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The Crystal Chemistry of Complex Niobium and Tantalum Oxides II. Composition and Structure of Wodginite

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Abstract

The structure of wodginite (non-centrosymmetric monoclinic space group *Cc*; ideal formula, $MnX_1X_2TaO_2$, where site X_2 contains 5-valent ions (and all the niobium) and the average valency of cations in site X_1 is 4) was determined by film methods to be an ordered form of the ixiolite structure. The *a* and *b* cell edges and angle β increase with manganese content, whereas *c* remains constant for wodginites from five localities in Western Australia.

Composition and Lattice Parameters

The characteristics of the mineral wodginite were clearly described by Nickel, Rowland, and McAdam (1963) for samples of the mineral from Wodgina, Australia, and Bernic Lake, Manitoba. The structure was not fully defined, and the effect of compositional variations on the structure could not therefore be discussed.

Table 1 shows the compositions and lattice parameters of wodginites from five localities in Western Australia and the average parameters quoted by Grice, Černy and Ferguson (1972) for the wodginites from the Tanco pegmatite at Bernic Lake, Manitoba. These values are by no means representative of the wodginites for the various localities, but they are quoted to demonstrate that there is a considerable variation in cell volume correlating to some degree with the Mn/(Fe + Mn) ratio, as shown graphically in Figure 1. There is also a strong correlation between manganese content and the *a* and *b* parameters and the monoclinic angle β; the chain length, *c*, remains constant.

Figure 2 demonstrates qualitatively how the metal content can vary within a small crystal fragment from a wodginite sample. This could indicate unmixing taking place at low temperatures, and makes it clear that a well-characterized structure may be difficult to achieve, particularly in a large crystal. Crystals of wodginite have been located that have small nuclei of cassiterite dotted throughout.

Structure Determination

A structure determination was carried out on a wodginite crystal fragment ($\sim$0.03 $\times$ 0.04 $\times$ 0.06 mm) from Wodgina, hand picked from a homogeneous region of a polished section. Electron probe analysis and powder X-ray diffraction (Hägg Guinier focussing camera) gave the cell dimensions and composition used in the calculations shown in Table 1. Data were collected photographically along two axes ([010] and [1$\bar{1}$2]) using a Nonius Integrating Weissenberg camera, equiinclination geometry, and Cu$K\alpha$ radiation. After the application of Lorenz and polarization corrections, these two sets of data were inter-correlated, and symmetrically similar reflections were averaged to give 555 independent observations. No correction was applied for absorption due to the difficulty of precisely describing the shape and orientation of such a small crystal with the apparatus available. This correction would have a small but significant effect ($\mu R \sim 4$), which would be partly offset, however, by the averaging of up to 8 separate intensity measurements to give a single observation.

Structure refinement was carried out in both the centrosymmetric $C2/c$ and the non-centrosymmetric space group *Cc* using the full matrix least-squares program of Busing, Martin, and Levy (1962) and the scattering factor data of Cromer and Weber (1965). The result was confirmed by Fourier methods. Refinement in the centrosymmetric space group gave an *R* factor of 14.3 percent with 21 variables, while the non-centrosymmetric space group gave $R = 13.1$ percent for 41 variables. The improvement is highly significant using Hamilton's (1965) criteria. The positional parameters of the atoms for the two refinements were not significantly different, but the absence of centrosymmetry allowed an ordering of the metal atoms that was not possible

TABLE 1. Composition and Unit Cell Dimensions of Various Wodginites

Specimen	Locality*	Cell Parameters (Å)				Vol (Å³)	Metal Content Normalized to 32 oxygens						Mn/Fe+Mn
		a	b	c	β		Ta	Nb	Mn	Fe	Sn	Ti	
2878	Greenbushes	9.468(5)	11.432(5)	5.110(2)	90.74(5)	553.1(1)	7.70	1.25	2.11	2.72	2.01	0.21	.437
MDC 1453	Mt. Matthew	9.448(5)	11.435(4)	5.099(3)	90.76(5)	550.8(1)	7.89	1.15	2.14	2.52	2.00	0.30	.459
S 388 B	Wodgina	9.530(7)	11.490(8)	5.098(4)	91.21(6)	558.1(2)	8.48	1.21	3.83	0.21	1.87	nil	.947
S 3315	Tabba Tabba	9.525(6)	11.479(8)	5.115(4)	91.25(6)	559.1(2)	8.13	0.68	4.24	0.05	2.64	0.26	.988
4292	Marble Bar	9.537(9)	11.47(1)	5.112(6)	91.24(9)	559.1(4)	8.56	0.61	4.06	0.52	1.80	0.46	.886
Grice *et al*	Bernic Lake	9.501(9)	11.453(2)	5.113(5)	91.00(6)	556.3(2)	7.94	0.36	3.33	0.98	2.54	0.95	.773

* All from Western Australia except Bernic Lake, Manitoba.

in the centrosymmetric space group no matter where the origin was placed. Electrostatic calculations (Part V) also showed that the non-centrosymmetric metal ordering is the most favored.

The ordering was determined by using an average scattering factor for the metals, and refining an occupancy factor and positional parameters. The fact that one fourfold metal site was occupied by Mn became immediately apparent. In the non-centrosymmetric space group, this method also indicated that one fourfold site was occupied exclusively by Ta while the other two fourfold sites were occupied by a mixture of the remaining cations. Table 2 shows the positional parameters for the atoms, and the bond lengths are shown in Figure 3. Oxygen parameters were not accurately obtainable in view of the large scattering factor of tantalum, so the

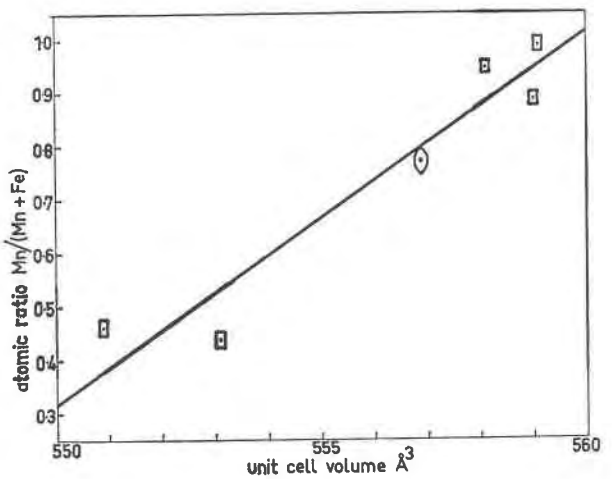

FIG. 1. Variation of unit cell volume of wodginite as a function of the atomic ratio Mn/(Mn + Fe).

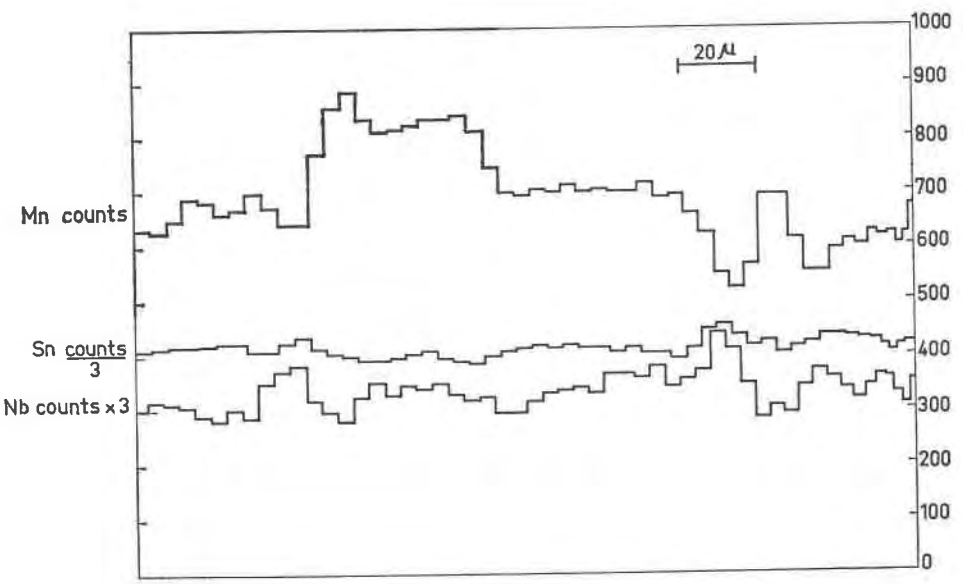

FIG. 2. Qualitative variation in composition of an inhomogeneous grain from a sample of wodginite. Electron microprobe step scan of XRF counts for Mn, Sn, and Nb over a 200μ interval of wodginite from sample S 388 B from Wodgina.

TABLE 2. Atomic Positional Parameters

	x	y	z	B
Ta	0.375(3)	0.414(1)	0.250(4)	0.4(1)
X1	0.375(3)	0.089(1)	0.750(4)	0.8(1)
X2	0.125(3)	0.169(1)	0.250(6)	0.8(1)
Mn	0.125(6)	0.343(1)	0.750(9)	0.7(2)
O1	0.255(9)	0.085(8)	0.088(16)	
O2	0.507(9)	0.438(8)	0.908(16)	
O3	0.266(9)	0.428(8)	0.555(16)	
O4	0.491(9)	0.051(8)	0.448(16)	
O5	0.256(9)	0.296(8)	0.102(16)	
O6	0.525(9)	0.183(8)	0.884(16)	
O7	0.247(9)	0.192(8)	0.577(16)	
O8	0.525(9)	0.312(8)	0.406(16)	

accuracy of these bond lengths is low (probably less than the computed accuracy, which was 0.08 Å for M-O bonds and 0.12 Å for the O-O bonds). The O-O distances fall in the normal range. The average metal-oxygen distances are Ta-O = 2.09 Å, X_1-O = 2.08 Å, Mn-O = 2.13 Å, and X_2-O = 1.97 Å. Observed and calculated structure factors are shown in Table 3.

The metal temperature factors were only refined subsequent to the determination of the occupancy, and because of the high correlation between scale factor, occupancy, and temperature factor, they are

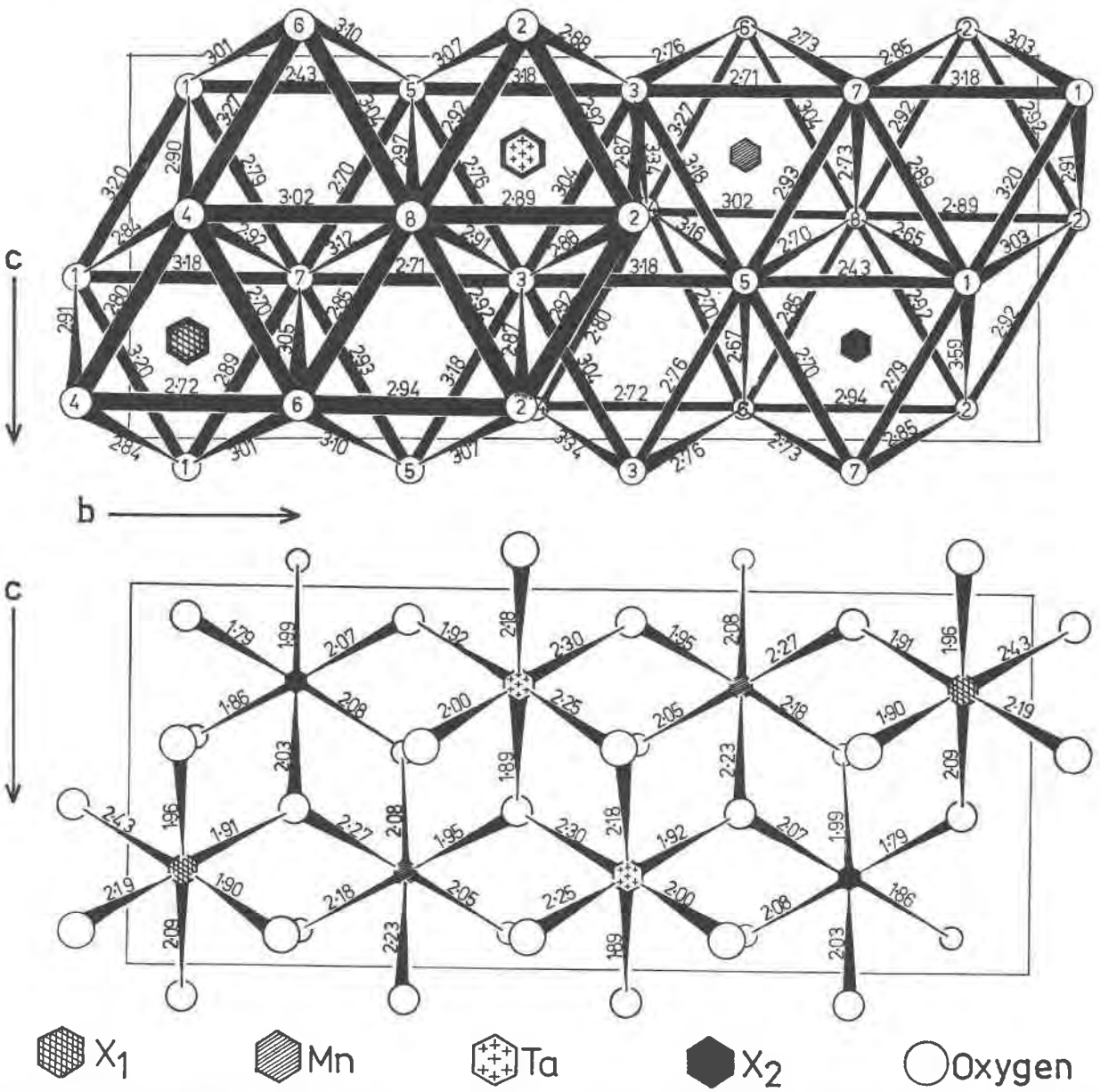

FIG. 3. Idealized projections of structure along the a axis from $a = 0$ to 0.5 showing oxygen-oxygen (top) and metal-oxygen (bottom) bond lengths in Å.

TABLE 3. Observed and Calculated Structure Factors for Wodginite

h	k	l	F(obs)	F(calc)	h	k	l	F(obs)	F(calc)	h	k	l	F(obs)	F(calc)	h	k	l	F(obs)	F(calc)	h	k	l	F(obs)	F(calc)
4	0	0	40.6	49.5	-8	2	2	5.1	3.3	-2	4	2	8.2	8.9	4	6	2	14.2	12.2	6	8	3	10.8	11.3
6	0	0	11.7	14.6	10	2	2	16.3	14.9	4	4	2	28.2	28.4	-4	6	2	17.7	14.6	-6	8	3	14.7	11.0
8	0	0	41.2	51.4	-10	2	2	17.2	15.2	-4	4	2	34.6	28.7	6	6	2	42.8	41.7	8	8	3	26.2	27.2
10	0	0	8.9	11.6	0	2	3	14.3	13.2	6	4	2	8.7	8.1	-6	6	2	55.6	43.4	-8	8	3	30.5	27.9
12	0	0	21.2	27.5	2	2	3	49.6	46.1	-6	4	2	12.6	9.0	8	6	2	12.3	13.1	0	8	4	9.9	12.2
0	0	2	58.2	58.2	-2	2	3	46.5	49.8	8	4	2	20.2	21.7	-8	6	2	11.1	9.2	2	8	4	7.7	5.6
2	0	2	6.7	3.5	4	2	3	14.4	13.0	-8	4	2	28.5	22.4	10	6	2	33.1	29.7	2	8	-4	5.6	1.4
2	0	-2	28.2	28.0	-4	2	3	11.6	11.8	10	4	2	8.5	7.5	-10	6	2	32.5	30.0	4	8	4	14.7	14.5
4	0	2	65.6	62.4	6	2	3	39.3	37.0	-10	4	2	6.8	6.2	0	6	3	4.6	3.4	4	8	-4	10.9	14.3
4	0	-2	54.8	62.7	-6	2	3	40.9	36.2	0	4	3	54.7	51.6	2	6	3	6.1	5.2	6	8	4	3.6	1.3
6	0	2	21.8	21.2	8	2	3	9.2	10.8	2	4	3	13.0	10.7	-2	6	3	9.4	3.6	6	8	-4	6.7	3.7
6	0	-2	7.4	7.9	-8	2	3	9.7	10.2	-2	4	3	12.1	10.3	4	6	3	4.7	3.7	0	8	5	24.7	29.7
8	0	2	31.9	38.0	-10	2	3	31.3	30.1	4	4	3	31.0	30.9	-4	6	3	6.6	3.6	2	8	5	8.3	10.7
8	0	-2	37.6	39.7	10	-2	3	25.7	28.3	-4	4	3	37.3	32.9	6	6	3	5.3	4.5	-2	8	5	5.8	9.8
10	0	2	4.9	8.8	0	2	4	7.9	7.0	6	4	3	9.9	10.0	-6	6	3	8.9	6.1	4	8	5	21.1	26.4
10	0	-2	10.5	13.0	2	2	4	24.9	22.0	-6	4	3	10.0	9.0	8	6	3	4.7	2.7	1	9	0	10.1	8.8
0	0	4	38.1	43.7	-2	2	4	21.3	20.0	8	4	3	34.0	33.6	-8	6	3	4.4	2.6	3	9	0	8.6	8.5
2	0	4	15.1	19.7	4	2	4	5.1	5.2	-8	4	3	40.0	33.2	0	6	4	12.2	12.7	5	9	0	8.1	7.2
2	0	-4	6.2	7.2	-4	2	4	5.8	3.3	10	4	3	5.8	8.3	2	6	4	42.0	39.7	7	9	0	8.9	6.4
4	0	4	43.1	45.6	6	2	4	18.4	17.5	10	4	-3	7.9	7.5	-2	6	4	39.0	39.1	9	9	0	7.6	6.4
4	0	-4	45.4	45.9	-6	2	4	21.9	19.5	0	4	4	26.1	24.7	4	6	4	11.3	11.8	1	9	1	5.7	6.1
6	0	4	6.6	8.0	-8	2	4	7.3	5.9	2	4	4	9.0	7.7	-4	6	4	12.5	9.5	-1	9	1	12.9	6.3
6	0	-4	14.8	14.4	8	-2	4	2.8	4.5	-2	4	4	9.5	8.7	6	6	4	31.3	33.4	3	9	1	3.5	3.7
8	0	4	22.3	30.6	0	2	5	7.1	9.5	4	4	4	22.6	22.0	-6	6	4	44.1	35.1	-3	9	1	6.4	5.6
8	0	-4	34.4	33.1	2	2	5	32.4	33.5	-4	4	4	25.2	22.6	8	-6	4	6.7	9.8	5	9	1	4.8	5.6
0	0	6	32.2	35.5	-2	2	5	32.3	33.2	6	4	4	8.4	8.1	8	6	-4	9.3	10.4	-5	9	1	4.8	4.6
2	0	6	5.9	10.6	4	2	5	9.2	10.8	-6	4	4	7.5	6.5	0	6	5	5.3	4.1	7	9	1	3.9	4.7
2	0	-6	8.9	10.2	-4	2	5	9.6	11.5	8	4	4	15.7	17.4	2	6	5	4.5	3.4	7	9	-1	5.5	4.2
4	0	6	17.0	26.7	-6	2	5	32.7	29.8	-8	4	4	21.2	18.1	-2	6	5	4.5	3.9	1	9	2	8.8	8.6
4	0	-6	23.6	28.7	6	-2	5	21.4	28.2	0	4	5	26.1	28.8	4	6	5	5.2	2.2	-1	9	2	8.9	7.9
1	1	0	6.7	7.3	0	2	6	4.3	4.7	2	4	5	4.2	5.1	-4	6	5	3.5	1.5	3	9	2	9.9	7.5
3	1	0	5.7	7.4	2	2	6	12.0	13.9	-2	4	5	12.3	11.8	1	7	0	3.4	5.4	3	9	-2	10.5	7.2
5	1	0	2.8	5.4	-2	2	6	16.5	16.3	4	4	5	27.5	30.1	3	7	0	3.4	4.8	5	9	2	6.9	7.5
7	1	0	4.1	6.0	-4	2	6	4.7	3.7	-4	4	5	33.0	30.4	5	7	0	4.6	4.9	-5	9	2	9.7	7.1
9	1	0	4.2	4.6	1	3	0	13.5	12.4	6	4	5	8.2	11.5	7	7	0	5.4	4.3	7	9	2	4.0	6.1
1	1	1	14.2	11.8	3	3	0	8.4	10.5	-6	4	5	3.2	5.8	9	-7	0	5.5	4.4	7	9	-2	8.5	7.2
-1	1	1	10.2	11.7	5	3	0	8.2	9.5	0	4	6	14.5	16.8	1	7	1	8.9	8.0	1	9	3	4.8	5.5
3	1	1	9.1	9.2	7	3	0	9.5	8.7	2	4	6	6.2	6.7	3	7	1	9.8	9.1	-1	9	3	7.2	3.9
-3	1	1	7.5	9.8	9	-3	0	10.5	7.2	-2	4	6	6.0	6.2	-3	7	1	9.0	10.5	3	9	3	4.3	4.2
5	1	1	8.9	9.3	11	-3	0	4.3	5.8	4	4	6	1.4	16.1	5	7	1	8.4	8.7	3	9	-3	4.8	6.0
-5	1	1	7.2	8.4	1	3	1	2.3	5.0	1	5	0	7.5	7.9	-5	7	1	7.3	7.5	5	9	3	4.2	6.5
7	1	1	6.7	7.3	-1	3	1	2.2	5.4	3	5	0	8.3	8.2	7	7	1	9.0	8.8	5	9	-3	4.2	4.9
-7	1	1	7.5	7.8	3	3	1	5.4	5.7	5	5	0	8.7	8.5	-7	7	1	9.6	7.1	1	9	4	3.9	6.7
9	1	1	7.4	7.5	-3	3	1	3.2	5.0	7	5	0	5.0	5.5	9	7	1	6.5	5.2	3	9	4	7.0	6.4
-9	1	1	6.9	7.5	5	3	1	2.8	4.7	9	5	0	8.1	6.3	-9	7	1	7.3	6.6	5	9	4	6.4	6.3
11	1	1	4.1	4.8	5	3	-1	3.7	4.6	1	5	1	6.6	7.8	0	7	-2	4.7	0.0	5	9	-4	5.6	6.3
1	1	2	4.9	6.2	7	3	1	4.1	5.2	-1	5	1	6.3	8.4	1	7	2	4.1	5.4	0	10	0	13.6	10.6
-1	1	2	5.4	6.8	-7	3	1	5.2	4.7	3	5	1	6.6	8.1	-1	7	2	4.6	4.9	2	10	0	25.2	26.5
3	1	2	7.4	7.2	9	3	1	4.5	3.9	-3	5	1	9.9	8.5	3	7	2	4.8	5.0	4	10	0	11.9	10.3
-3	1	2	2.9	5.7	-9	3	1	5.9	4.5	5	5	1	7.0	7.3	-3	7	2	3.8	4.3	6	10	0	27.9	24.0
5	1	2	4.0	5.0	1	3	2	9.8	9.6	-5	5	1	8.4	7.3	5	7	2	7.3	4.7	8	10	0	7.2	8.6
-5	1	2	5.1	6.6	-1	3	2	8.6	9.7	7	5	1	7.9	7.4	-5	7	2	5.7	4.8	0	10	1	7.0	8.1
7	1	2	4.4	6.6	3	3	2	12.2	10.6	-7	5	1	5.6	6.5	7	7	2	6.0	4.1	2	10	1	31.8	31.3
-7	1	2	6.8	6.1	-3	3	2	10.9	10.7	9	5	1	4.8	4.8	-7	7	2	5.3	4.6	-2	10	1	34.0	32.2
9	1	2	4.3	4.0	5	3	2	8.7	9.3	-9	5	1	5.1	5.2	9	7	2	4.6	4.6	4	10	1	9.5	8.1
-9	1	2	3.6	4.1	-5	3	2	10.0	9.6	1	5	2	8.6	8.5	-9	7	2	3.8	4.4	-4	10	1	4.6	5.8
1	1	3	11.7	10.2	7	3	2	9.5	7.7	-1	5	2	7.2	6.6	1	7	3	7.7	8.5	6	10	1	34.8	27.8
-1	1	3	7.2	7.5	-7	3	2	6.0	7.3	3	5	2	6.0	6.7	-1	7	3	9.1	8.9	6	10	-1	31.6	27.4
3	1	3	9.7	8.4	9	3	2	4.9	6.5	-3	5	2	8.3	8.2	3	7	3	9.5	9.2	8	10	1	5.6	5.5
-3	1	3	7.2	8.4	-9	3	2	9.8	6.4	5	5	2	9.9	8.3	-3	7	3	7.6	6.6	8	10	-1	8.5	7.6
5	1	3	8.4	8.5	11	3	2	6.5	5.8	-5	5	2	7.0	7.2	5	7	3	6.6	5.8	0	10	2	12.9	10.9
-5	1	3	6.6	8.1	-11	3	2	6.6	5.8	7	5	2	5.6	4.5	-5	7	3	9.8	8.2	2	10	2	25.6	25.1
7	1	3	5.1	5.5	1	3	3	3.5	4.6	-7	5	2	8.8	6.0	7	7	3	6.4	7.6	2	10	-2	27.7	25.4
-7	1	3	6.0	7.3	-1	3	3	4.3	5.3	9	5	2	5.8	6.8	-7	7	3	8.6	7.2	4	10	2	9.4	9.9
-9	1	3	5.7	5.9	3	3	3	4.8	5.8	-9	5	2	5.4	5.7	9	-7	3	3.2	5.0	-4	10	2	10.3	8.6
9	-1	3	6.0	6.9	-3	3	3	6.4	4.7	1	5	3	5.6	6.7	9	7	-3	4.8	5.6	6	10	2	19.5	20.6
1	1	4	4.0	4.8	5	3	3	5.0	4.1	-1	5	3	8.3	8.3	1	7	4	6.5	4.3	6	10	-2	23.9	20.8
-1	1	4	4.1	6.5	-5	3	3	4.7	5.3	3	5	3	7.4	7.3	-1	7	4	5.4	4.8	8	10	-2	8.0	9.1
3	1	4	5.7	6.8	7	3	3	5.1	5.0	-3	5	3	6.0	7.3	3	7	4	4.7	4.3	0	10	3	8.5	6.3
-3	1	4	4.0	5.3	-7	3	3	5.4	4.2	5	5	3	5.1	5.9	3	7	-4	5.4	4.9	2	10	3	28.0	27.2
5	1	4	4.4	4.2	9	3	3	4.1	4.1	-5	5	3	6.3	5.7	5	7	4	6.4	5.1	-2	10	3	27.1	28.7
-5	1	4	5.5	5.3	-9	3	3	4.2	3.8	7	5	3	4.9	6.5	5	7	-4	4.8	4.1	4	10	3	6.8	7.3
-7	1	4	4.1	4.4	1	3	4	9.1	8.3	-7	5	3	7.9	5.7	7	7	-4	2.4	3.5	4	10	-3	7.7	6.6
7	-1	4	3.5	5.9	-1	3	4	10.8	9.5	9	5	3	4.0	4.6	1	7	5	5.1	5.2	6	10	3	21.8	23.3
9	1	-4	2.6	4.9	3	3	4	7.5	7.1	-9	5	3	7.3	5.4	-1	7	5	4.0	7.0	6	10	-3	26.0	22.9
1	1	5	4.2	6.7	-3	3	4	5.3	7.7	1	5	4	8.2	8.5	3	7	5	8.6	7.8	2	10	4	16.3	19.8
-1	1	5	3.3	5.7	5	3	4	9.0	7.1	-1	5	4	5.6	6.6	-3	7	5	5.7	5.9	4	10	4	7.6	8.7
3	1	5	5.0	5.9	-5	3	4	5.9	6.5	3	5	4	5.1	3.4	5	7	5	2.4	4.9	1	11	0	8.0	7.7
-3	1	5	9.1	8.1	7	3	4	7.9	7.2	-3	5	4	6.7	6.5	5	7	-5	4.3	6.8	3	11	0	4.5	7.2
-5	1	5	5.3	6.2	-7	3	4	8.3	6.4	5	5	4	4.9	6.7	0	8	0	31.4	27.2	5	11	0	7.4	6.2
5	-1	5	6.5	7.9	-9	3	4	5.6	6.2	-5	5	4	4.7	4.3	2	8	0	3.9	2.1	7	11	0	8.3	7.2
-7	1	5	4.5	5.1	1	3	5	9.2	4.3	7	5	4	4.2	4.6	4	8	0	10.9	11.1	1	11	1	9.3	5.0
7	-1	5	2.4	4.3	-1	3	5	4.7	5.1	-7	5	4	6.3	6.1	6	8	0	6.0	2.3	-1	11	1	5.1	6.0
1	1	6	3.7	3.8	3	3	5	4.9	5.0	1	5	5	4.5	5.8	8	8	0	22.4	16.8	3	11	1	4.6	5.1
-1	1	6	6.7	5.7	-3	3	5	4.1	3.8	-1	5	5	5.8	5.8	10	-8	0	3.0	2.1	-3	11	1	4.8	6.1
-3	1	6	3.0	4.3	5	3	5	4.1	4.1	3	5	5	4.0	6.3	0	8	1	45.0	46.6	5	11	1	6.2	6.0
0	2	0	10.9	7.4	-5	3	5	5.2	4.8	-3	5	5	4.2	4.7	2	8	1	10.7	12.5	5	11	-1	8.0	5.0
2	2	0	34.6	35.7	7	3	-5	2.4	4.5	5	5	5	4.0	4.4	-2	8	1	14.5	14.9	7	11	-1	4.0	3.9
4	2	0	6.7	6.4	1	3	6	7.0	6.4	-5	5	5	6.5	5.8	4	8	1	39.2	40.7	1	11	2	6.6	7.1
6	2	0	20.6	22.1	-1	3	6	3.2	3.6	7	5	5	1.4	5.5	-4	8	1	45.6	41.3	3	11	2	7.4	8.9
8	2	0	6.9	5.5	3	3	6	6.3	6.5	1	5	6	5.1	6.3	6	8	1	13.1	13.3	-3	11	2	6.5	5.9
10	2	0	22.2	19.4	-3	3	6	4.9	5.1	0	6	0	17.2	14.0	-6	8	1	12.5	11.0	5	11	-2	8.5	7.3
0	2	1	19.3	16.5	0	4	0	40.6	36.4	2	6	0	60.0	58.1	8	8	1	34.9	32.4	7	11	2	5.3	6.1
2	2	1	66.2	60.1	2	4	0	11.7	10.6	4	6	0	17.1	14.3	-8	8	1	39.0	32.4	1	11	3	5.4	5.6
-2	2	1	48.7	59.8	4	4	0	32.7	33.7	6	6	0	43.0	43.7	-10	8	1	9.2	10.7	5	11	-3	3.3	4.8
4	2	1	17.1	15.9	6	4	0	10.2	9.2	8	6	0	12.0	11.5	10	-8	1	8.0	9.5	0	12	0	32.0	34.9
-4	2	1	10.9	11.0	8	4	0	25.5	22.9	10	-6	0	41.2	34.1	0	8	2	14.3	14.3	2	12	0	11.0	10.2
6	2	1	44.6	46.7	10	-4	0	5.9	7.1	0	6	1	3.6	4.4	2	8	2	4.7	3.3	4	12	0	37.3	34.0
-6	2	1	45.7	47.5	0	4	1	45.5	46.8	2	6	1	4.6	5.8	-2	8	2	10.2	7.3	6	12	0	11.7	9.6
8	2	1	9.0	10.1	2	4	1	23.4	24.3	-2	6	1	7.9	6.8	4	8	2	19.6	18.7	0	12	1	10.7	8.8
-8	2	1	13.9	13.6	-2	4	1	3.7	2.0	4	6	1	3.0	3.4	-4	8	2	20.8	18.5	2	12	1	4.2	2.9
10	2	1	31.8	30.3	4	4	1	43.4	52.3	-4	6	1	6.9	5.9	6	8	2	7.1	5.8	-2	12	1	9.4	8.4
-10	2	1	34.9	30.7	-4	4	1	52.4	52.5	6	6	1	7.5	3.8	-6	8	2	5.2	2.3	4	12	1	3.9	5.3
0	2	2	5.4	4.8	6	4	1	4.9	5.1	-6	6	1	5.2	3.4	8	8	2	11.4	10.6	4	12	-1	7.5	5.3
2	2	2	34.2	28.7	-6	4	1	19.6	16.4	8	6	1	4.6	4.6	-8	8	2	14.0	11.4	6	12	1	8.9	7.1
-2	2	2	27.9	28.0	8	4	1	30.6	31.5	-8	6	1	5.0	2.0	0	8	3	34.1	37.6	6	12	-1	2.4	3.4
4	2	2	6.7	5.8	-8	4	1	36.2	32.1	10	6	1	6.2	4.0	2	8	3	12.6	12.7	6	12	2	11.7	10.6
-4	2	2	9.9	8.9	10	4	1	11.7	11.7	-10	6	1	4.1	4.2	-2	8	3	12.4	11.8	-2	12	2	9.4	9.2
6	2	2	23.6	23.4	-10	4	1	5.7	6.5	0	6	2	15.7	13.8	4	8	3	34.6	36.0	4	12	2	29.9	30.4
-6	2	2	27.6	24.3	0	4	2	35.7	33.8	2	6	2	51.7	51.5	-4	8	3	38.8	36.7	-4	12	2	29.2	30.5
8	2	2	8.2	6.7	2	4	2	12.1	10.8	-2	6	2	51.1	50.2						2	12	3	2.4	5.2

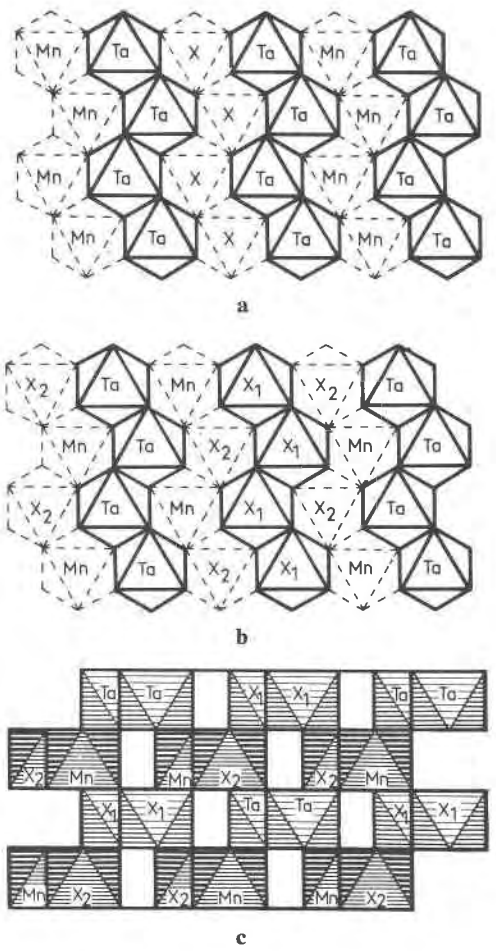

FIG. 4. Projections of the metal-oxygen octahedra in wodginite: (**a**) (100) projection of Grice's (1972) centrosymmetrical model; (**b**) and (**c**) (100) and (001) projections of the preferred non-centrosymmetric model. (**c**) is a view along the octahedral chains, and only the front octahedron can be fully seen.

of little significance. No refinement was made of the oxygen temperature factors which were arbitrarily set at 1.0.

Discussion

The centrosymmetric result approached as nearly as possible to that indicated by the non-centrosymmetric space group. The final metal ordering is shown in Figure 4. It was not possible to differentiate sites X_1 and X_2 on the basis of X-ray results alone, although X_2 is somewhat smaller in size. The Madelung energy is maximized if X_2 contains 5-valent ions and X_1 contains 4-valent ions (Part V), and this would suggest the assignment $X_1 = (Ta_{0.42}Sn_{0.47}Fe_{0.01}\square_{0.1})^{4+}$, $X_2 = (Ta_{0.7}Nb_{0.3})^{5+}$. X_1 and X_2 have similar scattering factors as required (average atomic number 54 and 63 respectively), and the only inconsistency is the small size of site X_2.

In most wodginites, the Mn site is probably occupied by a mixture of Mn and Fe, and vacancies do not occur on the X sites.

Subsequent to the completion of this work, Grice (1972) refined the structure, using diffractometer data, but in the centrosymmetric space group. Although the result gave only a moderate reliability index, Grice's choice of origin allowed a different ordering scheme (Fig. 4), which is slightly favored electrostatically over our centrosymmetric structure. This could have been reproduced by our non-centrosymmetric model (the lowest structure in Figure 4) which is electrostatically the more stable because the octahedrally coordinated low-charge Mn^{2+} is fully surrounded by octahedra containing the more highly charged X_2^{5+} edge-shared, and Ta^{5+} and X_1^{4+} corner-shared. As indicated in Figure 2, variations in composition could occur within the crystal fragment on which the structure was determined, and its average composition could differ from that quoted even though the probe analysis was made on wodginite from the same grain. Grice used quite large crystals which probably share the same problem. Continuing studies with electron microscope techniques are likely to give valuable information on whether there is further ordering in wodginite on a sub-micro scale not resolvable by X-ray methods. These structures are discussed further in Part V of this series.

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