The Canadian Mineralogist
Vol. 32, pp. 397-403 (1994)

JAHN–TELLER-DISTORTED $Mn^{3+}O_6$ OCTAHEDRA IN FREDRIKSSONITE, THE FOURTH POLYMORPH OF $Mg_2Mn^{3+}(BO_3)O_2$

PETER C. BURNS, MARK A. COOPER AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of fredrikssonite, $(Mg_{1.98}Fe_{0.02})(Mn^{3+}_{0.78}Fe^{3+}_{0.20}Al_{0.02})(BO_3)O_2$ according to results of an electron-microprobe analysis, orthorhombic, *a* 9.198(2), *b* 12.528(3), *c* 2.965(1) Å, *V* 341.7(1) Å^3, space group *Pbam*, $Z = 4$, has been refined by full-matrix least-squares methods to a conventional *R* index of 2.4% and a *wR* index of 2.8% for 555 unique observed $[I \geq 2.5\sigma(I)]$ reflections measured with Mo$K\alpha$ X-radiation. Fredrikssonite is isostructural with ludwigite and vonsenite, and it is the fourth polymorph of this composition; the others are pinakiolite, orthopinakiolite and takéuchiite. The *M*(1), *M*(2) and *M*(3) octahedral sites contain divalent cations, and only *M*(2) contains detectable Fe^{2+}. The *M*(4) site contains trivalent cations, and owing to the presence of Mn^{3+}, it is Jahn–Teller-distorted. The relationship between distortion (Δ) of $Mn^{3+}O_6$ octahedra and mean bond-length has been re-examined: the dependence has been fit to the equation $\langle Mn^{3+}–O\rangle = 1.991 + 7.47\Delta$.

Keywords: fredrikssonite, borate, structure refinement, trivalent manganese.

SOMMAIRE

Nous avons affiné la structure cristalline de la fredrikssonite, $(Mg_{1.98}Fe_{0.02})(Mn^{3+}_{0.78}Fe^{3+}_{0.20}Al_{0.02})(BO_3)O_2$ selon les résultats d'une analyse par microsonde électronique, orthorhombique, *a* 9.198(2), *b* 12.528(3), *c* 2.965(1) Å, *V* 341.7(1) Å^3, groupe spatial *Pbam*, $Z = 4$, par moindres carrés avec matrice entière, jusqu'à un résidu *R* de 2.4% (*R* pondéré = 2.8%), en utilisant 555 réflexions observées $[I \geq 2.5\sigma(I)]$ et mesurées avec rayonnement Mo$K\alpha$. La fredrikssonite est isostructurale avec ludwigite et vonsenite, et le quatrième polymorphe de cette composition (avec pinakiolite, orthopinakiolite et takéuchiïte). Les sites octaédriques *M*(1), *M*(2) et *M*(3) contiennent des cations bivalents, et seul *M*(2) contient une proportion mesurable de Fe^{2+}. Le site *M*(4) contient des cations trivalents; à cause de la présence de Mn^{3+}, ce site montre les effets d'une distorsion due à l'effet de Jahn–Teller. Nous examinons de nouveau la relation entre l'indice de distorsion Δ pour le polyèdre $Mn^{3+}O_6$ et la longueur moyenne de la liaison cation–oxygène. La dépendance répond à la relation $\langle Mn^{3+}–O\rangle = 1.991 + 7.47\Delta$.

(Traduit par la Rédaction)

Mots-clés: fredrikssonite, borate, affinement de la structure, manganèse trivalent.

INTRODUCTION

Fredrikssonite, ideally $Mg_2Mn^{3+}(BO_3)O_2$, from the Långban mine, Sweden, was described by Dunn *et al.* (1983). It belongs to the ludwigite group, which includes the isostructural minerals ludwigite, $Mg_2Fe^{3+}(BO_3)O_2$, and vonsenite, $Fe_2Fe^{3+}(BO_3)O_2$; these have recently been studied by Bonazzi & Menchetti (1989).

Fredrikssonite is one of four known polymorphs of $Mg_2Mn^{3+}(BO_3)O_2$; the others are pinakiolite (Moore & Araki 1974), orthopinakiolite (Takéuchi *et al.* 1978) and takéuchiite (Norrestam & Bovin 1987), all of which occur in the Långban mine. The relationship among the polymorphs is shown in Figure 1. Each structure may be regarded as a stack of monoclinic pseudocells, which are shown using dotted lines in Figure 1. Cation ordering is superimposed on the resulting frameworks, as described by Moore & Araki (1974), Takéuchi *et al.* (1978) and Norrestam & Bovin (1987).

Fredrikssonite contains an $Mn^{3+}O_6$ octahedron which, in a holosymmetric configuration, has an energetically degenerate e_g electronic state. The Jahn–Teller theorem (Jahn & Teller 1937) indicates that such an octahedron is unstable with respect to some distorted state, and that a spontaneous distortion of the $Mn^{3+}O_6$ octahedron will occur. The Jahn–Teller distortion of $Mn^{3+}O_6$ octahedra has long been recognized, but there still is a relatively small number of well-refined structures that contain Mn^{3+}. However, the distortion of $Mn^{3+}O_6$ octahedra, although similar in nature, is much less pronounced than the Jahn–Teller distortion of $Cu^{2+}O_6$ octahedra, which also is driven by an energetically degenerate e_g electronic state in the holosymmetric configuration.

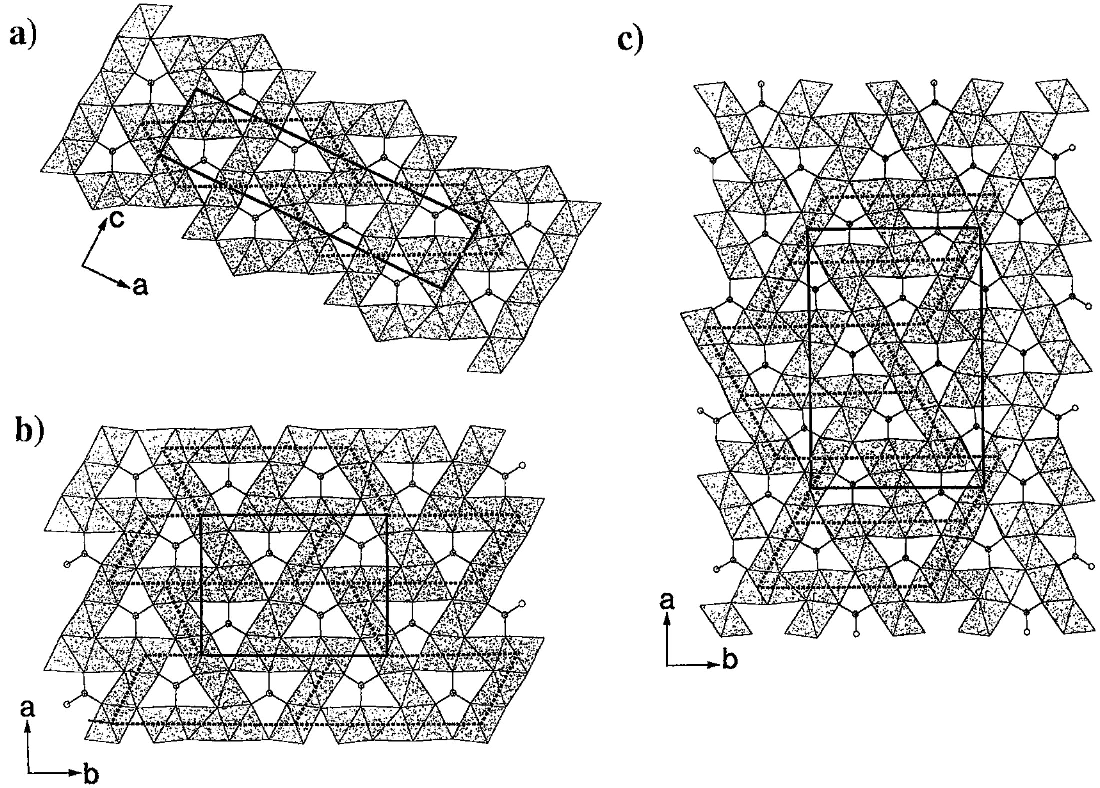

FIG. 1. Comparison of the structures of (a) pinakiolite, (b) fredrikssonite and (c) orthopinakiolite. The octahedral sites (Mg and Mn) are shaded with a random dot pattern. The unit cells are outlined with solid lines, the monoclinic pseudocell is outlined with dotted lines.

Here we report the results of a crystal-chemical study of fredrikssonite based upon results of electron-microprobe analyses and single-crystal X-ray structure refinement. These results provide the cation distributions and the geometry of the polyhedra, and may be compared to those observed in ludwigite and vonsenite (Bonazzi & Menchetti 1989) and the synthetic analogue of fredrikssonite (Norrestam *et al.* 1989a).

EXPERIMENTAL

X-ray data collection

A moderately equidimensional fragment of fredrikssonite from the type locality at Långban mine, Varmland, Sweden, was mounted on a Nicolet $R3m$ automated four-circle diffractometer. Twenty-five reflections were centered using graphite-monochromated Mo$K\alpha$ X-radiation. The unit-cell dimensions (Table 1) were derived by least-squares refinement of the setting angles of the twenty-five automatically aligned reflections. Data were collected using the $\theta/2\theta$ scan method with a 2.1° 2θ scan range and a variable scan-rate ranging from 4 to 29.3° 2θ/min. A total of 1103 reflections was measured; the ranges $0 \leq h \leq 13$, $0 \leq k \leq 18$, $-5 \leq l \leq 5$ were covered. Two standard reflections were measured every fifty-eight reflections; no significant change in their net intensities occurred during data collection. An empirical absorption correction based on 36 psi-scans for each of 12 reflections over the range ($8 \leq 2\theta \leq 59°$) was

TABLE 1. MISCELLANEOUS INFORMATION FOR REFINEMENT OF FREDRIKSSONITE

Space Group	Pbam	Crystal Size (mm)	0.09 x 0.11 x 0.13
a (Å)	9.198(2)	Total Ref.	1103
b (Å)	12.528(3)	Unique Ref.	588
c (Å)	2.965(1)	$[I \geq 2.5\sigma(I)]$	555
V (Å^3)	341.7(1)		
		Final R	2.4%
F(000)	377	Final wR	2.8%

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{½}$, $w=1/sig^2(F)$

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSIS* OF FREDRIKSSONITE

MgO Wt%	41.52	Mg	1.984
Mn_2O_3	32.07	Fe^{2+}	0.016
FeO	0.62		2.000
Fe_2O_3	8.26		
Al_2O_3	0.49	Mn^{3+}	0.782
B_2O_3	18.08	Fe^{3+}	0.199
Sum	101.04	Al	0.019
			1.000
		B	1.000

* Fe^{2+}/Fe^{3+} calculated on the basis of Mg + Mn + Fe + Al = 3.00 and on electroneutrality. The proportion of B_2O_3 is calculated on the basis of stoichiometry.

applied, reducing *R*(azimuthal) from 3.1 to 2.4%. The data were corrected for Lorentz, polarization and background effects, and equivalent reflections were merged with an *R*(int.) of 1.6%; of the 1103 reflections measured, there were 588 unique reflections, of which 555 were classed as observed [$I \geq 2.5\sigma(I)$].

Electron-microprobe analysis

The crystal used for X-ray data collection was mounted in epoxy, ground, polished and coated with carbon. The electron-microprobe analyses were done on a Cameca SX–50 instrument operating in wavelength-dispersion mode. The following standards were used: forsterite (Mg), spessartine (Mn), kyanite (Al) and arfvedsonite (Fe). Ten points were analyzed; the crystal was found to be homogeneous, and the average result of these analyses is given in Table 2. The formula unit (Table 2) was calculated on the basis of (1) the electroneutrality principle, and (2) Mg + Mn + Fe + Al = 3.00. We have assumed that all of the Mn is in the 3+ oxidation state. The level of B_2O_3 was calculated according to stoichiometry.

STRUCTURE REFINEMENT

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study. *R* indices are of the form given in Table 1, and are expressed as percentages.

Refinement of the structure was carried out in the space group *Pbam*, with the structure parameters for vonsenite (Bonazzi & Menchetti 1989) as the starting model. Refinement of the positional parameters and isotropic displacement parameters gave an *R* index of 3.3%. With a conversion to an anisotropic-displacement model, together with the refinement of all parameters, including cation site-scattering values, the refinement converged to an *R* index of 3.0%. A refinement was attempted using a refinable structure-factor weighting scheme, but the results were not improved. Inclusion of an isotropic extinction correction significantly improved the final refinement results, giving an *R* index of 2.4% and a *wR* index of 2.8%. Final positional parameters, equivalent isotopic displacement parameters and anisotropic displacement parameters are given in Table 3, selected bond-lengths, angles and polyhedral edge-lengths in Table 4, and a bond-valence analysis is given in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI National Research Council, Ottawa, Ontario K1A 0S2.

DISCUSSION

This structure refinement verifies that fredrikssonite is isostructural with ludwigite and vonsenite. This structure type has been described by Takéuchi *et al.* (1950), Bertaut (1950), Carvalho de Silva *et al.* (1955), Takéuchi (1956), Federico (1957), Mokeyeva (1968), Swinnea & Steinfink (1983), Bonazzi & Menchetti (1989), Norrestam *et al.* (1989a,b) and

TABLE 3. ATOMIC PARAMETERS FOR FREDRIKSSONITE

	x	*y*	*z*	$^*U_{eq}$	$^{**}U_{11}$	U_{22}	U_{33}	U_{12}
M(1)	0	0	0	62(4)	57(6)	58(6)	69(7)	-7(5)
M(2)	½	0	½	67(4)	71(6)	54(7)	75(7)	14(4)
M(3)	0.0048(1)	0.2800(1)	0	61(3)	62(4)	54(5)	67(5)	9(3)
M(4)	0.74115(5)	0.38458(3)	½	50(1)	44(2)	53(2)	54(2)	-1(2)
B	0.2782(4)	0.3598(3)	½	63(8)	88(14)	73(14)	27(13)	-6(11)
O(1)	0.8536(2)	0.0449(2)	½	73(6)	65(9)	76(10)	80(10)	15(7)
O(2)	0.3807(2)	0.0786(2)	0	68(5)	69(9)	52(9)	83(10)	-6(7)
O(3)	0.6277(2)	0.1423(2)	½	71(6)	58(9)	61(9)	93(10)	1(7)
O(4)	0.1130(2)	0.1422(2)	0	72(6)	64(9)	70(9)	82(11)	3(7)
O(5)	0.8559(2)	0.2349(2)	½	74(6)	65(9)	70(10)	87(11)	-16(7)

$^*U_{eq}=U_{eq}x10^4$, $^{**}U_{ij}=U_{ij}x10^4$, $U_{13}=U_{23}=0$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN FREDRIKSSONITE

M(1)-O(1)a,b,c,d	2.080(2) x4	M(2)-O(2),c,g,h	2.091(2) x4
M(1)-O(4),l	2.063(2) x2	M(2)-O(3),c	2.135(2) x2
<M(1)-O>	2.074	<M(2)-O>	2.106
M(3)-O(2)f	2.108(2)	M(4)-O(1)e	2.189(2)
M(3)-O(3)f,k	2.104(2) x2	M(4)-O(5)	2.151(2)
M(3)-O(4)	1.992(2)	M(4)-O(2)i,j	2.014(2) x2
M(3)-O(5)a,b	2.096(2) x2	M(4)-O(4)i,j	1.924(1) x2
<M(3)-O>	2.083	<M(4)-O>	2.036
B-O(1)f	1.381(4)		
B-O(3)f	1.384(4)		
B-O(5)f	1.385(4)		
<B-O>	1.383		
M(1) octahedron			
O(1)a-O(1)b	2.965(1) x2	O(1)a-M(1)-O(1)b	90.9(1) x2
O(1)a-O(1)c	2.918(4) x2	O(1)a-M(1)-O(1)c	89.1(1) x2
O(4)-O(1)a	3.062(3) x4	O(4)-M(1)-O(1)a	95.3(1) x4
O(4)-O(1)c	2.790(3) x4	O(4)-M(1)-O(1)c	84.7(1) x4
<O-O>	2.931	<O-M(1)-O>	90.0
M(2) octahedron			
O(2)-O(2)c	2.949(4) x2	O(2)-M(2)-O(2)c	89.7(1) x2
O(2)-O(2)g	2.965(1) x2	O(2)-M(2)-O(2)g	90.3(1) x2
O(3)-O(2)	2.828(3) x4	O(3)-M(2)-O(2)	84.0(1) x4
O(3)-O(2)c	3.140(3) x4	O(3)-M(2)-O(2)c	96.0(2) x4
<O-O>	2.975	<O-M(2)-O>	90.0
M(3) octahedron			
O(3)k-O(3)f	2.965(1) x2	O(3)k-M(3)-O(3)f	89.6(1) x2
O(3)k-O(5)b	2.936(3) x2	O(3)k-M(3)-O(5)b	88.7(1) x2
O(2)f-O(3)f	2.828(3) x2	O(2)f-M(3)-O(3)f	84.4(1) x2
O(2)f-O(5)a	2.776(3) x2	O(2)f-M(3)-O(5)a	82.7(1) x2
O(4)-O(3)f	3.083(3) x2	O(4)-M(3)-O(3)f	97.6(1) x2
O(4)-O(5)a	3.023(3) x2	O(4)-M(3)-O(5)a	95.4(1) x2
<O-O>	2.935	<O-M(3)-O>	89.8
M(4) octahedron			
O(2)j-O(2)i	2.965(1)	O(2)j-M(4)-O(2)i	94.8(1)
O(2)j-O(4)j	2.588(3) x2	O(2)j-M(4)-O(4)j	82.1(1) x2
O(4)i-O(4)j	2.965(1)	O(4)i-M(4)-O(4)j	100.8(1)
O(1)e-O(2)i	3.039(3) x2	O(1)e-M(4)-O(2)i	92.5(1) x2
O(1)e-O(4)i	2.790(3) x2	O(1)e-M(4)-O(4)i	85.2(1) x2
O(5)-O(2)i	2.776(3) x2	O(5)-M(4)-O(2)i	83.5(1) x2
O(5)-O(4)i	3.091(3) x2	O(5)-M(4)-O(4)i	98.5(1) x2
<O-O>	2.875	<O-M(4)-O>	89.9
B triangle			
O(1)f-O(3)f	2.410(3)	O(1)f-B-O(3)f	121.2(3)
O(1)f-O(5)f	2.381(3)	O(1)f-B-O(5)f	118.8(3)
O(3)f-O(5)f	2.398(3)	O(3)f-B-O(5)f	120.0(3)
<O-O>	2.396	<O-B-O>	120.0

a: x-1, y, z; b: x-1, y, -z; c: -x+1, -y, z; d: -x+1, -y, -z; e: -x+1.5, y+.5, z; f: x-.5, -y+.5, z; g: x, y, z+1; h: -x+1, -y, z+1; i: x+.5, -y+.5, z+1; j: x+.5, -y+.5, z; k: x-.5, -y+.5, -z; l: -x, -y, z

Takéuchi & Kogure (1992). In short, the structure belongs to the "3 Å fiber axis wallpaper structures" as described by Moore & Araki (1974). It contains four symmetrically distinct octahedral sites, and the boron is in triangular coordination.

TABLE 5. BOND-VALENCE* (v.u.) ANALYSIS FOR FREDRIKSSONITE

	M(1)	M(2)	M(3)	M(4)	B	Σ
O(1)	$0.347^{x4}\downarrow^{x2}\rightarrow$			0.334	0.991	2.019
O(2)		$0.338^{x4}\downarrow^{x2}\rightarrow$	0.325	$0.517^{x2}\downarrow^{x2}\rightarrow$		2.035
O(3)		$0.305^{x2}\downarrow$	$0.328^{x2}\downarrow^{x2}\rightarrow$		0.982	1.943
O(4)	$0.362^{x2}\downarrow$		0.428	$0.642^{x2}\downarrow^{x2}\rightarrow$		2.074
O(5)			$0.334^{x2}\downarrow^{x2}\rightarrow$	0.367	0.980	2.015
	2.112	1.962	2.077	3.019	2.953	

* Bond-valence parameters from Brown (1981)

Our designations of the octahedral sites [*M*(1) to *M*(4)] are consistent with the usage of Bonazzi & Menchetti (1989). However, the nomenclature used for the *M* sites in this structure type is by no means consistent. Recently, in their study of the synthetic analogue of fredrikssonite, Norrestam *et al.* (1989a) used *M*(4) and *M*(3) to designate our *M*(3) and *M*(4) sites, respectively. In their study of ludwigite, Takéuchi & Kogure (1992) used *M*(3) and *M*(2) to designate our *M*(2) and *M*(3) sites, respectively.

M(1) and M(3) octahedra

Site-scattering refinement indicates that the *M*(1) and *M*(3) sites are occupied only by Mg. The mean octahedral bond-lengths, <*M*(1)–O> = 2.074 Å, and <*M*(3)–O> = 2.083 Å, are similar to those reported in ludwigite [(<*M*(1)–O> = 2.086 Å, <*M*(3)–O> = 2.090 Å; Bonazzi & Menchetti (1989)]. The *M*(1) and *M*(3) octahedra are slightly smaller in the fredrikssonite crystal examined here, and this is consistent with small amounts of Fe^{2+} at the *M*(1) and *M*(3) sites of ludwigite, as reported by Bonazzi & Menchetti (1989).

M(2) octahedron

The site-scattering refinement indicates that the *M*(2) octahedron contains approximately 92% Mg and 8% of a heavier cation, in this case either Fe^{2+} or Mn^{2+}. The somewhat longer <*M*(2)–O>, equal to 2.106 Å, is consistent with the presence of a larger divalent cation, but owing to its low concentration, it is not possible to distinguish between Fe^{2+} and Mn^{2+}. The *M*(2) site occurs on a *2/m* position in the space group *Pbam*; thus 8% Fe^{2+} or Mn^{2+} at this site corresponds to 0.04 atoms per formula unit, a value similar to that obtained *via* normalization of the electron-microprobe results (Table 2).

M(4) octahedron

Site-scattering refinement shows that the *M*(4) site contains only Mn and Fe, and the electroneutrality principle requires that these cations be in the trivalent state. Normalization of the electron-microprobe data indicates that the site-population is approximately 78% Mn^{3+}, 20% Fe^{3+} and 2% Al^{3+}.

The structure of $Mg_{1.93}Mn_{1.07}O_2BO_3$, a synthetic analogue of fredrikssonite, was reported by Norrestam *et al.* (1989a). They derived significantly different octahedral-site occupancies for the *M*(2) and *M*(4) sites (our notation); in the synthetic material, *M*(2) contains 65.4% Mg and 34.6% Mn, whereas *M*(4) contains 27.4% Mg and 72.6% Mn. Samples of lugwigite and vonsenite studied by Bonazzi & Menchetti (1989) also contain significant levels of trivalent cations at both the *M*(2) and *M*(4) sites. In fredrikssonite, trivalent cations are located only in the *M*(4) site, as shown by site-scattering refinement, and the bond-valence sums calculated for the *M* sites in fredrikssonite (Table 5) are consistent with these assignments of occupancy.

The Jahn–Teller theorem (Jahn & Teller 1937) indicates that the presence of Mn^{3+} in the *M*(4) octahedron will lead to a distortion of the octahedron environment. Bonding arguments (Dunitz & Orgel 1960) show that a tetragonal (4+2)- or (2+4)-distortion of the ligand arrangement will serve to lift the electronic degeneracy. Examination of $Mn^{3+}O_6$ octahedra in reported structures indicates that the (4+2)-distorted geometry is almost invariably adopted.

In the case of vonsenite, the *M*(4) octahedron is occupied mainly by Fe^{3+}, and the Jahn–Teller theorem does not apply. The vonsenite structure, and the *M*(4) octahedron contained therein (Table 6), may be regarded as the prototype structure, which is perturbed by the Jahn–Teller effect in fredrikssonite. Comparison of the *M*(4) site in these structures (Table 6) shows that the *M*(4) octahedron in fredrikssonite is strongly distorted in comparison to the *M*(4) octahedron in vonsenite. However, the *M*(4) octahedron in fredrikssonite is not tetragonally (4+2)-distorted, as is commonly observed for $Mn^{3+}O_6$ octahedra, but is [(2+2)+2] distorted, *i.e.*, there are two short (equatorial) *M*(4)–O bonds, two intermediate (equatorial) *M*(4)–O bonds and two long (apical) *M*(4)–O bonds. Examination of the local environment of the *M*(4) octahedron reveals the cause of this additional distortion.

The *M*(4) octahedron is located on a mirror plane, and includes only four symmetrically distinct ligands. The cation bonds to two pairs of symmetrically equivalent ligands [O(2) and O(4)]; in these cases, the equivalent ligands are in a *cis* arrangement. It is not possible to obtain a (4+2)-distorted octahedron by lengthening either pair of bonds. A (4+2)-distorted octahedron may only be obtained by lengthening both the *M*(4)–O(1) and *M*(4)–O(5) bonds, and by shortening the *M*(4)–O(2) and *M*(4)–O(4) bonds to continue to satisfy the valence requirements of the cation. Consideration of thirty-four $Mn^{3+}O_6$ octahedra in well-refined structures (see below) gives average equatorial and apical Mn^{3+}–O distances of 1.93 Å and 2.24 Å, respectively. The *M*(4)–O(4) bond-length is in line with these averages, but the *M*(4)–O(2) distance is considerably longer than expected for an equatorial bond (Table 6). The O(4) anion is bonded to one *M*(1), one *M*(3) and two *M*(4) cations (Table 5); the bonds to *M*(1) and *M*(3) supply 0.790 v.u. to O(4), and its remaining bond-valence requirements are compatible with short bonds to Mn^{3+} at *M*(4). The coordination number of O(2) is [5] rather than [4], as is the case for O(4), and O(2) receives 1.001 v.u. from *M*(2) and *M*(3); the remaining bond-valence requirements of O(2) are compatible with intermediate length bonds to Mn^{3+} at *M*(4). Thus the [(2+2)+2] coordination of Mn^{3+} in fredrikssonite is the result of local bond-valence requirements stemming from different coordination numbers of the equatorial anions.

TABLE 6. COMPARISON OF THE M(4) BOND-LENGTHS (Å) IN VONSENITE* AND FREDRIKSSONITE

	Vonsenite	Fredrikssonite
M(4)-O(1)	2.073(1)	2.189(2)
M(4)-O(5)	2.078(1)	2.151(2)
M(4)-O(2) x2	2.089(1)	2.014(2)
M(4)-O(4) x2	2.001(1)	1.924(1)
<M(4)-O>	2.055	2.036
Δ	0.0004	0.0025

* Bonazzi & Menchetti (1989)

Effect of distortion of $Mn^{3+}O_6$ octahedra on mean bond-length

Shannon *et al.* (1975) reported the effects of distortion of $Mn^{3+}O_6$ octahedra on the $\langle Mn^{3+}–O\rangle$ bond-length based on nine well-refined structures containing 16 symmetrically distinct $Mn^{3+}O_6$ octahedra. We have selected an additional 13 structures that contain 18 symmetrically distinct $Mn^{3+}O_6$ octahedra; each of the structures is well refined, and there is no evidence of significant cationic substitution at the Mn^{3+} site. The new data, in addition to the data given by Shannon *et al.* (1975), are given in Figure 2, and shows the dependence of $\langle Mn^{3+}–O\rangle$ on distortion of the octahedra, $\Delta = 1/6\Sigma[(L_i-\bar{L})/\bar{L}]^2$, where L_i is an individual Mn^{3+}–O bond-length and $\bar{L}$ is $\langle Mn^{3+}–O\rangle$. The relationship derived from these data is $\langle Mn^{3+}–O\rangle =$

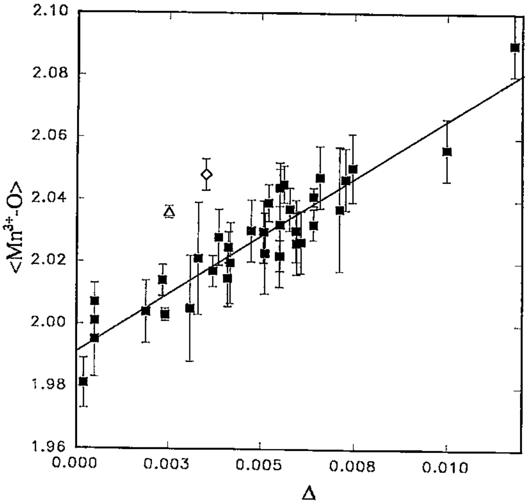

FIG. 2. Mean Mn^{3+}–O (Å) *versus* distortion for $Mn^{3+}O_6$ octahedra from well-refined structures. Vertical error-bars are from the original authors.

1.991 + 7.47Δ (correlation coefficient = 0.87), close to that reported by Shannon *et al.* (1975).

The maximum distortion (Δ) for any $Mn^{3+}O_6$ octahedron is 0.012, observed in the structure of β-$NaMnO_2$ (Hoppe *et al.* 1975). This value, although almost twice the maximum given by Shannon *et al.* (1975), is only about one-third of the maximum value observed for $Cu^{2+}O_6$ octahedra.

The *M*(4) site in fredrikssonite is given as an open triangle in Figure 2, and the open diamond represents the *M*(3) site in pinakiolite. Fredrikssonite contains significant Fe^{3+} at the Mn^{3+} site. Shannon (1976) listed Fe^{3+} and Mn^{3+} as having the same radius (0.645 Å), and the $<Mn^{3+}–O>$ distance in Figure 2 (~2.03 Å) is compatible with this. However, it is also apparent from Figure 2 that an undistorted $Mn^{3+}O_6$ octahedron has a mean bond-length of approximately 1.99 Å; hence Mn^{3+} does have a smaller ionic radius than Fe^{3+}, but the increase in mean bond-lengths produced by the large (Jahn–Teller) distortions in $Mn^{3+}O_6$ octahedra result in $<Mn^{3+}–O>$ values that are similar to $<Fe^{3+}–O>$ values. This means that substitution of Fe^{3+} for Mn^{3+} should lead to positive deviations from the $<Mn^{3+}–O>$ *versus* Δ relationship of Figure 2, and this is exactly what is observed for fredrikssonite and pinakiolite.

ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of Operating, Infrastructure and Equipment grants to FCH, and by the University of Manitoba in the form of a Graduate Fellowship and the J.L. Lightcap award to PCB. The manuscript was improved following a review by Dr. Paola Bonazzi and editorial work by Dr. Robert Martin.

REFERENCES

BERTAUT, E.F. (1950): Structures des boroferrites. *Acta Crystallogr.* **3**, 473-474.

BONAZZI, P. & MENCHETTI, S. (1989): Contribution to the crystal chemistry of the minerals of the ludwigite–vonsenite series. *Neues Jahrb. Mineral., Monatsh.*, 69-83.

BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Natvrotsky, eds.), Academic Press, New York (1-30).

CARVALHO DA SILVA, J., CLARK, J.R. & CHRIST, C.L. (1955): Crystal structure of ludwigite, $Mg_2Fe'''BO_3O_2$. *Geol. Soc. Am. Bull.* **66**, 1540-1541 (abstr.).

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

________ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

DUNITZ, J.D. & ORGEL, L.E. (1960): Stereochemistry of ionic solids. *Adv. Inorg. Chem.* **2**, 1-60.

DUNN, P.J., PEACOR, W.B., SIMMONS, W.B. & NEWBURY, D. (1983): Fredrikssonite, a new member of the pinakiolite group from Långban, Sweden. *Geol. Fören. Stockholm Förh.* **105**(4), 335-340.

FEDERICO, M. (1957): Sulla breislakite. *Per. Mineral.* **26**, 191-214.

HOPPE, V.R., BRACHTEL, G. & JANSEN, M. (1975): Über $LiMnO_2$ und β-$NaMnO_2$. *Z. Anorg. Allg. Chem.* **417**, 1-10.

JAHN, H.A. & TELLER, E. (1937): Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy. *Proc. Royal Soc.* **A161**, 220-235.

MOKEYEVA, V.I. (1968): Refinement of the structure of ludwigite $(Mg_{1.85}Fe^{2+}_{0.15})(Fe^{3+}_{0.60}Al_{0.40})BO_3O_2$ and distribution of Mg^{2+} and Fe^{2+} among the cation sites of the structure. *Geochem. Int.* **5**, 809-813.

MOORE, P.B. & ARAKI, T. (1974): Pinakiolite, $Mg_2Mn^{3+}O_2[BO_3]$; warwickite, $Mg(Mg_{0.5}Ti_{0.5})O[BO_3]$; wightmanite, $Mg_3(O)(OH)_5[BO_3]\cdot nH_2O$: crystal chemistry of complex 3 Å wallpaper structures. *Am. Mineral.* **59**, 985-1004.

NORRESTAM, R. & BOVIN, J.-O. (1987): The crystal structure of takéuchiite, $Mg_{1.71}Mn_{1.29}BO_5$, a combined single crystal X-ray and HRTEM study. *Z. Kristallogr.* **181**, 135-149.

________, DAHL, S. & BOVIN, J.-O. (1989b): The crystal structure of magnesium–aluminum ludwigite, $Mg_{2.11}Al_{0.31}Fe_{0.53}Ti_{0.05}Sb_{0.01}BO_5$, a combined single crystal X-ray and HREM study. *Z. Kristallogr.* **187**, 201-211.

________, NIELSEN, K., SØTOFTE, I. & THORUP, N. (1989a): Structural investigation of two synthetic oxyborates: the mixed magnesium–manganese and the pure cobalt ludwigites, $Mg_{1.93(2)}Mn_{1.07(2)}O_2BO_3$ and $Co_3O_2BO_3$. *Z. Kristallogr.* **189**, 33-41.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

________, GUMERMAN, P.S. & CHENAVAS, J. (1975): Effect of octahedral distortion on mean Mn^{3+}–O distances. *Am. Mineral.* **60**, 714-716.

SWINNEA, J.S. & STEINFINK, H. (1983): Crystal structure and Mössbauer spectrum of vonsenite, $2FeO{\cdot}FeBO_3$. *Am. Mineral.* **68**, 827-832.

TAKÉUCHI, Y. (1956): The crystal structure of vonsenite. *Mineral. Soc. Japan* **2**, 19-26.

________, HAGA, N., KATO, T. & MIURA, Y. (1978): Orthopinakiolite, $Me_{2.95}O_2[BO_3]$: its crystal structure and relationship to pinakiolite, $Me_{2.90}O_2[BO_3]$. *Can. Mineral.* **16**, 475-485.

________ & KOGURE, T. (1992): The structure type of ludwigite. *Z. Kristallogr.* **200**, 161-167.

________, WATANABE, T. & ITO, T. (1950): The crystal structures of warwickite, ludwigite and pinakiolite. *Acta Crystallogr.* **3**, 98-107.

Received March 15, 1993, revised manuscript accepted September 1, 1993.