Concatenated Nets of an *Orthorhombically Distorted* Si-in-$ThSi_2$ Type with Equal Intra- and Internet Bond Lengths: PSP-32, PSP-33 and PSP-34

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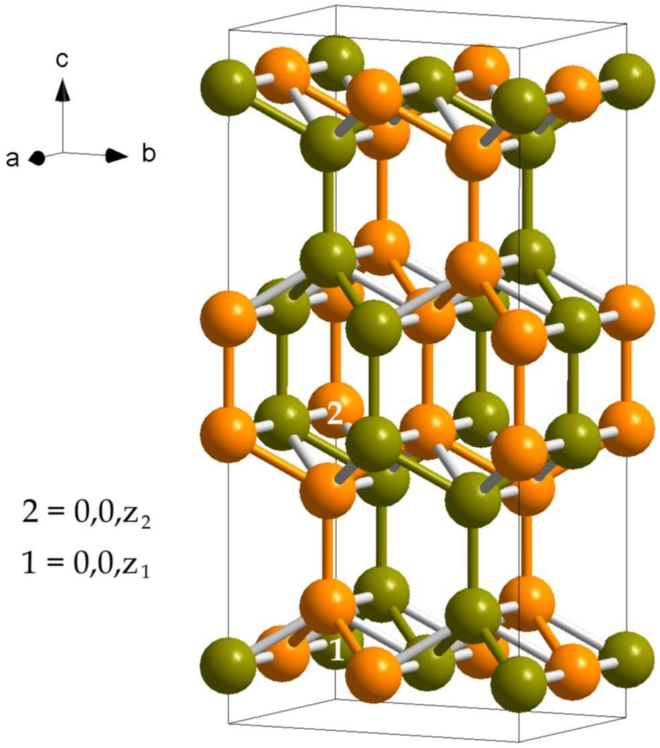


Space group *Fddd* (# 70),

Wyckoff positions *16g*,

coordinates 00*z*.

Note that the constituting three-connected sphere packing has been tabulated as type 3/10/t4 (i.e. pseudo-*tetragonal*) instead of 3/10/oX even though it may be *orthorhombically* distorted.

a) Ideal configuration (equal interatomic distances, all *intra*net bond angles 120°, *intra*net angle between strands of zigzag-chains 90°):

$z_1 = {}^1/_{12}$,

$z_2 = {}^5/_{12}$,

$a = b$,

$c/a = c/b = \sqrt{6}$.

This is identical with PSP-7 (tetragonal), a *five*-connected structure.

b) General configuration (equal interatomic distances, variable bond angles, variable *intra*net angle between strands of zigzag-chains):

Relationship between the parameters of the two concatenated structures *1* and *2*:

$z_2 = 0.5 - z_1$.

*Intra*net distances along c:

$d_C = c \cdot 2z_1 = c \cdot 2(0.5 - z_2)$ which has to be smaller than or equal to 0.25c so as to fit into the unit cell, hence $z_1 \leq 0.125$.

Transversally *inclined* distances (not parallel to c; also all *inter*net distances of this kind):

$$d_{TRI} = \sqrt{0.0625a^2 + 0.0625b^2 + (0.25 - 2z_1)^2 c^2} = \sqrt{0.0625a^2 + 0.0625b^2 + (2z_2 - 0.75)^2 c^2} .$$

Strictly *transversal* distances (i.e. those in the *a*-*b*-plane):

$d_{TR} = 0.5a$, assuming $b > a$. (Or alternatively $d_{TR} = 0.5b$ if $a > b$.)

1. Absence of strictly transversal contacts

Make all distances equal:

$d_C = d_{TRI}$, or

$$c \cdot 2z_1 = \sqrt{0.0625a^2 + 0.0625b^2 + (0.25 - 2z_1)^2 c^2}$$, and hence

$$4{z_1}^2 c^2 = 0.0625a^2 + 0.0625b^2 + (0.25 - 2z_1)^2 c^2$$, or

$$4{z_1}^2 c^2 = 0.0625a^2 + 0.0625b^2 + 0.0625c^2 - z_1 c^2 + 4{z_1}^2 c^2$$, so that

$$z_1 = 0.0625 \cdot (a/c)^2 + 0.0625 \cdot (b/c)^2 + 0.0625 ,$$

i.e. z_1 has to be larger than 0.0625 (in order for z_1-0.0625 to remain positive), which together with the above limit of the *intra*net distance means that $0.0625 < z_1 \leq 0.125$.

Thus the *five*-connected PSP-32 is obtained.

2. Strictly transversal contacts established as well

The structure becomes *seven*-connected if the two concatenated nets establish contact in one strictly transversal direction as well, i.e.

$d_{TR} = d_C$, or $0.5a = 2cz_1$ (assuming *b*>*a*), and thus $z_1 = 0.25 \cdot (a/c)$.

This substituted in the above expression for z_1 yields

$$0 = 0.0625 \cdot \left[(a/c)^2 - 4 \cdot (a/c) + (b/c)^2 + 1\right], \text{ or } 4 = \left[(a/c) - 2\right]^2 + (b/c)^2 + 1, \text{ so that}$$

$$b/c = \sqrt{3 - \left[(a/c) - 2\right]^2}\,.$$

Thus PSP-33 is obtained.

In the special case of *a* = *b* two further strictly transversal contacts are formed in addition to the two formed as described above and the foregoing expression yields

$$0 = (a/c)^2 - 2 \cdot (a/c) + 0.5, \text{ or } 1 = \left[(a/c) - 1\right]^2 + 0.5, \text{ so that}$$

$$a/c = \sqrt{1/2} + 1,$$

(here the *negative* value of the square root applies in order for z_1 to fall within the allowed range according to $z_1 = 0.125 \cdot (a/c)^2 + 0.0625$, or $z_1 = 0.25 \cdot a/c$); this arrangement corresponds to the *nine*-connected tetragonal structure of PSP-31.

If, starting from this arrangement, one wished to further decrease z_1 one would have to increase either *c*/*a* or *c*/*b* or both, i.e. for a given *c* one would have to decrease *a* (or *b*). This would, however, entail a reduction in length of the strictly transverse connections to a greater degree than that of the transversally inclined connections. Collisions in a strictly transverse direction must thus ensue and it is, therefore, not possible to further decrease z_1 below the absolute minimum value given by

$$z_1 = 0.25 \cdot a/c = 0.25 \cdot (\sqrt{1/2} + 1), \text{ or} \approx 0.073223,$$

in complete analogy to PSP-7.

For z_1 = 0.125 and *a* = *b*, *c*/*a* = √2 and the concatenated arrangement corresponds to the cubic primitive structure of PSP-8 (*six*-connected).

For a certain value of the *a*/*b* ratio the symmetry becomes hexagonal, viz. when the projection along *c* acquires a structure corresponding to a plane-filling arrangement of regular triangles, the necessary condition being

$$0.5a = 0.25\sqrt{a^2 + b^2}, \text{ or } b = a \cdot \sqrt{3},$$

so that the previous equation for z_1 becomes

$$z_1 = 0.0625 \cdot (a/c)^2 + 3 \cdot 0.0625 \cdot (a/c)^2 + 0.0625, \text{ or}$$

$z_1 = 0.25 \cdot (a/c)^2 + 0.0625$.

At the same time, $d_{TR} \geq d_C$ must apply, i.e.

$0.5a \geq 2cz_1$, or $0.5a \geq 2c \cdot [0.25 \cdot (a/c)^2 + 0.0625]$, and hence

$a/c \geq (a/c)^2 + 0.25$, or $0 \geq (a/c)^2 - a/c + 0.25$, and thus

$0 \geq [(a/c) - 0.5]^2$, which requires that $a/c = 0.5$, or

$c = 2a$.

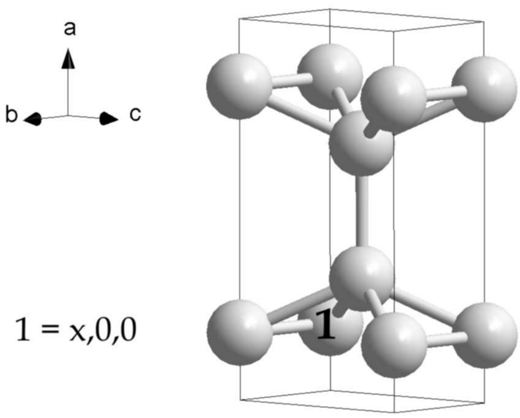
From this and the previous equation it follows that

$z_1 = 0.125$.

Thus PSP-34 is obtained, identical to the *eight*-connected primitive hexagonal structure.

c) The previously known homogeneous sphere packings which correspond to PSP-32 and PSP-33:

Both these PSPs can be realized in the form of 7/3/o5 – even PSP-32 although this is only five-connected. The sphere packing which corresponds to the latter has, in fact, been designated as "orthorhombic" 5/4/t6 (i.e. pseudo-*tetragonal*) rather than 5/4/oX despite the fact that it may be *orthorhombically* distorted.



Space group *Immm* (# 71),

Wyckoff positions *4e*,

coordinates *x*00.

As compared to the above case of space group *Fddd* (# 70) with doubly occupied *16g* Wyckoff position the lattice parameters are half as large and interchanged (*a* in place of *c*, *b* in place of *a*, *c* in place of *b*), hence the parameter x (in place of z_1) has to be twice as large.