

MANGANOSTIBITE: A NOVEL CUBIC CLOSE-PACKED
STRUCTURE TYPEPAUL B. MOORE, *Department of the Geophysical Sciences*
University of Chicago, Chicago, Illinois, 60637

ABSTRACT

Manganostibite is orthorhombic, space group *Ibmm*, with $a=8.727$ (5), $b=18.847$ (6), $c=6.062$ (4) Å. The ideal formula is $Mn^{2+}_7Sb^{5+}As^{5+}O_{12}$, $Z=4$. Regrouping of cations according to coordination number leads to the general formula $M_6O_2[T_3O_{10}]$, where $M=(Mn_6Sb)^{VI}$ and $T=(Mn_2As)^{IV}$.

Oxygen atoms occur in a cubic close-packed arrangement and their layers are stacked parallel to {130}. The structure includes populated octahedral edge-sharing chains . . . Mn—Mn—Sb—Mn—Mn—Sb . . . which run parallel to the y -axis and these further share edges with Mn—O octahedral edge-sharing walls. The walls are three octahedra wide along the y -axis and run parallel to the z -axis. The tetrahedra share corners with the octahedra and occur as $[T_3O_{10}]$ triple groups. Manganostibite belongs to an homologous series $M_{2n}O_{n-1}[T_nO_{3n+1}]$, where $n=3$; the simplest member of this series is the spinel structure type.

Average Me—O distances are $M(1)$ —O 2.15, $M(2)$ —O 2.20, $M(3)$ —O 2.22, Sb—O 1.99, $T(1)$ —O 2.04 and As—O 1.67 Å.

INTRODUCTION

Manganostibite is a peculiar compound known only from the abandoned Brattfors Mine, Nordmarks Odalfält, Värmland, Sweden where it occurred in skarn bands associated with sonolite and catoptrite in marble. Originally named "manganostibiit" and described by Igelström (1884), the mineral possessed uncertain status as a species until a paper by Moore (1968a) reported its crystal chemistry. The crystal chemistry of manganostibite proved so unusual that no unambiguous formula unit could be assigned the mineral and a detailed crystal structure analysis was undertaken, the results of which are reported herein. This remarkable compound is shown to belong to a novel structure type based on cubic closed-packed oxygen atoms; it possesses a formula unit $Mn^{2+}_7Sb^{5+}As^{5+}O_{12}$. Grouping of cations according to their coordination numbers leads to $(Mn_6Sb)^{VI}(Mn_2As)^{IV}O_{12}$. The structure adds new knowledge to the crystal chemistry of dense-packed systems and offers one of the few examples of a crystal involving the combination of Mn^{2+} , Sb^{5+} and As^{5+} cations.

EXPERIMENTAL

All crystals of manganostibite used in this study were obtained from specimen number 28939, kindly loaned by the Swedish Natural History Museum. A finely ground single crystal mixed with silicon standard ($a=5.4301$ Å) and diluted with rubber cement provided a small sphere from which a Buerger camera powder pattern (Fe/Mn radiation, 114.6

TABLE 1. MANGANOSTIBITE. CRYSTAL DATA.

	1	2
<i>a</i>	8.72 Å	8.727(5)
<i>b</i>	18.86	18.847(6)
<i>c</i>	6.06	6.062(4)
<i>V</i>	999.6 Å ³	997.1 (6)
<i>Z</i>		4
Space group		<i>Ibmm</i>
$\rho(\text{obs.})$	4.949 g/cm ³	
$\rho(\text{calc.})$	—	5.00 g/cm ³
Ideal Formula		Mn ₇ ²⁺ Sb ₆ ⁵⁺ As ₅ ⁵⁺ O ₁₂

1. Moore (1968a). Estimated standard errors not stated. The ideal formula proposed was Mn²⁺₂Mn⁴⁺₄Sb⁵⁺₂O₁₅, *Z* = 4.

2. This study. The calculated density is based on the following cell contents: (Mn_{25.0}Fe_{0.7}Zn_{0.4}Mg_{1.9})Sb_{4.0}(As_{3.2}Si_{0.8})O_{48.0}.

mm camera diameter) was obtained. All powder lines were unambiguously indexed using the strong three-dimensional single crystal intensities as a guide. These data were refined by conventional least-squares techniques to yield the cell parameters in Table 1. The powder data in Table 2 are more complete and superior to those previously reported by Moore (1968a), although the major changes appear only in the revision of some ascribed Miller indices; the new cell parameters are in very good agreement with those previously reported.

1362 symmetry independent intensities were gathered on a PAILRED automated diffractometer using MoK α radiation with a silicon monochromator to $2\theta = 100^\circ$. These data span the 0- to 12-levels with *a* as the rotation axis. The crystal, a flat bead of 0.0039 mm³ volume, required careful polyhedral transmission and absorption anisotropy correction, since $\mu = 155 \text{ cm}^{-1}$. 836 intensities were "non-zero" and were the only ones used in the ensuing analysis, after obtaining F_0 data through conventional procedures.

More detailed work should be offered on the method of data collection. The raw data included the integrated intensities I_{hkl} and their symmetry equivalent $I_{h\bar{k}l}$. Twenty second background readings were taken on either side of the maxima, employing a half-angle scan of 2.4° and a peak scan rate of $2.5^\circ/\text{minute}$. The three-dimensional data set further revealed the extinction criteria hkl , $h+k+l \neq 2n$; $0kl$, $k \neq 2n$ (where *n* is any integer), confirming the earlier report of Moore (1968a) which was based on film data. Fortuitously, the crystal shape exhibited approximate *mmm* point symmetry, resulting in I_{hkl} , $I_{h\bar{k}l}$ reflection pairs which were identical in intensity. These pairs were averaged and the polyhedral transmission and absorption anisotropy corrections applied to the remaining data, utilizing a local modified version of the GNABS program of Burnham (pers. commun.). Subsequent parameter refinements were based on a local version of the familiar least-squares program of Busing, Martin and Levy (1962). No corrections for anomalous dispersion were applied.

STRUCTURE ANALYSIS

The Patterson projection, $P(uv)$, immediately revealed that the oxygen atoms were situated in cubic close-packed layers which are stacked parallel to {130}. It was then discovered that the manganostibite cell can be related to spinel through the transformations $[100]_m = [\bar{1}00]_s$, $[010]_m = [110]_s$, and $[001]_m = [\bar{1}10]_s$; the magnitudes are $a_m \approx a_s$, $b_m \approx 3/\sqrt{2}$

TABLE 2. MANGANOSTIBITE. POWDER DATA^a

I/I_0	$d(\text{obs})$	$d(\text{calc})$	hkl	I/I_0	$d(\text{obs})$	$d(\text{calc})$	hkl
4	9.313	9.423	020 ^b	1	1.7906	1.7919	460
6	4.965	4.978	101 ^b	1	1.7615	1.7626	1.10.1
4	4.694	4.712	040 ^b	1	1.7101	1.7111	282
6	4.380	4.363	200	1	1.6749	1.6773	501
2	3.945	3.960	220	2	1.6669	1.6681	163
3	3.477	3.480	211	1	1.5808	1.5839	550
1	3.196	3.201	240	2	1.5675	1.5706	0.12.0
2	3.024	3.031	002	5	1.5418	1.5425	462
3	2.873	2.875	310	2	1.5147	1.5155	004
4	2.823	2.831	112	1	1.4769	1.4763	3.11.0
10	2.651	2.657	161	1	1.4684	1.4702	1.11.2
4	2.616	2.623	301	1	1.3937	1.3945	0.12.2
2	2.576	2.581	251	1	1.3461	1.3474	3.12.1
2	2.536	2.527	321	1	1.3425	1.3406	314
1	2.485	2.489	202	1	1.3259	1.3283	2.12.2
1	2.405	2.407	222	1	1.3227	1.3209	503
2	2.289	2.303	350	2	1.2736	1.2747	4.12.0
2	2.280	2.280	152	2	1.1470	1.1464	5.12.1
5	2.179	2.181	062	1	1.1395	1.1407	3.12.3
1	2.128	2.126	420	2	1.0910	1.0906	0.12.4
1	2.038	2.041	411	1	1.0252	1.0246	1.18.1
1	1.9591	1.9614	172	1	1.0117	1.0109	5.12.3
1	1.8190	1.8250	213				

^a FeK α_1 , 114.6 mm camera diameter; silicon standard $a = 5.4301$ Å.

^b Reflections excluded from cell refinement due to absorption effects.

a_s , and $c_m \approx 1/\sqrt{2} a_s$. Consideration of these relationships requires that manganostibite have 48 oxygen atoms in the unit cell, not 60 as reported previously by Moore (1968a). Further word on this difference appears in latter discussion. According to Moore (1968a) the cell formula was stated as $\text{Mn}_{22.8}\text{Mg}_{1.9}\text{Fe}_{0.7}\text{Zn}_{0.4}\text{Sb}_{4.4}\text{As}_{1.1}\text{Si}_{0.8}\text{O}_{59.8}$. With only 48 oxygen atoms in the cell, nearly all Mn must have formal charge close to 2+.

The next step was to decipher the ordering relationship over the octahedral and tetrahedral voids consistent with the assumed space group $Ibmm$, the cell contents, local charge balance and the F_0 data. Solutions of cubic and hexagonal close-packed structures often prove difficult due to the high geometrical correlation among atomic positions and manganostibite proved no exception. The key rested in the assumption that 4Sb in the cell were ordered over the point position $2/m$ at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; etc. Alternative choice of point position $2/m$ at $0, 0, 0$; etc. leads to an electrostatically implausible arrangement since Sb-O polyhedra must share edges. The Patterson projection further provided information on the relative density of other octahedral and tetrahedral populations through consideration of the Sb- Me vectors. Unambiguous three-dimensional interpretation of the structure was realized after tests of the several trial models thus obtained.

REFINEMENT

Of the 836 non-zero reflections, 166 were within twice the background error which was assessed from PAILRED scans, the these were excluded from further refinement. Further-

TABLE 3. CELL MULTIPLICITIES, ATOMIC COORDINATES, AND ISOTROPIC TEMPERATURE FACTORS FOR MANGANOSTIBITE.

	<i>M</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ⁻²)
Sb	4	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.32(3)
As	4	0.3678(6)	0	$\frac{3}{4}$.50(6)
<i>T</i> (1)	8	.3817(5)	0.1746(2)	$\frac{3}{4}$.39(5)
<i>M</i> (1)	4	0	0	0	.46(7)
<i>M</i> (2)	8	0	.1575(2)	0	.50(6)
<i>M</i> (3)	8	.2794(5)	.0821(3)	$\frac{1}{4}$.66(6)
O(1)	8	.0228(24)	.0755(10)	$\frac{1}{4}$.57(26)
O(2)	8	.0236(22)	.2400(10)	$\frac{1}{4}$.47(24)
O(3)	8	-.0265(23)	.4280(9)	$\frac{1}{4}$.45(24)
O(4)	8	.2589(26)	0	-.0193(31)	.60(23)
O(5)	16	.2538(19)	.1728(6)	.0268(19)	.30(14)

more, 13 of the strongest low-angle reflections suffered severe secondary extinction effects and were excluded. Convergence to $R_{hkl}=0.11$ for the remaining 657 reflections was obtained through conventional least-squares atomic coordinate and isotropic temperature factor refinement; $R_{hkl}=0.12$ for all 836 "non-zero" reflections. Scattering tables were prepared from MacGillavry and Rieck (1962) for half-ionized species, with *T*(1), *M*(1), *M*(2), *M*(3) = Mn⁺. Atomic coordinates, cell multiplicities, and isotropic temperature factors appear in Table 3; the F_o-F_c data appear in Table 4.¹ It was not necessary during this study to consider the possibility of non-centrosymmetry since the refined data and the electrostatic model are compatible with *Ibmm*. Errors in the F_o data are believed to be principally contributed by the uncertainties in the absorption anisotropy correction, especially with respect to the atomic absorption coefficients of the heavy species such as Mn, Sb and As and the polyhedral approximation of the crystal shape.

DISCUSSION OF THE STRUCTURE

Topology. A polyhedral diagram over the unit cell of the manganostibite atomic arrangement is presented in Figure 1. Infinite edge-sharing octahedral chains run parallel to the *y*-axis with the population sequence . . . Mn-Mn-Sb-Mn-Mn-Sb . . . at alternate levels $z=\frac{1}{4}$ and $z=\frac{3}{4}$. These link by edge-sharing to Mn-O octahedral edge-sharing walls, which are three octahedra wide along the *y*-axis. These walls run parallel to the *z*-axis. Finally, tetrahedral corner-sharing triplets occur, with composition MnAsMnO₁₀, and link to the octahedra by corner-sharing. The bonding arrangement is rather evenly distributed in three-dimensions; consequently, manganostibite exhibits no good cleavage directions.

¹ To obtain a copy of Table 4, order NAPS Document #01051 from ASIS National Auxiliary Publications service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York, 10022 remitting \$5.00 for microfiche or \$2.00 for photocopies, payable to CCMIC-NAPS.

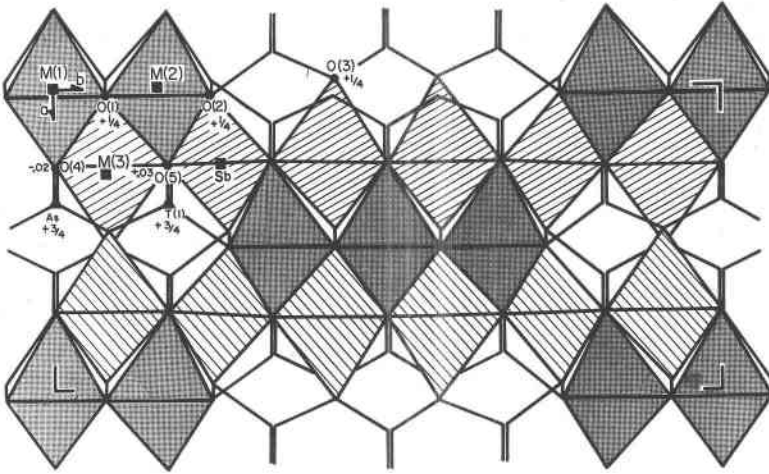


FIG. 1. Polyhedral diagram of the manganostibite atomic arrangement in one unit cell. Octahedra centered at $z=0$ and $\frac{1}{2}$ are stippled. Octahedra centered at $z=\frac{1}{4}$ are ruled NE-SW and octahedra at $z=\frac{3}{4}$ are ruled NW-SE. Tetrahedral populations are represented at T -O spokes.

Discussion of the manganostibite topology has already appeared in a paper by Moore and Smith (1969). Briefly, the compound belongs to an homologous series $M_{2n}O_{n-1}[T_nO_{3n+1}]$, with space group $Ibmm$, where M = octahedral populations and T = tetrahedral populations. Noting that $Ibmm$ is the orthorhombic subgroup of spinel $Fd3m$, the numbers $n=1, 2$ and 3 yield the formulae for spinel, β - Mg_2SiO_4 and manganostibite, respectively; that is $M_2[TO_4]$, $M_4O[T_2O_7]$, and $M_6O_2[T_3O_{10}]$. Idealized polyhedral diagrams of these three members are illustrated in the aforementioned paper and are not repeated here. The manganostibite formula is obtained by setting $M_6 = Mn_5Sb$ and $T_3 = Mn_2As$. It is worthy of note that the ordering of Mn, Sb over M; and Mn, As over T in manganostibite leaves the space group of the idealized homologous series invariant.

Crystal chemistry. The M -O, T -O and O-O' interatomic distances are presented in Table 5. Mean M -O and T -O distances provide information on the valence states of the cations and should be consistent with the electrostatic model.

First, the chemical constituency of manganostibite must be discussed in more detail. The calculated density based on the ideal cell formula $Mn_{28}Sb_4As_4O_{48}$ is much higher than the experimental determination (Table 1). The chemical contents of a manganostibite unit cell on the basis of Igelström's (1884) analysis and a corrected ARL electron probe analysis

TABLE 5. OCTAHEDRAL AND TETRAHEDRAL DISTANCES IN MANGANOSTIBITE^a.
(ESTIMATED STANDARD ERRORS: ME-O ± 0.019, O-O' ± 0.027 Å)

<i>M</i> (1)		<i>M</i> (2)	
4 <i>M</i> (1)-O(1)	2.088 Å	2 <i>M</i> (2)-O(1)	2.174
2 <i>M</i> (1)-O(4)	2.262	2 <i>M</i> (2)-O(2)	2.181
		2 <i>M</i> (2)-O(5)	2.239
aver.	2.146 Å		2.198
2O(1)-O(1) ^{II}	2.846 ^b	2O(2)-O(5)	2.908 ^b
4O(1)-O(4)	2.989 ^b	2O(1)-O(5)	3.043 ^b
2O(1)-O(1) ^I	3.057 ^b	2O(2)-O(5) ^I	3.049
4O(1)-O(4) ^I	3.166	1O(1)-O(1) ^I	3.057 ^b
		1O(2)-O(2) ^I	3.059
aver.	3.035	2O(1)-O(2)	3.100 ^b
		2O(1)-O(5) ^I	3.465
			3.104
<i>M</i> (3)			
1 <i>M</i> (3)-O(3) ^{III}	2.164	Sb	
2 <i>M</i> (3)-O(5)	3.191		
1 <i>M</i> (3)-O(1)	2.243	2Sb-O(2)	1.985
2 <i>M</i> (3)-O(4)	2.256	4Sb-O(5)	1.987
	2.217		1.986
1O(5)-O(5) ^{IV}	2.706 ^b	2O(5)-O(5) ^{IV}	2.706 ^b
2O(1)-O(4)	2.989 ^b	4O(5)-O(2)	2.733 ^b
2O(1)-O(5)	3.043 ^b	4O(2)-O(5) ^{III}	2.882
2O(4)-O(3) ^{III}	3.156	2O(5)-O(5) ^{III}	2.911
1O(4)-O(4) ^{IV}	3.265		
2O(4)-O(5)	3.269		
2O(5)-O(3) ^{III}	3.332		
	3.129		
		T(1)	
		2T(1)-O(5)	2.016
		1T(1)-O(2) ^V	2.031
		1T(1)-O(3) ^V	2.093
As			
2As-O(3) ^V	1.641		
2As-O(4)	1.691		
	1.666	2O(5)-O(3) ^V	3.178
		2O(5)-O(2) ^V	3.326
4O(4)-O(3) ^V	2.703	1O(5)-O(5) ^{IV}	3.356
1O(3) ^V -O(3) ^{VI}	2.714	1O(2) ^V -O(3) ^V	3.570
1O(4)-O(4) ^{IV}	2.797		
	2.721		3.322

^a Superscripts refer to symmetry equivalent oxygen atoms, obtained by the following transformations of the data in Table 3: I = \bar{x} , \bar{y} , \bar{z} ; II = x , \bar{y} , \bar{z} ; III = $\frac{1}{2} - x$, $\frac{1}{2} - y$, z ; IV = x , y , $\frac{1}{2} - z$; V = $\frac{1}{2} + x$, $\frac{1}{2} - y$, \bar{z} ; VI = $\frac{1}{2} + x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$.

^b Shared octahedral edges.

Moore, 1968a) were calculated as $\text{Mn}_{22.8}\text{Mg}_{1.9}\text{Fe}_{0.7}\text{Zn}_{0.4}\text{Sb}_{4.4}\cdot\text{As}_{1.1}\text{Si}_{0.8}\text{O}_{59.8}$ using the latter results. Arsenic, determined from a metal standard, is now known to be too low, by at least a factor of two. Indeed, Igelström reported a much higher arsenic content, but his other oxide determinations—with the exception of a slightly higher manganese oxide content—agree fairly well with the probe results. Rewriting the cell formula by adding the requisite manganese so that the “large” cations sum to 28, assuming the antimony content is exactly 4, adding enough arsenic to silicon to yield an aggregate cell content of 4, and substituting 48 oxygen atoms in the formula yields $\text{Mn}_{25.0}\text{Mg}_{1.9}\text{Fe}_{0.7}\text{Zn}_{0.4}\text{Sb}_{4.0}\text{As}_{3.2}\cdot\text{Si}_{0.8}\text{O}_{48.0}$. The calculated density of 5.00 gm/cm³ is in a fair agreement with the observed value and this formula is selected as a working approximation to the true cell contents of a manganostibite crystal.

It should be noted that the cell oxygen content cannot be assessed by packing considerations alone. With 60 oxygen atoms in the cell, the packing index is 16.6 Å³/oxygen; with 48 oxygens, this value is 20.7 Å³/oxygen. Since the valence states of the cations were largely unknown, no choice of oxygen content could be made and Moore (1968a) suggested the end-member formula $\text{Mn}^{2+}_2\text{Mn}^{4+}_4\text{Sb}^{5+}_2\text{O}_{16}$, $Z = 4$. Since most cations are in high valence states for this formula, the oxygen packing efficiency is expected to increase considerably and is similar to the index for braunite, $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$, which is 17.1 Å³/oxygen. The correct value proves to be much closer to that of manganosite, MnO, which possesses the rocksalt structure and has a packing index of 21.8 Å³/oxygen. Again, nearly all manganese atoms are probably in the divalent state for manganostibite.

The Me-O and O-O' interatomic distances in Table 5 show that typical Mn^{2+} -O averages (2.19–2.21 Å) occur for $M(2)$ and $M(3)$. The Sb-O and As-O averages agree well with the valence states Sb^{5+} and As^{5+} respectively. Si^{4+} evidently replaces As^{5+} to a limited extent since their crystal radii are similar; the isotropic temperature factor for As^{5+} ($B = 0.50/\text{Å}^2$) is higher than expected for a dense-packed structure and supports the argument that limited Si^{4+} substitutes for this cation. The mean T(1)-O distance of 2.04 Å suggests Mn^{2+} in tetrahedral coordination. Examples of refined structures with Mn^{2+} in tetrahedral coordination are rare; computing Mn^{IV} -O for galaxite, Al_2MnO_4 , using the approximate structural data in Wyckoff (1965) yields Mn^{IV} -O = 2.00 Å. The rare trigonal bipyramidal coordination for Mn^{2+} has been recently reported by Moore and Smyth (1968) in the mineral eveite, $\text{Mn}_2(\text{OH})(\text{AsO}_4)$, which is isotypic to andalusite. The Mn^{V} -O mean distance is 2.12 Å in this crystal and is intermediate between Mn^{IV} -O and Mn^{VI} -O distances. Thus, it is reasonable to state that Mn^{IV} -O \approx 2.00–2.04 Å average distances are indicative of the divalent state.

TABLE 6. ELECTROSTATIC VALENCE BALANCES (Σ) FOR THE ANIONS IN MANGANOSTIBITE.

			Σ
O(1)	$2M(1)+2M(2)+M(3)$	$2/6+2/6+2/6+2/6+2/6$	1.67
O(2)	$2M(2)+Sb+T(1)$	$2/6+2/6+5/6+2/4$	2.00
O(3)	$M(3)+As+T(1)$	$2/6+5/4+2/4$	2.08
O(4)	$M(1)+2M(3)+As$	$2/6+2/6+2/6+5/4$	2.25
O(5)	$M(2)+M(3)+Sb+T(1)$	$2/6+2/6+5/6+2/4$	2.00

The $M(1)$ -O average of 2.15 Å is significantly short for the Mn^{2+} -O octahedral distance. It is unlikely that Mg reported in the analysis preferentially populates this site since the isotropic temperature factor is not anomalously high. Two explanations are offered and are obvious if the individual interatomic distances are compared. There exist $4M(1)$ -O(1) 2.09 and $2M(1)$ -O(4) 2.26 Å distances. This may result from a tetragonal Jahn-Teller distortion, that is, partial occupancy of Mn^{3+} over the $M(1)$ sites. I believe that this explanation plays only a limited role in the manganostibite structure since excess positive charge would result over the crystal with the addition of Mn^{3+} . This may be compensated by $Si^{4+} \rightarrow As^{5+}$ substitution, but the substitution appears to be quite limited in extent. An alternative and more plausible explanation can be found in Table 6. O(1), with $\Sigma=1.67$, is highly undersaturated with respect to cations whereas O(4), with $\Sigma=2.25$, is considerably oversaturated. Thus, Me -O(1) distances appear shorter than average, and Me -O(4) are longer than average, as clearly shown in Table 5. The remaining anions, O(2), O(3) and O(5) are very nearly neutral.

From the foregoing discussion, the ideal crystal-chemical formula for manganostibite is $(Mn^{2+}_5Sb^{5+})^{VI}O_2[(Mn^{2+}_2As^{5+})^{IV}O_{10}]$. Grouping octahedral and tetrahedral populations without regard to cationic species leads to $M_6T_3O_{12}$, that is, M_2TO_4 . Thus, manganostibite is crystallochemically as dense as spinel.

SOME REMARKS ON THE CRYSTAL-CHEMICAL BEHAVIOR OF Sb^{5+} IN SKARNS

Only a few examples of skarn minerals containing essential Sb^{5+} are known; these compounds are very interesting since their crystallochemical behavior appears to be unique among minerals. It has been demonstrated by Moore (1968b) that Sb^{5+} possesses a crystal radius nearly identical to that of Fe^{3+} and that statistical distribution of $(Sb^{5+}_{0.5}Fe^{3+}_{0.5})$ over Ti^{4+} sites in ilmenite structures exists in the compound melanostibite.

On the other hand, no examples of Sb^{5+} replacing Mn^{2+} , Mn^{3+} or Mn^{4+}

are known. The crystal radii of Mn^{2+} and Mn^{4+} render any such substitution unlikely, the former being too large and the latter too small. Mn^{3+} , which in octahedral coordination exhibits violent Jahn-Teller distortion, possesses crystallochemically distinct behavior and Sb^{5+} substitution would probably be limited for this reason.

In many respects, Sb^{5+} behaves crystallochemically like Fe^{3+} , possessing similar $Me-O$ distances and rather regular octahedral coordination by oxygen atoms. Like Fe^{3+} , there may be a weak tendency toward tetrahedral coordination. On the other hand, the pentavalent state results in a distinctly different local charge balance and, in the absence of Fe^{3+} , would permit crystal chemistries distinct from well-known complex Fe^{3+} oxides.

Several compounds have been reported which are crystallochemically akin to manganostibite and which occur in a similar paragenesis. Moore (1966) discussed the crystal chemistry of catoptrite and yeatmanite, species which are closely related, the former occurring in close association with manganostibite. Their structures are probably based on close-packed oxygen atoms and possess substructures akin to pyrochroite. The formula proposed by Moore (1966) for catoptrite is $Mn^{2+}_{14}Sb^{5+}_2Al_4Si_2O_{29}$, but a footnote in that paper states that 28 oxygens probably occur in the structure since one extra oxygen atom would have to be stuffed in between the close-packed layers. This suggested the presence of Sb^{3+} instead of Sb^{5+} . On the basis of the structure determination of manganostibite and the coexistence of the two species, it is unlikely that catoptrite contains Sb^{3+} , but more likely contains fewer divalent cations. This is supported by the crystallochemical calculation in Table 7, based on the observed density and cell parameters reported by Moore (1966) and the chemical analysis of Flink (1917). The revised formula for catoptrite is $Mn^{2+}_{13}Sb^{5+}_2Al_4Si_2O_{28}$, with yeatmanite being $(Mn, Zn)^{2+}_{13}Sb^{5+}_2Si_4Zn_2O_{28}$.

Långbanite, a species with a controversial history, was suggested by Moore (1968a) to have the formula $Mn^{2+}_2Mn^{3+}_{11}Sb^{3+}Si_2O_{24}$. However, this compound probably contains antimony in the pentavalent state, since some of the manganese ions must possess valence states greater than $2+$. Early analyses on långbanites report Sb as Sb_2O_3 and Mn as MnO, or MnO and MnO_2 ; but older wet chemical analyses were notoriously unreliable for assessing mixed valence states. Strunz (1944) demonstrated a close relationship between the cells of långbanite and braunite ($Mn^{2+}Mn^{3+}_6SiO_{12}$) and stated that the two minerals were probably dimorphs of each other. Although the structures are certainly related, the consistent presence of 12–15% Sb in långbanites and its absence in braunite throws this conclusion into question. In other words, antimony is probably ordered in the langbanite structure. I suggest the ideal

TABLE 7. CRYSTAL-CHEMICAL CALCULATIONS FOR CATOPTRITE AND LÅNGBANITE.

	1		2	
	Weight percent	Atoms in cell	Weight percent	Atoms in cell
CaO	0.58	0.33	1.73	1.16
FeO	2.44	1.07	—	—
MnO	52.61	23.33	20.53	10.88
MgO	3.06	2.39	0.54	0.50
Mn ₂ O ₃	—	—	50.14	23.88(Mn ³⁺)
Fe ₂ O ₃	3.58	1.42(Fe)	3.44	1.62(Fe ³⁺)
Al ₂ O ₃	9.50	5.86(Al)	—	—
Sb ₂ O ₅	20.76	4.04	14.03	3.26(Sb ⁵⁺)
SiO ₂	7.75	4.06	9.59	6.01
H ₂ O	0.11	—	—	—
	100.39		100.00	

1. Catoptrite analysis of Flink (1917) using crystal cell criteria of Moore (1966). The formula is written $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})_{26.40}\text{Sb}_{4.04}(\text{Al}, \text{Fe}^{3+}, \text{Fe}^{2+})_{8.00}\text{Si}_{4.06}\text{O}_{56.62}$.

2. Långbanite, assuming Sb⁵⁺, Mn²⁺ and Mn³⁺. Analysis of Bäckström in Magnusson (1930), stated as Sb₂O₃ 12.58, SiO₂ 9.58, Fe₂O₃ 3.44, MnO₂ 35.06, MnO 36.82, MgO 0.53, CaO 1.73=99.74. Using the cell criteria in Moore (1968a) and $\rho=4.92$, the formula is written as $(\text{Mn}^{2+}, \text{Ca}, \text{Mg})_{12.54}(\text{Mn}^{3+}, \text{Fe})_{25.50}\text{Sb}^{5+}_{3.26}\text{Si}_{6.01}\text{O}_{70.91}$.

formula $\text{Mn}^{2+}_4\text{Mn}^{3+}_9\text{Sb}^{5+}\text{Si}_2\text{O}_{24}$ for långbanite; this formula is in fair agreement with crystallochemical calculation in Table 7 for the analysis of Bäckström in Magnusson (1930), assuming the valence states Mn²⁺, Mn³⁺ and Sb⁵⁺.

Table 8 presents a summary of the Sb⁵⁺-bearing compounds which occur in association with skarns. Listed as their ideal endmember formulae, their mutual relationships are evident. Summing all cations, the

TABLE 8. CRYSTALLOCHEMICALLY RELATED SPECIES CONTAINING Sb⁵⁺.

species	formula ^a	$R_x\text{O}_y$ ^b	volume/ oxygen ^c
manganostibite	$\text{Mn}^{2+}_{14}\text{Sb}^{5+}_2\text{As}^{5+}_2\text{O}_{24}$	$R_3\text{O}_4$	20.7 Å ³
catoptrite	$\text{Mn}^{2+}_{13}\text{Sb}^{5+}_2\text{Al}_4\text{Si}_2\text{O}_{28}$	$R_3\text{O}_4$	20.5
yeatmanite	$(\text{Mn}, \text{Zn})^{2+}_{13}\text{Sb}^{5+}_2\text{Si}_4\text{Zn}_2\text{O}_{28}$	$R_3\text{O}_4$	19.6
melanostibite	$\text{Mn}^{2+}_8\text{Fe}^{3+}_4\text{Sb}^{5+}_4\text{O}_{24}$	$R_2\text{O}_3$	18.8
långbanite	$\text{Mn}^{2+}_4\text{Mn}^{3+}_9\text{Sb}^{5+}\text{Si}_2\text{O}_{24}$	$R_2\text{O}_3$	17.6

^a Based on 24 or 28 oxygen atoms for comparative purposes.

^b R = sum of cations, simple oxide formula.

^c Computed from cell parameters cited in Moore (1966) and Moore (1968a).

compounds can be expressed either as R_2O_3 or R_3O_4 derivatives. The packing indices, expressed as volume per oxygen atom, closely follow the crystal radii of the cations and the assumption that these structures involve close-packed oxygen atoms.

ACKNOWLEDGMENT

This work was supported by NSF grant GA-10932.

REFERENCES

- BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least squares program. *U.S. Oak Ridge Nat. Lab. Rep. ORNL-TM-305*.
- FLINK, G. (1917) Einige Neuigkeiten in Schwedischen Mineralogie. *Geol. Foren. Forch.* **40**, 431-438.
- IGELSTRÖM, L. J. (1884) Manganostibiit, ett nytt mineral från Nordmarks grufvor i Vermland. *Kongl. Vetens. Akads. Forch.* **4**, 89-93.
- MACGILLAVRY, C. H., AND G. D. RIECK, Eds. (1962) *International Tables for X-ray Crystallography, Vol. 3*. The Kynoch Press, Birmingham, England.
- MAGNUSSON, N. H. (1930) Långbans Malms-trakt. *Svenska Geol. Unders. Ser. Ca*, No. 23, p. 55.
- MOORE, P. B. (1966) Catoptrite and yeatmanite-stuffed pyrochroite structures? *Amer. Mineral.* **51**, 1494-1500.
- (1968a) Contributions to Swedish mineralogy II. Melanostibite and manganostibite, two unusual antimony minerals. *Ark. Mineral. Geol.* **4**, 449-458.
- (1968b) Substitutions of the type $(Sb_{0.5}^{5+}Fe_{0.5}^{3+}) \rightleftharpoons (Ti^{4+})$: the crystal structure of melanostibite. *Amer. Mineral.* **53**, 1104-1109.
- AND J. R. SMYTH (1968) Crystal chemistry of the basic manganese arsenates III. The crystal structure of eveite. *Amer. Mineral.* **53**, 1841-1845.
- AND J. V. SMITH (1969) High pressure modification of Mg_2SiO_4 : crystal structure and crystallochemical and geophysical implications. *Nature* **221**, 653-655.
- STRUNZ, H. (1944) Wahrscheinliche Dimorphie Zwischen Braunite und Långbanite. *Neues Jahrb. Mineral. Geol. Monatsh.* **A1944**, 241-243.
- WYCKOFF, R. W. G. (1965) *Crystal Structures, Vol. 2, 2nd Ed.*, Interscience Publishers, New York.

Manuscript received, January 20, 1970; accepted for publication, April 2, 1970.