undersaturated or oversaturated electrostatically with respect to cations. Table 4 reveals that O(12), O(5), and O(7) are considerably undersaturated with $\Delta\Sigma = -.25$, $-.35$, and $-.42$ respectively; whereas O(6) and O(9) are considerably oversaturated both with $\Delta\Sigma = +0.25$. The remaining cations deviate only slightly from electrostatic neutrality.

Table 5 presents the Me-O and O-O' polyhedral distances in the arsenoclasite crystal structure. The polyhedral averages are Mn(1)^V-O 2.19, Mn(2)^{VI}-O 2.25, Mn(3)^{VI}-O 2.22, Mn(4)^{VI}-O 2.19, Mn(5)^{IV}-O 2.13, As(1)^{IV}-O 1.67 and As(2)^{IV}-O 1.69 Å. The Mn^{2+VI}-O and As^{5+IV}-O averages are typical for their polyhedra and have been recorded for numerous structures. The Mn^{2+V}-O trigonal bipyramidal average is considerably longer than the Mn^V-O 2.12 Å distance in eveite, Mn₂(OH)(AsO₄) (an isotype of andalusite) reported by Moore and Smyth (1968), but the environments in the two structures are quite different. The Mn^{2+IV}-O distance is considerably longer than the Mn^{IV}-O 2.04 Å tetrahedron reported by Moore (1970c) for manganostibite, Mn₅^{2+VI}Mn₂^{2+IV}Sb⁵⁺As⁵⁺O₁₂. It is difficult to suggest reasons for these differences without much speculation since the number of refined structures with Mn²⁺ in tetrahedral or five-fold oxygen coordination are few and no survey is practicable. Geometrically, the trigonal bipyramid is capable of continuous distortion and passes into the square pyramid. As for Mn(5)^{IV}-O in

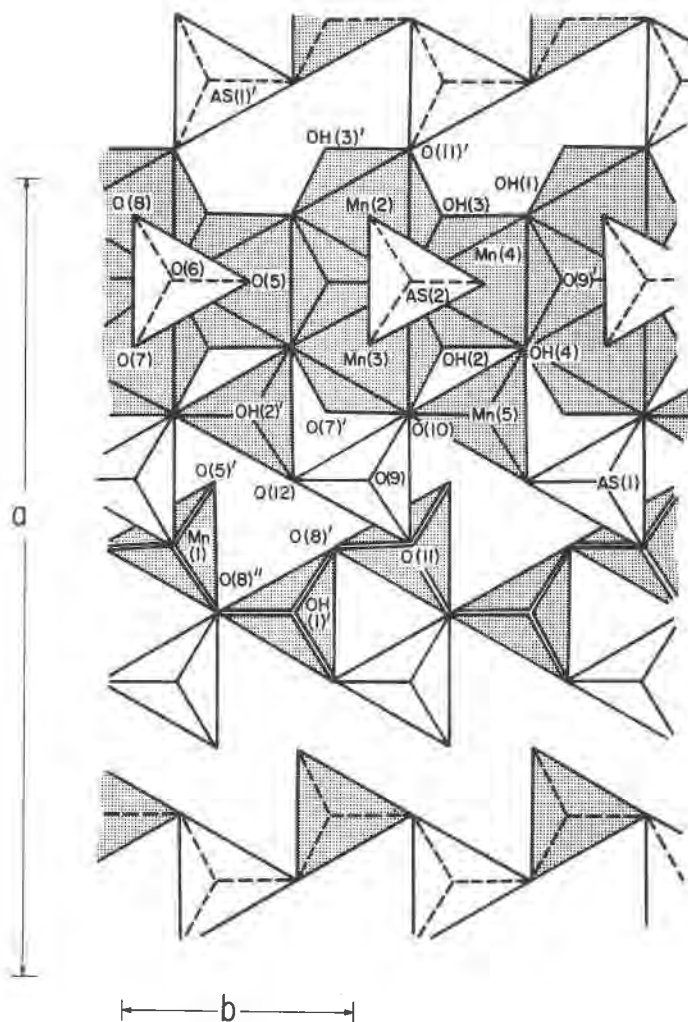


FIG. 5. Idealized polyhedral diagram of the arsenoclasite atomic arrangement down the *c*-axis, built from the components in Figure 3. All Mn-O polyhedra are stippled and the As-O tetrahedra are unshaded. The Mn(2)-, Mn(3)-, Mn(4)-O octahedral wall is centered at $z \sim \frac{3}{4}$. Labelling of the atoms conforms to the convention in Table 5. Comprehension of the three-dimensional polyhedral arrangement is further assisted by Figure 2.

arsenoclasite, the coordination polyhedron deviates considerably from a cation-centered tetrahedron since Mn(5) resides nearly in the plane of the base. For geometrical discussion, the oxygen polyhedron is tetrahedral in shape, but from an electronic standpoint, it is more properly

TABLE 4. ARSENOCLASITE: ELECTROSTATIC VALENCE BALANCES (Σ) ABOUT ANIONS^a.

| | | | Σ | $\Delta \Sigma$ |
|-------|-------------------------------|-----------------|----------|-----------------|
| OH(1) | Mn(1) + Mn(2) + Mn(4) | 2/5+2/6+2/6 | 1.07 | + .07 |
| OH(2) | Mn(3) + Mn(4) + Mn(5) | 2/6+2/6+2/4 | 1.17 | + .17 |
| OH(3) | Mn(2) + Mn(2) + Mn(4) | 2/6+2/6+2/6 | 1.00 | + .00 |
| OH(4) | Mn(3) + Mn(4) + Mn(5) | 2/6+2/6+2/4 | 1.17 | + .17 |
| O(5) | As(2) + Mn(1) | 5/4+2/5 | 1.65 | - .35 |
| O(6) | As(2) + Mn(2) + Mn(3) + Mn(4) | 5/4+2/6+2/6+2/6 | 2.25 | + .25 |
| O(7) | As(2) + Mn(3) | 5/4+2/6 | 1.58 | - .42 |
| O(8) | As(2) + Mn(1) + Mn(1) | 5/4+2/5+2/5 | 2.05 | + .05 |
| O(9) | As(1) + Mn(2) + Mn(3) + Mn(4) | 5/4+2/6+2/6+2/6 | 2.25 | + .25 |
| O(10) | As(1) + Mn(3) + Mn(5) | 5/4+2/6+2/4 | 2.08 | + .08 |
| O(11) | As(1) + Mn(1) + Mn(2) | 5/4+2/5+2/6 | 1.98 | - .02 |
| O(12) | As(1) + Mn(5) | 5/4+2/4 | 1.75 | - .25 |
| | | | | +0.00 |

^aThe $\Delta \Sigma$ for severely oversaturated or undersaturated anions are italicized.

a trigonal pyramid. The distinction between Mn(1)^V-O and Mn(5)^{IV}-O results from their cation locations in the stacking sequence (. . . ch . . .). Mn(1)^V is located at $z \sim \frac{1}{4}$ and $\frac{3}{4}$, which in Figure 1 are the centers of the hexagonal close-packed blocks and the cation must coordinate to apical anions above and below. Mn(5)^{IV} however, is located at $z \sim 0, \frac{1}{2}$, which are centers of the cubic close-packed blocks. Consequently, Mn(5)^{IV} coordinates to an apical anion above (below) but the apical anion below (above) is not present.

The only polyhedra which share edges are the Mn(2)-, Mn(3)- and Mn(4)-oxygen octahedra. As shown in Table 5, shared edges tend to be among the shortest for their polyhedra. The effects of electrostatic deviations from neutrality about anions are also apparent: the undersaturated anions show short Me-O distances on the average, whereas the oversaturated anions have longer Me-O distances than average. These accord with generally observed trends in oxysalt crystals add yet further confidence to the contention that three distinct coordination polyhedra for Mn²⁺ occur in arsenoclasite.

ACKNOWLEDGEMENTS

This study was supported by a Dreyfus Foundation grant and the NSF grant GA-10932 awarded to the senior author.

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Manuscript received, February 22, 1971; accepted for publication, April 14, 1971.