

## The Crystal Structure of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>

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Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> is orthorhombic, space group *Ima2*, with  $a = 40.91$ ,  $b = 4.93$ ,  $c = 5.27$  Å. The asymmetric structural unit contains one octahedron, three sevenfold coordinated ions, and one square antiprism, and its relations to the fluorite and ZrO<sub>2</sub> structures are discussed. Variations in compositions can be accounted for by increasing or decreasing the number of sevenfold coordinated ions in the structure.

### Introduction

Zirconium dioxide would be an attractive material for high temperature applications if it did not contain the disruptive-monoclinic to tetragonal phase transition. Dense polycrystalline zirconia ceramics are useful at high temperatures only if the material is "stabilized" in some other crystal structure. The cubic fluorite structure can be obtained by using CaO (or MgO) or by using Y<sub>2</sub>O<sub>3</sub> (or some of the heavier rare earth oxides). This cubic phase is then anion deficient with only a partial tendency, if any, for ordered oxygen vacancies to occur, of the type described for the Sc<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> system (1) and the CaO-ZrO<sub>2</sub> system (2).

It has long been known that Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> form an orthorhombic phase with ZrO<sub>2</sub> at a composition of about Nb<sub>2</sub>O<sub>5</sub>·6ZrO<sub>2</sub> (3). Recently this phase has been shown to have a superstructure, which varies with composition over a range from about Nb<sub>2</sub>O<sub>5</sub>·5ZrO<sub>2</sub> to Nb<sub>2</sub>O<sub>5</sub>·8ZrO<sub>2</sub> (4). These compositions were reported to belong to a continuous homologous series M<sub>n</sub>O<sub>2n+1</sub>, where  $n$  varies from ~7 to 10. The superstructure occurs only in one direction with a multiple cell varying from ~7 to 10 times the ~5 Å cell of the basic fluorite structure. Single crystals from the previous work (4) have

been utilized in the present study to solve the structure of the phase Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>.

### Experimental

Colorless crystals of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> were picked from a mixture of Nb<sub>2</sub>O<sub>5</sub>·6ZrO<sub>2</sub>, which was slowly cooled from 1200°C in a BaO-V<sub>2</sub>O<sub>5</sub> flux. Annealing at 1450°C for 60 hours improved the quality of the superstructure spots. The symmetry and approximate unit-cell size were determined by single crystal methods using precession (4), rotation, and Weissenberg photographs. The crystal was mounted on a Nonius CAD-3 automatic diffractometer.

The cell parameters listed in Table I were refined from the diffractometer data. Intensities

TABLE I  
CRYSTAL DATA OF Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>

|                              |
|------------------------------|
| $a = 40.92(2)$ Å             |
| $b = 4.93(1)$                |
| $c = 5.27(1)$                |
| Volume = 1064 Å <sup>3</sup> |
| $D_{\text{calc}} = 6.27$     |
| $Z = 4$                      |
| Space group = <i>Ima2</i>    |

were recorded with  $\text{MoK}\alpha$  radiation for the reciprocal lattice points within one octant with  $\theta < 40^\circ$ . A  $\theta$ - $2\theta$  scanning mode was used with each reflection scanned until the counting statistics were favorable (with a limit of 10 scans). In the calculations, 921 reflections with  $\sigma(I)/I < 0.5$  were used. No absorption corrections have been made; the crystal measured less than 0.04 mm in the maximum dimension.

### Structure Determination

The two space groups consistent with the symmetry and the systematic extinctions are *Ima2* or *Imam*. From the three-dimensional Patterson function it has been possible by considering the  $Z_r$ - $Z_r$  vectors to exclude the space group *Imam*.

All the calculations were performed on an IBM 360-44. The programs used were written by M. Saux and J. Galy. The full matrix least-squares program is an adaptation of the Busing, Martin, and Levy program (5).

The scattering factors of zirconium and oxygen atoms given by McMaster et al. (6) were used with dispersion corrections. Niobium is considered in the calculations as having the same scattering factor as a zirconium atom. A structure has been proposed on the basis of a theoretical model consistent with the Patterson map.

This model was based on several considerations. Figure 1 is a representation of the fluorite-type structure,  $\text{MO}_2$ . If one of two strings of oxygen atoms in alternate planes is moved in the

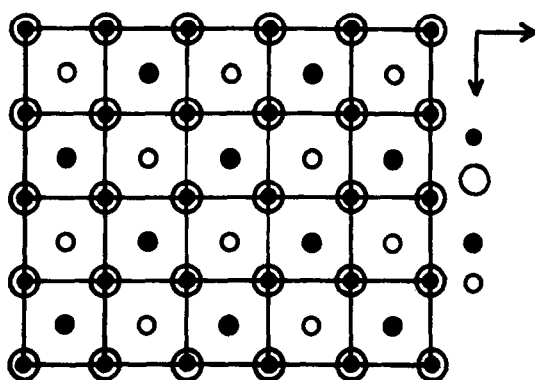


FIG. 1. The fluorite-type structure with composition  $\text{MO}_2$  composed of cubes with the metal atom in eightfold coordination. ●, oxygen at  $y = \frac{3}{4}$ ; ○, oxygen at  $y = \frac{1}{4}$ ; ●, metal at  $y = \frac{1}{2}$ ; ○, metal at  $y = 0$ .

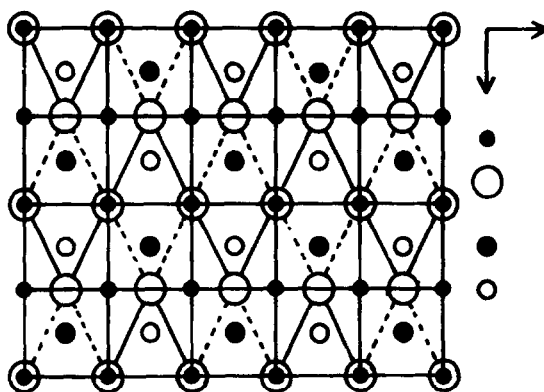


Fig. 2. A hypothetical structure with  $\text{MO}_2$  composition composed of sevenfold coordinated metal atoms formed by "pulling the string" of alternate rows of oxygen atoms. ●, oxygen at  $y = \frac{3}{4}$ ; ○, oxygen at  $y = \frac{1}{4}$ ; ●, metal at  $y = \frac{1}{2}$ ; ○, metal at  $y = 0$ .

$z$  direction as shown in Fig. 2, we get a structure, still with the  $\text{MO}_2$  composition, in which the metal atom coordination decreases from 8 to 7. This concept of "pulling the string" of oxygen atoms in a structure to change the coordination of a cation while the composition is left unchanged was originated by S. Andersson (personal communication). Note that if the "string" of oxygen atoms in the second plane at alternate levels is also "pulled" the polyhedra become trigonal antiprisms or octahedra. Finally, it was also necessary to find a way to change the composition in order to obtain an  $\text{MO}_{2+x}$

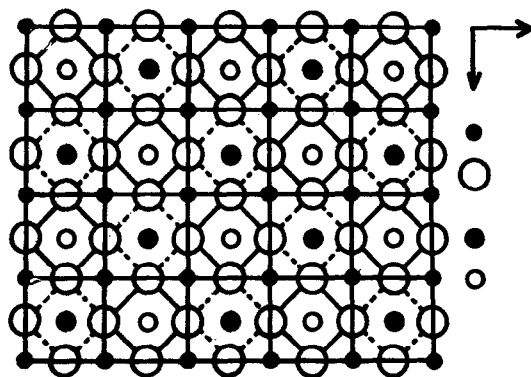


FIG. 3. A hypothetical structure with composition  $\text{MO}_3$  composed of square antiprisms (eightfold coordination). ●, oxygen at  $y = \frac{3}{4}$ ; ○, oxygen at  $y = \frac{1}{4}$ ; ●, metal at  $y = \frac{1}{2}$ ; ○, metal at  $y = 0$ .

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub><sup>a</sup>

|                | $x/a$         | $y/b$         | $z/c$         | $B(\text{\AA}^2)$ |
|----------------|---------------|---------------|---------------|-------------------|
| M <sub>1</sub> | 0             | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.39(6)           |
| M <sub>2</sub> | $\frac{1}{4}$ | 0.5151(9)     | 0.5087(9)     | 0.44(6)           |
| M <sub>3</sub> | 0.06500(7)    | -0.0152(8)    | 0.5894(6)     | 0.70(4)           |
| M <sub>4</sub> | 0.12780(6)    | 0.5138(8)     | 0.5136(8)     | 0.42(4)           |
| M <sub>5</sub> | 0.18965(6)    | -0.0151(9)    | 0.5861(9)     | 0.56(5)           |
| O <sub>1</sub> | $\frac{1}{4}$ | 0.3564(54)    | 0.1537(55)    | 0.78(33)          |
| O <sub>2</sub> | 0.1976(4)     | 0.3485(36)    | 0.4426(38)    | 0.43(20)          |
| O <sub>3</sub> | 0.2195(6)     | 0.8082(35)    | 0.3110(52)    | 0.09(20)          |
| O <sub>4</sub> | 0.1589(5)     | 0.7925(34)    | 0.3251(60)    | 0.75(40)          |
| O <sub>5</sub> | 0.0956(4)     | 0.7915(43)    | 0.2785(45)    | -0.14(22)         |
| O <sub>6</sub> | 0.0362(5)     | 0.7505(52)    | 0.3797(45)    | 0.86(31)          |
| O <sub>7</sub> | 0.0827(5)     | 0.2994(47)    | 0.4251(52)    | 0.48(29)          |
| O <sub>8</sub> | 0.0249(5)     | 0.2973(47)    | 0.1839(48)    | 0.46(28)          |
| O <sub>9</sub> | 0.1419(5)     | 0.3421(44)    | 0.1826(49)    | 0.63(30)          |

<sup>a</sup> The numbers in parentheses are standard deviations in the last significant figures.

formula. Therefore, square antiprisms have been introduced to increase the anion content. It is possible to imagine a hypothetical structure built with square antiprisms only (Fig. 3), with the composition MO<sub>3</sub>.

The model obtained was then: 1 square antiprism, eightfold coordination, located on the mirror plane; 1 cube, eightfold coordination, on the twofold axis; and 3 polyhedra with sevenfold coordination, which permit the linkage of

cubes and square antiprisms. Figure 4 gives an ideal picture of this model with the composition M<sub>8</sub>O<sub>17</sub> or Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>.

### Refinement

Least-squares refinement of atomic coordinates and isotropic thermal parameters reduced the conventional  $R$  value to 0.057 for the 921 reflections and the results of this refinement are listed in Table II. Observed and calculated structure factors are reported in Table III. The space group *Ima2* is noncentrosymmetric, so the  $z$  coordinate for the atom Zr<sub>1</sub> was fixed at  $z = \frac{1}{2}$ . The interatomic distances are given in Table IV.

### Description of the Structure

A ball and spoke model of the structure projected on (010) is given in Fig. 5. The refined structure is distinctly different from the model shown in Fig. 4. The structure contains three types of coordination polyhedra, all distorted. The metal atoms in M<sub>1</sub> positions are surrounded by six oxygens forming an octahedron; M<sub>1</sub> is on the twofold axis parallel to the  $z$  axis. The other position M<sub>2</sub> is at the center of a distorted square antiprism centered on the mirror plane at  $x = \frac{1}{4}$ . Finally, M<sub>3</sub>, M<sub>4</sub>, and M<sub>5</sub> positions correspond to metal atoms surrounded by seven oxygens. The type of coordination and polyhedral linkage of M<sub>4</sub> and M<sub>5</sub> is also found, for example, in the monoclinic form of ZrO<sub>2</sub>, and

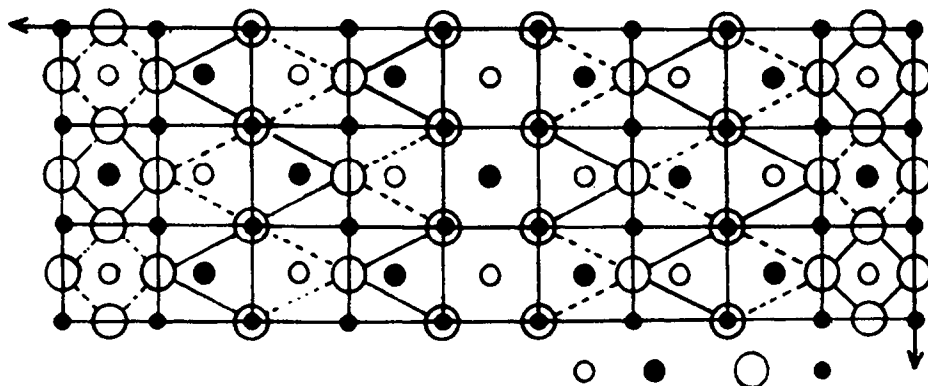


FIG. 4. A hypothetical structure having the composition M<sub>8</sub>O<sub>17</sub> composed of combinations of the polyhedra shown in Figs. 1, 2, and 3. The ideal model used for least-squares refinement of the structure Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>. ●, oxygen at  $y = \frac{3}{4}$ ; ○, oxygen at  $y = \frac{1}{4}$ ; ●, metal at  $y = \frac{1}{2}$ ; ○, metal at  $y = 0$ .





TABLE IV

SELECTED INTERATOMIC DISTANCES IN ANGSTROMS OF  
 $\text{Nb}_2\text{Zr}_6\text{O}_{17}^a$ (Estimated Standard Deviations  $\text{M}-\text{O} = 0.012$  and  
 $\text{O}-\text{O} = 0.025$ )

|                                  |       |   |
|----------------------------------|-------|---|
| <b>M<sub>1</sub></b>             |       |   |
| O <sub>6</sub> (2)               | 2.032 |   |
| O <sub>8</sub> (2)               | 2.195 |   |
| O <sub>81</sub> (2)              | 2.032 | M <sub>1</sub> —O = 2.086 C.N.6         |
| O <sub>61</sub> (2)              | 2.778 |   |
| <b>M<sub>2</sub></b>             |       |   |
| O <sub>1</sub>                   | 2.029 |   |
| O <sub>11</sub>                  | 1.986 |   |
| O <sub>2</sub> (2)               | 2.322 | M <sub>2</sub> —O = 2.177 C.N.8         |
| O <sub>3</sub> (2)               | 2.176 |   |
| O <sub>31</sub> (2)              | 2.204 |   |
| <b>M<sub>3</sub></b>             |       |   |
| O <sub>7</sub>                   | 1.919 |   |
| O <sub>71</sub>                  | 2.189 |   |
| O <sub>81</sub>                  | 2.024 |   |
| O <sub>6</sub>                   | 2.001 | M <sub>3</sub> —O = 2.114 C.N.7         |
| O <sub>61</sub>                  | 2.266 |   |
| O <sub>5</sub>                   | 2.283 |   |
| O <sub>51</sub>                  | 2.118 |   |
| <b>M<sub>4</sub></b>             |       |   |
| O <sub>5</sub>                   | 2.269 |   |
| O <sub>51</sub>                  | 2.147 |   |
| O <sub>7</sub>                   | 2.177 |   |
| O <sub>4</sub>                   | 2.121 | M <sub>4</sub> —O = 2.154 C.N.7         |
| O <sub>41</sub>                  | 2.024 |   |
| O <sub>91</sub>                  | 2.052 |   |
| <b>M<sub>5</sub></b>             |       |   |
| O <sub>91</sub>                  | 2.190 |   |
| O <sub>2</sub>                   | 1.974 |   |
| O <sub>21</sub>                  | 2.030 |   |
| O <sub>4</sub>                   | 2.091 | M <sub>5</sub> —O = 2.122 C.N.7         |
| O <sub>41</sub>                  | 2.248 |   |
| O <sub>3</sub>                   | 2.088 |   |
| O <sub>31</sub>                  | 2.235 |   |
| O <sub>1</sub> —O <sub>2</sub>   | 2.630 | O <sub>5</sub> —O <sub>6</sub> 2.496    |
| O <sub>2</sub> —O <sub>11</sub>  | 2.619 | O <sub>5</sub> —O <sub>51</sub> 2.668   |
| O <sub>1</sub> —O <sub>3</sub>   | 2.686 | O <sub>6</sub> —O <sub>61</sub> 2.637   |
| O <sub>2</sub> —O <sub>9</sub>   | 2.660 | O <sub>6</sub> —O <sub>82</sub> 2.715   |
| O <sub>2</sub> —O <sub>21</sub>  | 2.760 | O <sub>6</sub> —O <sub>8</sub> 2.506    |
| O <sub>2</sub> —O <sub>91</sub>  | 2.771 | O <sub>61</sub> —O <sub>51</sub> 2.496  |
| O <sub>2</sub> —O <sub>31</sub>  | 2.728 | O <sub>7</sub> —O <sub>8</sub> 2.685    |
| O <sub>2</sub> —O <sub>4</sub>   | 2.773 | O <sub>7</sub> —O <sub>81</sub> 2.772   |
| O <sub>2</sub> —O <sub>41</sub>  | 3.113 | O <sub>7</sub> —O <sub>6</sub> 2.937    |
| O <sub>21</sub> —O <sub>41</sub> | 3.213 | O <sub>7</sub> —O <sub>51</sub> 2.797   |
| O <sub>21</sub> —O <sub>91</sub> | 2.633 | O <sub>7</sub> —O <sub>91</sub> 2.863   |
| O <sub>3</sub> —O <sub>31</sub>  | 2.698 | O <sub>8</sub> —O <sub>81</sub> 2.677   |
| O <sub>3</sub> —O <sub>4</sub>   | 2.482 | O <sub>8</sub> —O <sub>62</sub> 2.715   |
| O <sub>3</sub> —O <sub>2</sub>   | 2.535 | O <sub>81</sub> —O <sub>612</sub> 2.715 |

TABLE IV—continued

|                                  |       |                                 |       |
|----------------------------------|-------|---------------------------------|-------|
| O <sub>3</sub> —O <sub>32</sub>  | 2.496 | O <sub>81</sub> —O <sub>7</sub> | 2.772 |
| O <sub>31</sub> —O <sub>11</sub> | 3.091 | O <sub>9</sub> —O <sub>91</sub> | 2.789 |
| O <sub>31</sub> —O <sub>21</sub> | 2.884 |                                 |       |
| O <sub>4</sub> —O <sub>41</sub>  | 2.670 |                                 |       |
| O <sub>4</sub> —O <sub>5</sub>   | 2.602 |                                 |       |
| O <sub>4</sub> —O <sub>9</sub>   | 2.446 |                                 |       |
| O <sub>4</sub> —O <sub>91</sub>  | 3.720 |                                 |       |

<sup>a</sup> Numbers in parentheses indicate an average of two values.

Mumme and Wadsley (7) have adequately described the geometry of sevenfold coordinated ions.

These polyhedra sharing edges and corners form the network of the stoichiometric phase  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  (or  $\text{M}_8\text{O}_{17}$ ). Figure 6 shows how these polyhedra are linked together at one level (metal atoms approximately at  $y = 0$ ).

### Discussion

The phase  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  is known to be in the middle of a "solid-solution" or "homologous series" field in the  $\text{Nb}_2\text{O}_5$ — $\text{ZrO}_2$  phase diagram (4). The position of the superstructure lines in the X-ray diffraction powder patterns varies smoothly with composition, and a two-phase field has never been observed in this region. Electron diffraction patterns indicate that the unit cell of any individual crystal of intermediate composition can be exceedingly large (4).

It should be obvious from Fig. 6 that the basic unit of one octahedron, three sevenfold coordinated ions, and one square antiprism can be varied by increasing or decreasing the total number of any of these three types of polyhedra: (1) The basic unit of one octahedron and three sevenfold coordinated ions can be incorporated with an increasing number of square antiprisms; (2) the basic unit of three sevenfold coordinated ions and one square antiprism can be incorporated with an increasing number of octahedra; and (3) one octahedra and one square antiprism can be incorporated with an increasing or decreasing number of sevenfold coordinated ions. All three of these possible ways of varying the structure result in an increase or decrease in the multiplicity ( $m$ ) of the subcell.

In the first case, increasing or decreasing the number of square antiprisms results in a variation

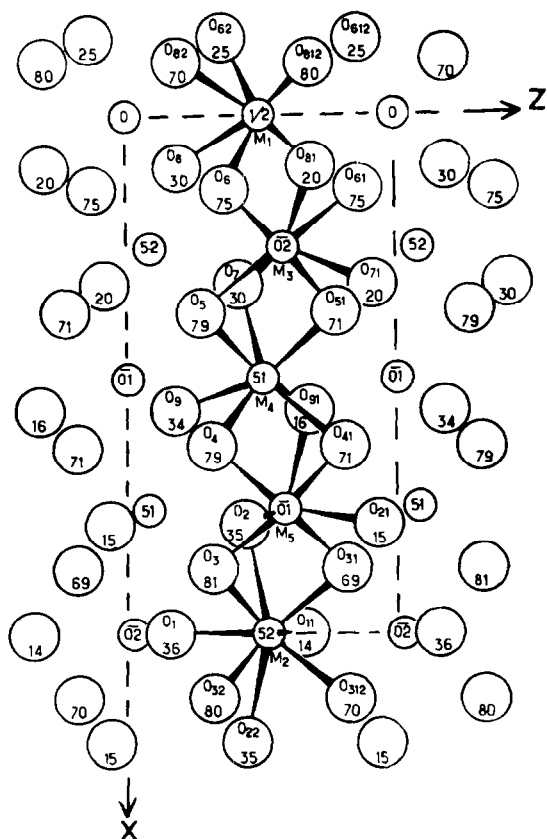


FIG. 5. A ball and spoke model of the structure of  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  after refinement, projected on (010). Numbers inside metals (M) and oxygens (O) indicate  $y$ -parameter of atom.  $M_1$ —octahedron,  $M_2$ —square antiprism,  $M_3$ — $M_4$ — $M_5$ —sevenfold coordinated polyhedra.

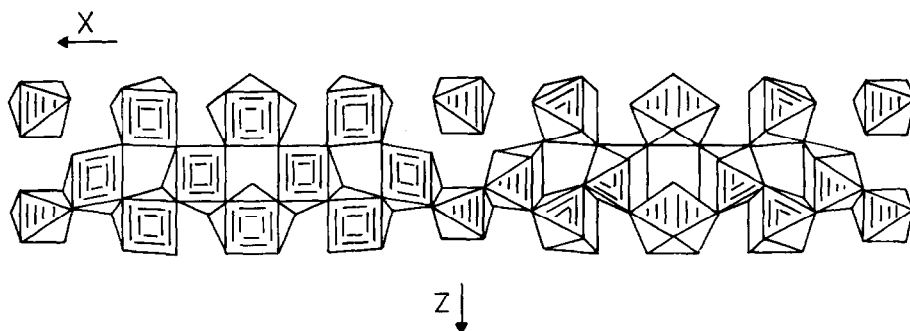


FIG. 6. Representation, at one level, of the refined structure of  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  as polyhedra linked together by edge and corner sharing (metal atoms approximately at  $y=0$ ). The "apparently isolated" octahedra are actually edge-shared with the sevenfold coordinated polyhedra of the adjacent unit cell, as shown in the postulated structure of  $m=6$ , Fig. 7.

of the multiplicity from  $m=7$  for *no* square antiprisms to  $m=10$  for three square antiprisms. However, the metal/oxygen ratio is incorrect.

In the second case, increasing or decreasing the number of octahedra also results in a variation of the multiplicity from  $m=7$  for *no* octahedra to  $m=10$  for three octahedra. The metal/oxygen ratio is in agreement with the observed chemistry.

In the third case, increasing or decreasing the number of sevenfold coordinated ions results in a variation of the multiplicity from a minimum of  $m=4$  for one sevenfold coordinated ion to a value of  $m=10$  for four sevenfold coordinated ions. A structure with *no* sevenfold coordinated ions is not possible, since this ion is necessary to link the octahedra to the square antiprism.

It may be assumed that the octahedra shown in Fig. 6 are occupied by  $\text{Nb}^{5+}$  ions and account for one-half the niobium content of the unit cell. The remaining niobium ions may be either in the square antiprisms or disordered in the sevenfold coordinated polyhedra. The crystal structure of  $\text{Ta}_2\text{Zr}_8\text{O}_{21}$  ( $m=10$ ) now under study should reveal more structural information.

Figure 7 illustrates the proposed structures of the homologous series  $M_n\text{O}_{2n+1}$ , where  $n$  equals the multiplicity. For the solid solution series in the  $\text{Nb}_2\text{O}_5$ – $\text{ZrO}_2$  system the multiplicity ( $m$ ) varies from not quite  $m=7$  to exactly  $m=10$ . The diagram labeled  $m=10$  is therefore our proposed structure for  $\text{Nb}_2\text{Zr}_8\text{O}_{21}$ . Obviously any intermediate multiplicity can be made up of units of one of the pictured structures, ordered (or partially ordered) with units of the next

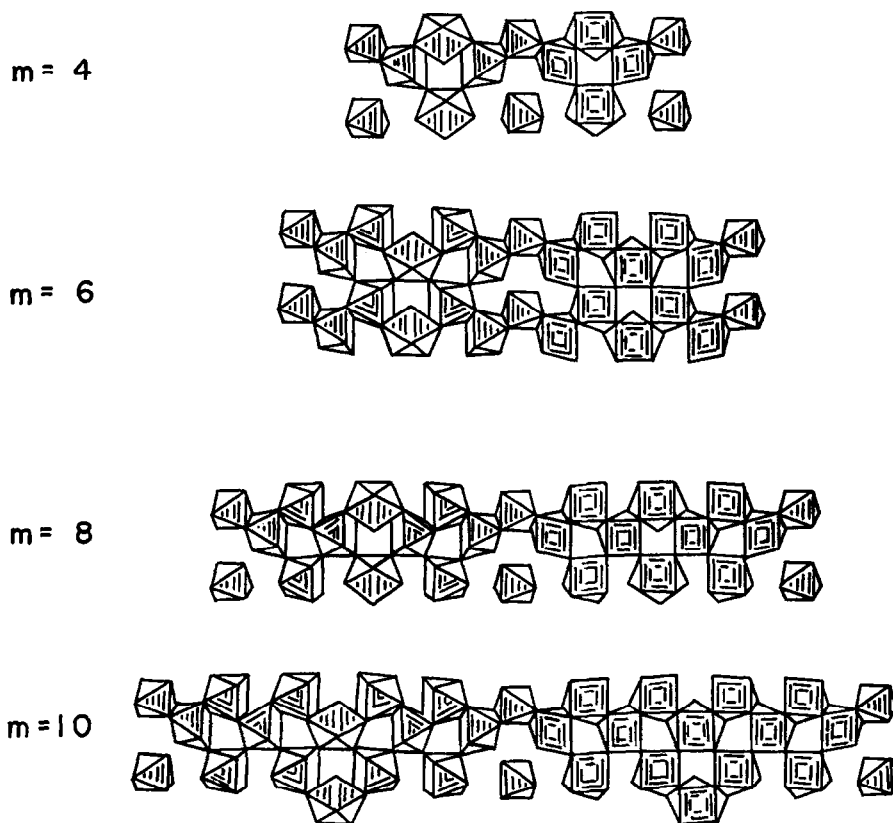


FIG. 7. Polyhedral representations of the structures proposed for the phases in the homologous series  $M_nO_{2n+1}$  with  $n = 4, 6, 8,$  and  $10$ , based on the structure of  $Nb_2Zr_6O_{17}$  ( $m = 8$ ). The diagram for  $m = 10$  is the proposed structure of  $Nb_2Zr_8O_{21}$  and  $m = 6$  is the proposed structure of  $Y_6O_5F_8$ . The "apparently isolated" octahedra are actually edge-shared with the sevenfold coordinated polyhedra of the adjacent unit cell, as shown in the postulated structure of  $m = 6$ .

structure. In such ordering only the structures shown in Fig. 7 would be body centered and all intermediate phases would belong to another space group, in accordance with observation (4).

Orthorhombic phases similar to those in this region in the  $Nb_2O_5$ - $ZrO_2$  system have been reported in the system  $Y$ - $O$ - $F$  (8, 9). They were assigned to an homologous series  $Y_nO_{n-1}F_{n+2}$ , where the multiplicity varies from not quite 4 to about 8. It is interesting that 4 is the absolute minimum of the proposed series and great similarities should exist between the two series.

Figure 8 is an ideal representation of the structures shown in Fig. 7. Note that the square antiprisms are distorted differently from those shown in the ideal  $MO_3$  structure of Fig. 3 and in the ideal structure of Fig. 4. Figure 8 illustrates that there are actually two different kinds of sevenfold coordinated ions. The type of sevenfold coordination shown in Figs. 2 and 4 is actually

present only for the ions immediately adjacent to the octahedra,  $M_3$  of Fig. 5. This coordination is necessary to link the octahedron to either another sevenfold polyhedron or to a square antiprism. However, the next two sevenfold coordinated ions in the structure of  $Nb_2Zr_6O_{17}$ ,  $M_4$  and  $M_5$  of Fig. 5, are actually distorted cubes where the eighth oxygen is too far removed to be considered part of the real coordination.

It seems obvious that these structures shown in Figs. 6 and 7 account for all the anion excess fluorite phases found to have orthorhombic symmetry and superstructure in one direction. The principle of the square antiprism polyhedron may also be a more general mechanism to account for excess anions in a lattice of cubic coordination. Square antiprisms occurring disordered or partly ordered in a fluorite structure are thus an alternate explanation for non-stoichiometry in  $UO_{2+x}$  (10) and  $CaF_2$  with a



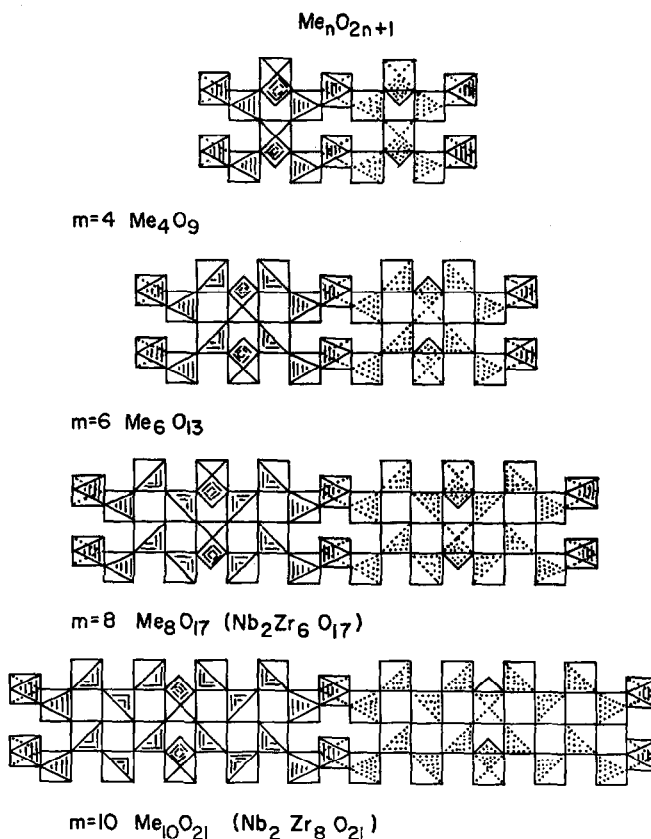


FIG. 8. The ideal models of the structures shown in Fig. 7. Note the differences between  $m=8$  ( $\text{Me}_8\text{O}_{17}$ ) of this figure and the ideal model shown in Fig. 4. Solid lines indicate faces of polyhedra which point upward and dotted lines indicate faces of polyhedra which point down.

small amount of rare earth trifluoride in solid solution (11).

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