

## Jubilite: A 4-,8-connected Cubic Structural Pattern in Space Group Pm3

Michael J. Bucknum<sup>1</sup> and Eduardo A. Castro<sup>2,\*</sup>

<sup>1</sup> Georgia College & State University, Department of Chemistry and Physics, CBX 82, Milledgeville, GA 31061, U.S.A.

<sup>2</sup> INIFTA, Theoretical Chemistry Division, Suc.4, C.C. 16, La Plata 1900, Argentina

\* Author to whom correspondence should be addressed; e-mail: castro@quimica.unlp.edu.ar / direccion@inifta.unlp.edu.ar

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**Abstract:** In the course of investigating structural modifications of the 3-,4-connected net known as the Pt<sub>3</sub>O<sub>4</sub> structure-type (waserite), a novel 4-,8-connected structure-type was discovered. This lattice is generated by replacing the 3-connected trigonal planar vertices of the Pt<sub>3</sub>O<sub>4</sub> structure-type with 4-connected tetrahedral vertices, to achieve a structure which possesses a generic empirical formula of JK<sub>6</sub>L<sub>8</sub>. In such a topological modification, the four 3-fold axes of the parent cubic, Pm3n, Pt<sub>3</sub>O<sub>4</sub> structure-type are retained. Thus the 4-connected tetrahedral vertices are oriented so as to preserve cubic symmetry in the resulting Pm3, JK<sub>6</sub>L<sub>8</sub> (jubilite) lattice. The unit cell contains a single 8-connected cube-centered vertex, six 4-connected distorted square planar vertices and eight 4-connected distorted tetrahedral vertices. It is a Wellsean structure with a Wells point symbol given by (4<sup>16</sup>6<sup>4</sup>8<sup>4</sup>)(4<sup>2</sup>8<sup>2</sup>)<sub>6</sub>(4<sup>3</sup>8<sup>3</sup>)<sub>8</sub> and a Schläfli symbol of (5<sup>3/4</sup>, 4.2667). This latter index reveals a decrease in the lattice's polygonality and concomitant increase in the connectivity through the transformation from waserite to jubilite. The topology of the parent waserite lattice (Pt<sub>3</sub>O<sub>4</sub>) corresponds to that of the Catalan structures with the Wells point symbol (8<sup>4</sup>)<sub>3</sub>(8<sup>3</sup>)<sub>4</sub>, which has the Schläfli symbol (8, 3.4285). Finally, it can be seen that a sequence of structure-types starting with waserite (Pt<sub>3</sub>O<sub>4</sub>) and moving to jubilite (JK<sub>6</sub>L<sub>8</sub>) and finally to fluorite (CaF<sub>2</sub>) represents a continuous crystallographic structural transformation in which the symmetry and topology undergo concomitant changes from one structure-type (waserite) to the other structure-types. The topology of the fluorite lattice, represented by the Wells point symbol (4<sup>24</sup>)(4<sup>6</sup>)<sub>2</sub>, and the Schläfli symbol (4, 5<sup>1/3</sup>), indicates a discontinuous topological transformation from the intermediate jubilite lattice;

like the discontinuous topological transformation from  $\text{Pt}_3\text{O}_4$  to  $\text{JK}_6\text{L}_8$ ; in which the polygonality is again reduced, in this step from  $5^{3/4}$  to 4, and the connectivity is concomitantly increased, from 4.2667 to  $5^{1/3}$ , during the continuous structural transformation. The  $l$  index, a topological measure of the form of a structure-type in terms of the ratio of the weighted average polygonality to the weighted average connectivity in the unit cell, decreases in the sequence from  $\text{Pt}_3\text{O}_4$  (2.3333) to jubilate (1.3476) to fluorite (0.7500). This indicates the discontinuous, though monotonic, appearance of more closed networks upon increasing the connectivity and concomitantly decreasing the polygonality in the structural sequence. Interestingly, the ratios of the form indexes of the adjacent members in this series:  $l_{\text{waserite}}/l_{\text{jubilate}}$  and  $l_{\text{jubilate}}/l_{\text{fluorite}}$ , are approximately equal to each other.

**Keywords:** Jubilate, Cubic structural pattern, Space Group  $\text{Pm}\bar{3}$ .

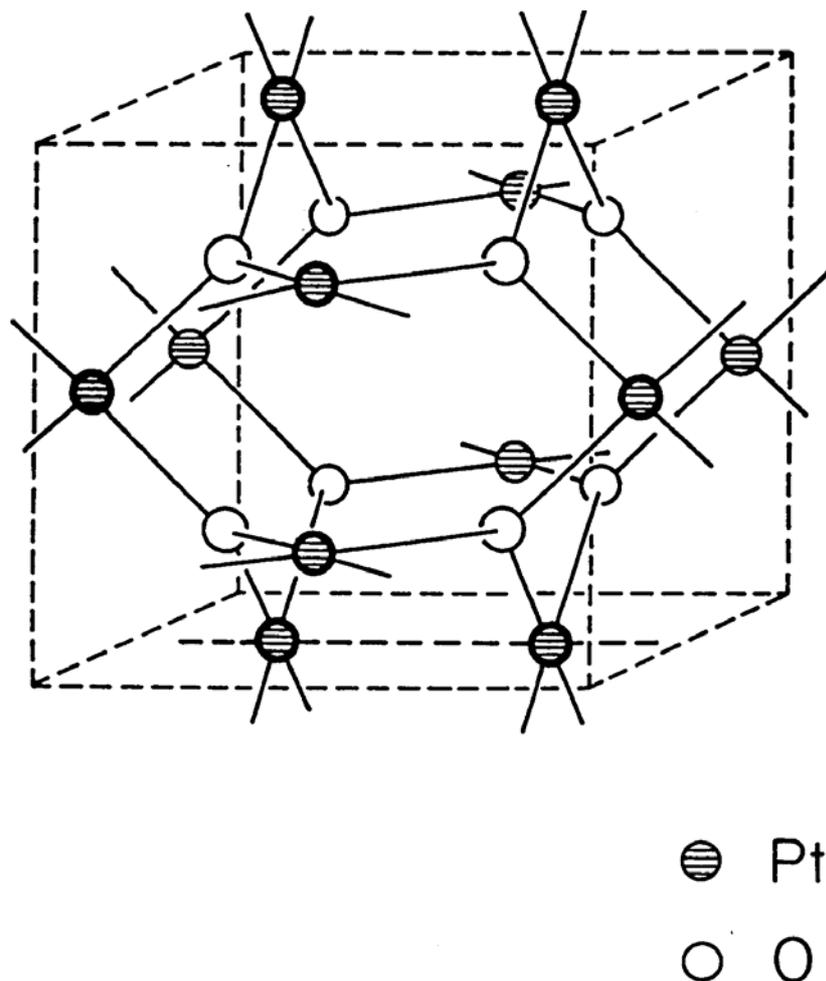
## Introduction

Waser and McClanahan solved the structure of a novel sodium platinate lattice,  $\text{NaPt}_3\text{O}_4$ , in 1954 [1]. This structure was synthesized as a jet black powder by the reaction of dry sodium chloroplatinate with dry sodium carbonate in a platinum crucible heated to a temperature at which the powdered material became molten, as is shown in Equation 1 below:



Upon cooling the molten mixture, the resulting black powder of the product sodium platinate was purified and conductivity and powder diffraction studies were carried out [1]. Conductivity measurements showed that the product phase  $\text{NaPt}_3\text{O}_4$  was a good sodium ion conductor (specific resistance at room temperature measured as  $\approx 10^4$  ohm-cm) because of the loose association of the  $\text{Na}^+$  ions in the lattice coordinated to the oxygen atoms at a relatively large distance of 2.46 Å. According to the investigators, the sodium ions could be reversibly removed from the  $\text{Pt}_3\text{O}_4$  host lattice to some extent, but the sodium ions could not be completely removed. The  $\text{Pt}_3\text{O}_4$  host lattice, herein called waserite in honor of its discoverer, is shown in Figure 1.

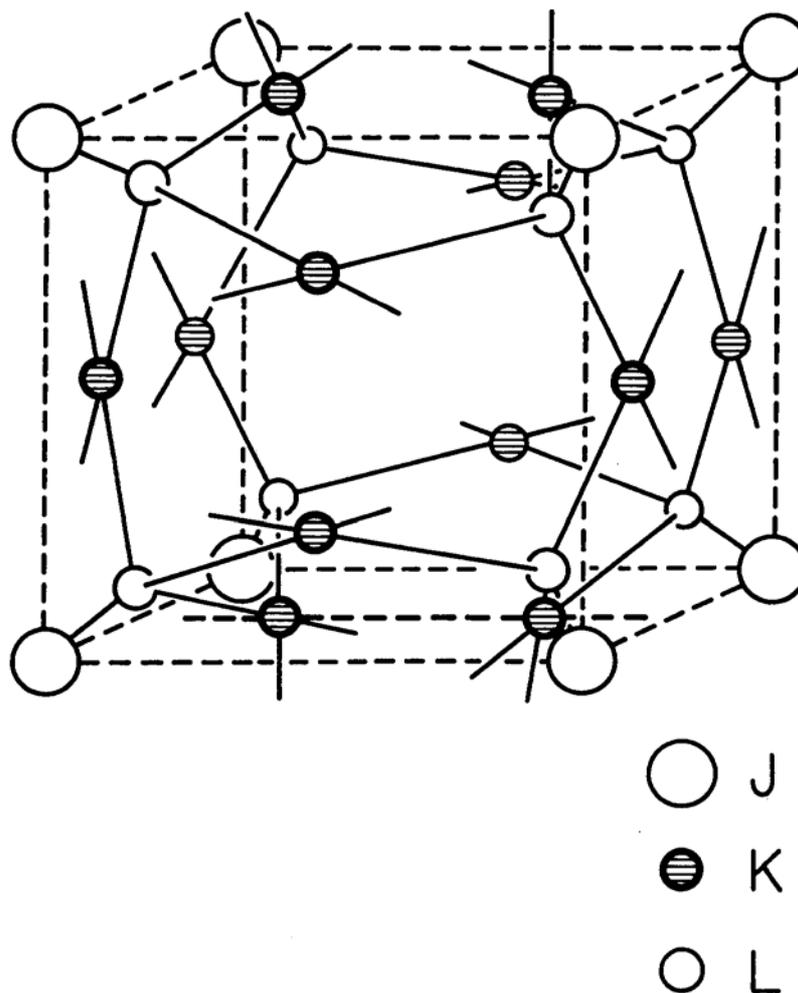
This cubic structure-type represents a unique 3-,4-connected net which, to some degree, complements the hexagonal phenacite structure-type discovered in 1930 by Bragg and Zachariasen [2]. Both networks consist of 3- and 4-connected vertices that alternate in 3 dimensions, giving rise to a connectivity index (weighted average atomic valency),  $p$ , of about 3.4285 [3]. Interestingly, this index represents a continued fraction, and evidently the presence of high symmetry in these lattices does not preclude a connectivity index which is irrational [4].  $\text{Pt}_3\text{O}_4$  lies in space group  $\text{Pm}\bar{3}\text{n}$ , number 223, with 6 Pt's in the Wyckoff positions  $6(\text{c}) \pm(1/4, 0, 1/2)$  and 8 O's in the Wyckoff positions  $8(\text{e}) \pm(1/4, 1/4, 1/4)$  [5]. In contrast, the phenacite structure-type, in a binary stoichiometry of  $\text{A}_3\text{B}_4$ , lies in space group  $\text{P}6_3/\text{m}$ , number 176, with three sets of atomic positions: N(1)  $2(\text{c}) \pm(1/3, 2/3, 1/4)$ , N(2)  $6(\text{h}) (\pm(u, v, 1/4); \pm(-v, u-v, 1/4); \pm(v-u, -u, 1/4))$  and Si  $6(\text{h}) (\pm(u, v, 1/4); \pm(-v, u-v, 1/4); \pm(v-u, -u, 1/4))$  [6].

**Figure 1.** Waserite structure-type.

The present communication describes a novel structure-type derived from waserite by replacing the trigonal planar, 3-connected vertices in  $\text{Pt}_3\text{O}_4$  with tetrahedral, 4-connected vertices. In its most obvious form such a structure would possess 8 tetrahedral O vertices; in the Wyckoff positions  $8(i) \pm(x, x, x)$  of a  $\text{Pm}\bar{3}$  space group, number 200. Upon transforming waserite into the new structure-type by replacing the trigonal planar vertices with tetrahedral vertices, an 8-connected cube centered vertex is introduced into the unit cell, while the six 4-connected square planar vertices are retained, albeit slightly distorted, from waserite's structure. This novel structure-type is shown in Figure 2 [7].

The new structure-type, hereafter called jubilate because of its discovery at the beginning of the new millenium, is cubic and lies in space group  $\text{Pm}\bar{3}$ , number 200, with 1 atom in the Wyckoff position 1(a) (0, 0, 0), 6 atoms in the Wyckoff positions 6(f)  $\pm(x, 0, 1/2)$  and 8 atoms in the Wyckoff positions 8(i)  $\pm(x, x, x)$ . It therefore has 15 atoms in the cubic unit cell, with a generic composition  $\text{JK}_6\text{L}_8$ . J is an 8-connected cube centered vertex, the 6 K correspond to the slightly distorted square planar vertices in Figure 2, and the 8 L correspond to the slightly distorted tetrahedral vertices in Figure 2.

Figure 2. Jubilite structure-type.



The 4-connected vertices, both the square planar and the tetrahedral atoms, are forced to be distorted from their ideal bond angles of  $90^\circ$  (square planar) and  $109.47^\circ$  (tetrahedral) by the geometry of the lattice. In contrast, in waserite the 3-connected trigonal planar vertices and 4-connected square planar vertices are both completely undistorted from their ideal angles of  $120^\circ$  (trigonal planar) and  $90^\circ$  (square planar), respectively.

### Transformations and Topology of the Jubilite Lattice

As has been previously discussed, the topological characteristics of crystalline materials may be described with reference to the two secondary topological parameters called the polygonality,  $n$ , and the connectivity,  $p$ , of the unit of pattern [8]. The polygonality refers to a weighted average of all the shortest circuits about all of the atoms (vertices) in the unit cell of the structure; the connectivity is the weighted average valence over the atoms (vertices) in the unit cell. These parameters,  $n$  and  $p$ , are rigorously determined in all crystalline matter where links (bonds) between atoms are unambiguous. For some structure-types, it may be useful to view the lattice as consisting of interpenetrating component lattices with their respective polygonalities and connectivities.

As topological parameters, the polygonality and connectivity originate from the Euler relation for the sphere [9] which rigorously describes the relation between the vertices,  $V$ , edges,  $E$ , and faces,  $F$ , of convex polyhedra; as shown in Equation 2.

$$V - E + F = 2 \quad (2)$$

This relation holds for any division of the sphere into vertices, edges and faces. By recognizing the identities,  $nF = 2E$  and  $pV = 2E$ , one may relate the secondary topological indexes,  $n$  and  $p$ , to the primary topological indexes,  $V$ ,  $E$  and  $F$ , as is shown in Equation 3 [10].

$$\frac{1}{n} - \frac{1}{2} + \frac{1}{p} = \frac{1}{E} \tag{3}$$

Equation 3 is rigorous for the polyhedra and polygons, but it does not hold for 2-dimensional and 3-dimensional extended structures. Evidently, the Euler relation needs to be modified in order to describe the structure of crystalline materials in a topological sense. At any event, the values of  $n$  and  $p$  can be rigorously calculated for any arbitrary unit cell and these indexes can be used to characterize the material topologically, as, for example, in the topology map shown in Figure 3 below [11]. The ordered pair of numbers  $(n, p)$  is called the Schläfli symbol of the unit of pattern. One can apply these ideas to topologically characterize the waserite, jubilite and fluorite lattices, which are related to each other through a continuous crystallographic structural transformation.

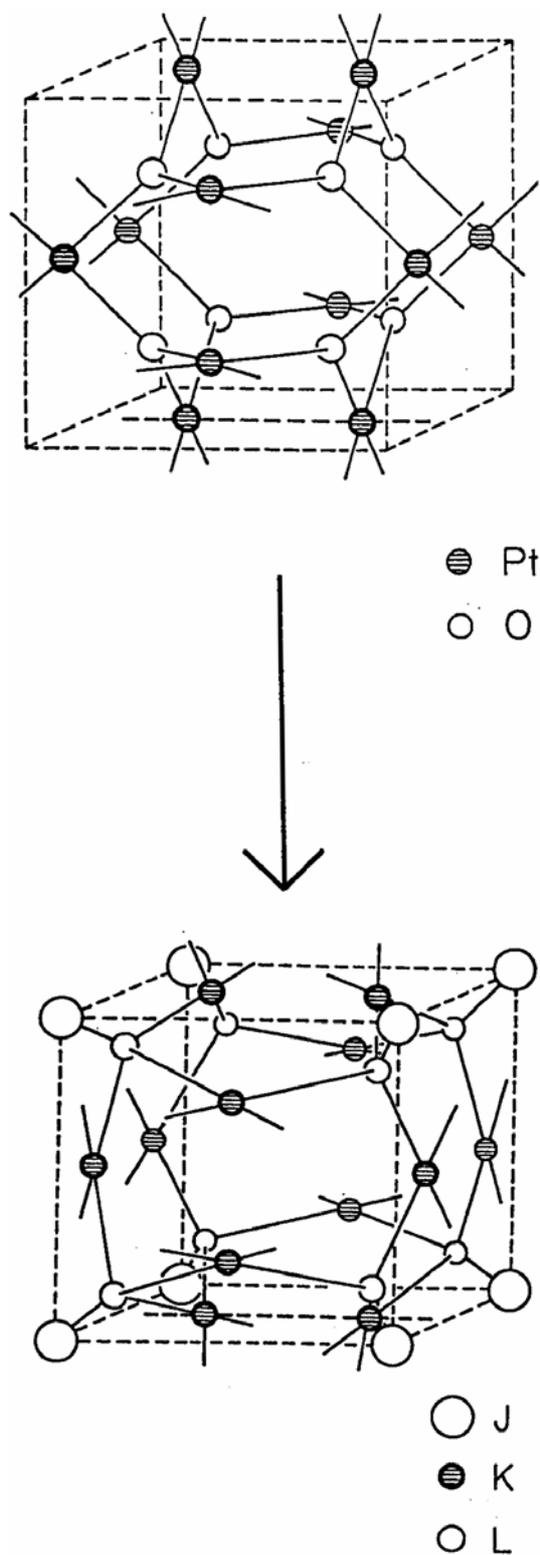
**Figure 3.** Topology map of regular structures.

		p					
n	3	4	5	6	7	8	...
3	t	o	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
⋮							

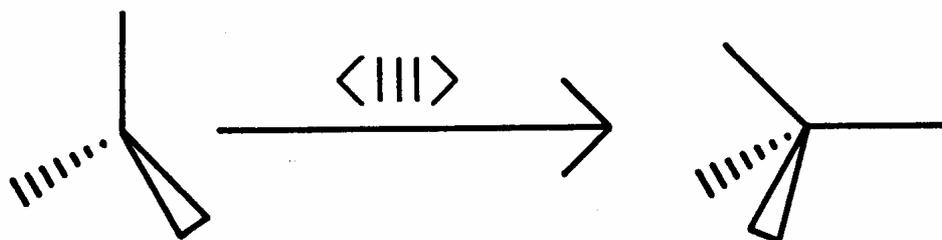
Beginning with the waserite lattice, shown on the top side in Figure 4, one can envision a structural transformation in which the eight trigonal planar vertices, in Wyckoff positions 8(e)  $\pm(1/4, 1/4, 1/4)$  of  $Pm3n$ , are deformed continuously by drawing these atoms towards their respective, adjacent cube vertices along the  $\langle 111 \rangle$  axes, and preserving 3-fold symmetry along the continuous deformation pathway, to generate eight tetrahedral vertices, in Wyckoff positions 8(i)  $\pm(x, x, x)$  of  $Pm3$  of the jubilite lattice, shown on the bottom side of Figure 4. During this continuous, cubic symmetry preserving structural transformation, the six 4-connected square planar vertices, originally in the Wyckoff positions 6(c)  $\pm(1/4, 0, 1/2)$  of  $Pm3n$  of the waserite lattice, are held fixed relative to the deformation of the eight 3-connected trigonal planar vertices (in 8(e)  $\pm(1/4, 1/4, 1/4)$  of  $Pm3n$ ), and are

transformed, through the change in space group symmetry, to occupy the Wyckoff positions 6(f)  $\pm(x, 0, 1/2)$  in Pm3 of the product jubilate lattice.

**Figure 4.** Continuous structural transformation of waserite to jubilate.



The structural transformation is termed continuous because the deformation of the eight 3-connected trigonal planar vertices along  $\langle 111 \rangle$ , to form eight 4-connected tetrahedral vertices, which is shown schematically in Figure 5, can occur virtually infinitesimally inside the unit cell.

**Figure 5.** Cubic symmetry preserving distortion of trigonal planar vertex into tetrahedral vertex.

During this structural transformation, the topology of the original waserite unit cell, given by the Schläfli symbol  $(8, 3.4285)$ , with the Wells point symbol  $(8^4)_3(8^3)_4$ , is discontinuously transformed into a topology represented by the Schläfli symbol  $(5^{3/4}, 4.2667)$  of the jubilite unit cell, with a Wells point symbol given by  $(4^{16}6^48^4)(4^28^2)_6(4^38^3)_8$ . In the topological change accompanying the structural transformation, the polygonality is compressed from a value of  $n = 8$  in waserite to  $n = 5^{3/4}$  in the latter jubilite structure-type. In contrast, the change from trigonal planar connectivity to tetrahedral connectivity results in the connectivity index increasing from 3.4285 to 4.2667. The space group symmetry is concomitantly lowered from  $Pm\bar{3}n$ , number 223, in waserite to  $Pm\bar{3}$ , number 200, in the jubilite lattice.

In a subsequent continuous structural transformation, the jubilite lattice, shown on the top in Figure 6, is continuously transformed into the fluorite lattice, shown on the bottom of Figure 6, by coalescing the six 4-connected square planar vertices in  $6(f) \pm(x, 0, 1/2)$  of  $Pm\bar{3}$  jubilite into three 8-connected cube centered vertices (the fourth 8-connected cube centered vertex located at  $(0, 0, 0)$  is retained undeformed from the parent jubilite lattice) in Wyckoff positions  $4(a) (0, 0, 0)$  of  $Fm\bar{3}m$ , number 225, fluorite [12]. In such a structural transformation, each of three pairs of adjacent 4-connected square planar vertices in  $\{100\}$  of jubilite is condensed into each of three corresponding single 8-connected cube centered vertices in  $\{100\}$  of fluorite. It is interesting to note that once again, as in the original waserite lattice, in the fluorite lattice there is no angle strain as the resulting eight 4-connected tetrahedral vertices in  $8(c) \pm(1/4, 1/4, 1/4)$  all have the ideal tetrahedral angle of  $109.47^\circ$  and all four 8-connected cube centered vertices, in  $4(a) (0, 0, 0)$  of  $Fm\bar{3}m$  of fluorite, have the ideal cubical angle of  $70.53^\circ$ .

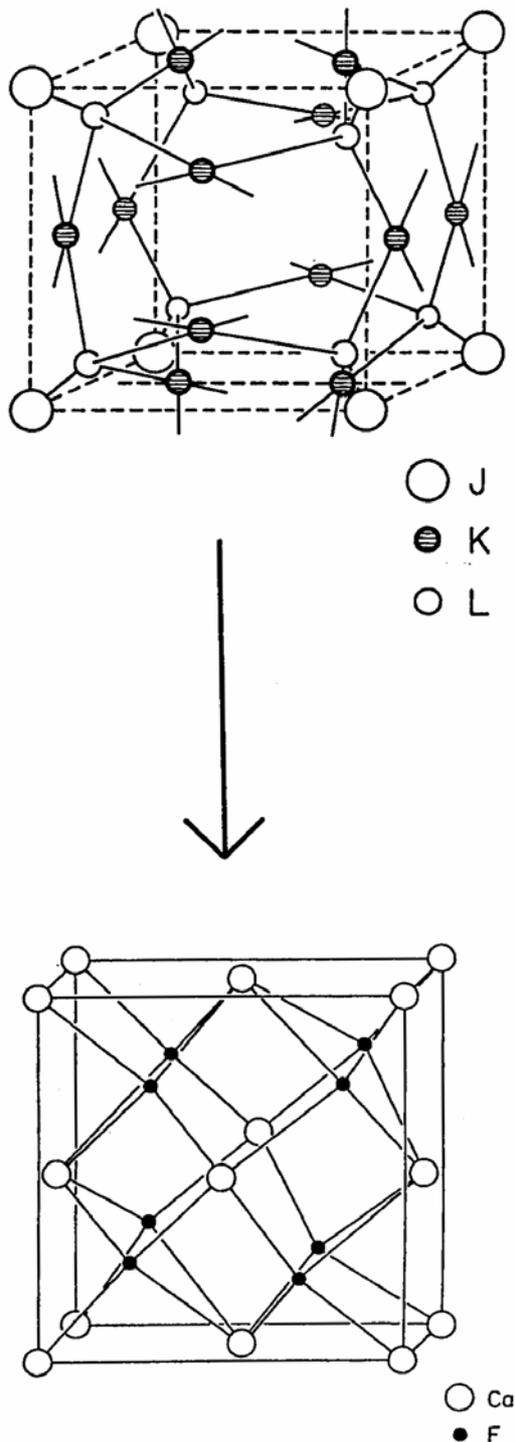
During the continuous structural transformation from jubilite to fluorite, the topology once again changes discontinuously as the polygonality is reduced from jubilite  $(5^{3/4}, 4.2667)$  to fluorite  $(4, 5^{1/3})$ , represented by the Wells point symbol  $(4^{24})(4^6)_2$ , and the connectivity is once again increased in the structural transformation; this time from 4.2667 to 5.3333. The symmetry of the lattice is curiously decreased from waserite in  $Pm\bar{3}n$ , number 223, to jubilite in  $Pm\bar{3}$ , number 200, and then increased from jubilite to fluorite in  $Fm\bar{3}m$ , number 225. Finally, the  $l$  index [9]; which is a measure of the form of a structural pattern in terms of the ratio, shown in Equation 4, of the average polygonality in the unit cell,  $n$ , to the average connectivity in the unit cell,  $p$ ;

$$l = \frac{n}{p} \quad (4)$$

decreases monotonically in the sequence from waserite, where  $l$  is 2.3333, to jubilite, where  $l$  is 1.3476, to fluorite, where  $l$  is 0.7500. This change in  $l$  to some extent reflects a transition from a relatively

open structure (waserite) into more highly connected structures which are topologically more closed (jubilate and fluorite).

**Figure 6.** Continuous structural transformation of jubilate into fluorite.



It is quite interesting in this connection to compare the ratios of the form indexes for the members in this series of 3 patterns related through a continuous crystallographic structural transformation. The ratios  $I_{\text{waserite}}/I_{\text{jubilate}}$  and  $I_{\text{jubilate}}/I_{\text{fluorite}}$  can be formed and their values compared, as shown in Equation 5:

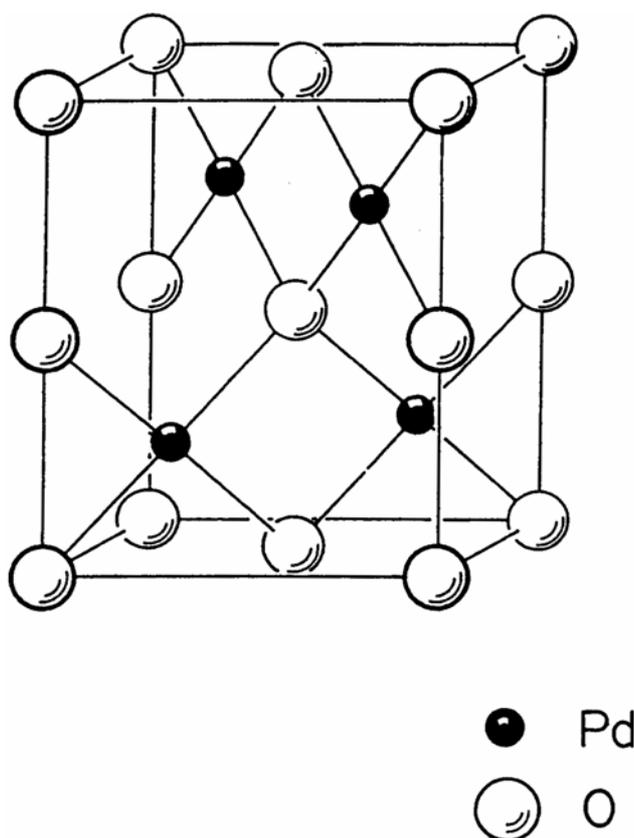
$$\frac{I_{\text{Waserite}}}{I_{\text{jubilate}}} \approx \frac{I_{\text{jubilate}}}{I_{\text{fluorite}}} \approx 1.7 \quad (5)$$

Evidently, the transformation of the topological form of the structure in changing from waserite to jubilite and then from jubilite to fluorite, manifests as nearly the same number. The similarity of the form change reveals the transformations are in some sense proportional, in other words the ratio of polygonality change to connectivity change is proportional in the 2 related continuous structural transformations.

### Presence of Strain in Jubilite

In the structural transformations represented in Figures 4 and 6, one sees the generation of a strained intermediate lattice, jubilite, occurring between the continuous structural transformation from one unstrained structure-type, waserite, into another unstrained structure-type, fluorite. The question naturally arises as to the occurrence of structure-types with strain in them. One prominent example of a strained lattice is the cooperite structure-type shown in Figure 7 [13].

**Figure 7.** Cooperite structure-type.

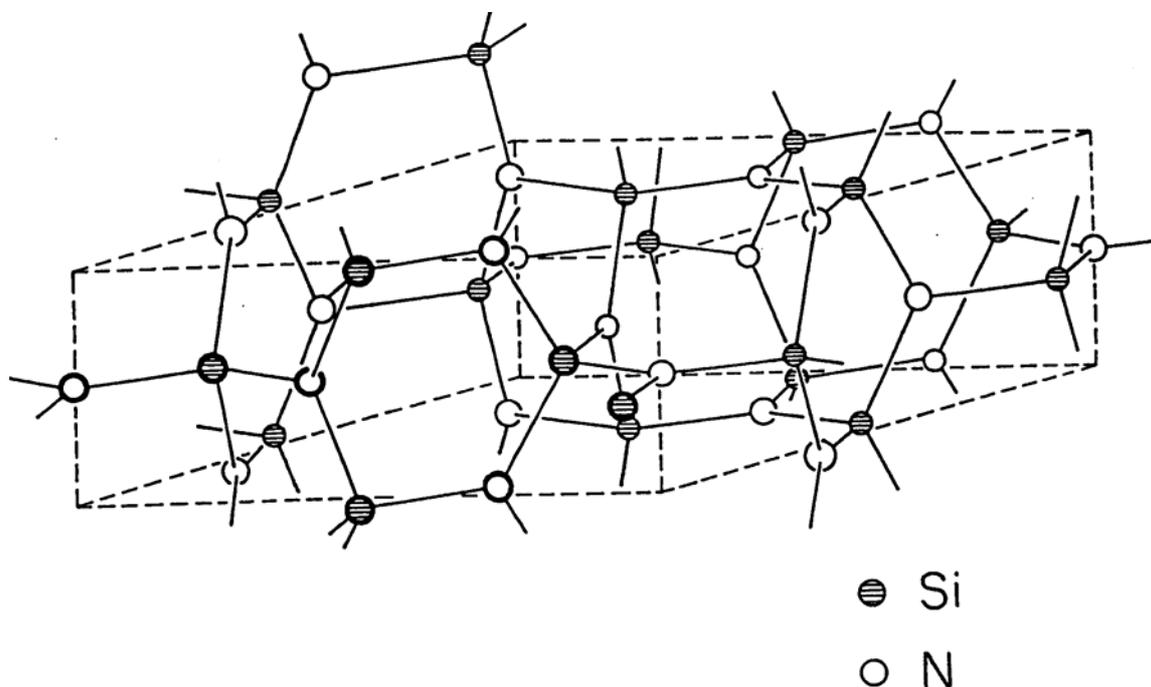


This structure-type is observed as the sulfide mineral PtS, and the oxide PdO. The lattice lies in space group  $P4_2/mmc$ , number 131. The structure, which contains one 4-connected tetrahedral vertex, the S or O atom, and one 4-connected square planar vertex, the Pt or Pd atom, is forced by its geometry to have strain. The bond angles observed in the lattice are distorted from the ideal tetrahedral angle of  $109.47^\circ$ , and the ideal square planar angle of  $90^\circ$  [11].

Yet another prominent example of a strained lattice is the phenacite structure-type [2], which is the structure of  $Si_3N_4$  and  $Ge_3N_4$  and several other oxides and fluorides [14]. Its structure is shown in Figure 8, for a binary stoichiometry it has the space group symmetry  $P6_3/m$ , number 176, as discussed above. The lattice contains three 4-connected tetrahedral vertices and four 3-connected trigonal planar

vertices in the unit of pattern. Once again, the geometry of the lattice forces the trigonal planar and tetrahedral vertices to be distorted from their ideal bond angle values of  $120^\circ$  and  $109.47^\circ$ , respectively.

**Figure 8.** Phenacite structure-type.



It is interesting to speculate whether in analogy to the waserite-jubilite-fluorite triad, there may exist strain-free end-member structures that are related to the strained lattices of cooperite and phenacite through continuous structural transformations.

Finally, some important groundbreaking theoretical [15] and synthetic [16] work has been carried out on the jubilite structure-type very recently in 2004. The work of Balakrishnarajan et al. includes theoretical analysis of the bonding in a potential transition metal realization of the jubilite structure-type that suggests that quadruply bonded transition metal dumbbell pairs may be stabilized in the cube faces of the structure (atom “K” in Figure 2) when atom “J” is an alkaline earth metal and atom “L” is a chalcogenide, in Figure 2. In other work by Pley et al., a Pt-containing cluster anion has been synthesized that exhibits the core jubilite structure.

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  15. Professor Roald Hoffmann's group in theoretical chemistry at Cornell University has studied the jubilate structure-type and has discovered that it is compatible in its structure with the presence of quadruple transition metal M-M bonded dumbbell pairs in the cube faces of the jubilate lattice (the element symbolized as "K" in Figure 2), see M.M. Balakrishnarajan, P. Kroll, M.J. Bucknum and R. Hoffmann, *New Journal of Chemistry*, **2004**, 28, 185.
  16. Pley et al. have synthesized a Pt-containing transition metal cluster anion with the core jubilate structure, see M. Pley and M.S. Wickleder, *Angewandte Chemie International Edition*, **2004**, 43(32), 4168.