Concatenated Nets of the Si-in-$ThSi_2$ Type with Equal Intra- and Internet Bond Lengths: PSP-7, PSP-8 and PSP-31 (Tetragonal)

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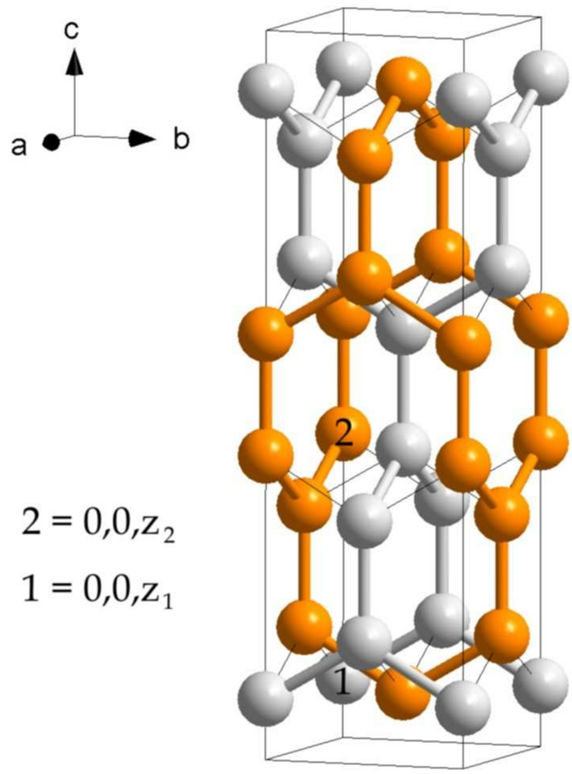
(August 2018)



Space group *I*4_1/*amd* (# 141),

Wyckoff positions *8e*,

coordinates 00*z*.

a) Ideal configuration (PSP-7, equal interatomic distances, all *intra*net bond angles 120°):

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

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

$c/a = 2\sqrt{3}$.

The structure is *five*-connected.

b) General configuration (PSP-7, equal interatomic distances, variable bond angles):

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 0.25*c* so as to fit into the unit cell, hence $z_1 \leq 0.125$.

Transversally *inclined* distances (not parallel to *c*; also the *inter*net distances):

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

Now make all distances equal:

$d_C = d_{TRI}$, or

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

$z_1 = 0.0625 + 0.25/(c/a)^2$, or

$c/a = \sqrt{0.25/(z_1 - 0.0625)}$, i.e. z_1 has to be larger than 0.0625, which together with the above limit of the *intra*net distance means that $0.0625 < z_1 \leq 0.125$ and therefore $2 \leq c/a < \infty$.

The structure is *five*-connected.

c) Special configurations (PSP-8 and PSP-31):

For $z_1 = 0.125$ (maximum allowed value) and hence $c/a = 2$ (i.e. minimum allowed value) the concatenated structure corresponds to the *six*-connected cubic primitive arrangement (PSP-8).

At a sufficiently large value of *c*/*a* the structure becomes *nine*-connected (PSP-31) due to additional contacts between strictly *transversally* situated (i.e. in the *a*-*b*-plane) atoms, as follows.

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

$d_{TR} = a/\sqrt{2}$.

Make this equal to d_C as calculated previously:

$a/\sqrt{2} = c \cdot 2z_1$.

Thus:

$$c/a = 1/\left(2\sqrt{2}\cdot z_1\right)$$

and by substituting this for *c/a* in the earlier expression for z_1 we obtain

$$z_1 = 0.0625 + 0.25/(c/a)^2 = 0.0625 + 2z_1^{\ 2}$$, or

$$2z_1^{\ 2} - z_1 + 0.0625 = 0$$, or

$$z_1^{\ 2} - 0.5z_1 + 0.0625 = 0.03125$$, or

$z_1 - 0.25 = \pm\sqrt{0.03125}$, i.e. $z_1 = \pm\sqrt{0.03125} + 0.25$ = 0.426777 or 0.0732233.

Only the second of these two values lies in the admissible range for z_1. Then, from the previous equation, *c/a* = 2+2√2 = 4.828427.

Since *c/a* may not be increased any further without d_{TR} becoming smaller than d_C (and d_{TRI}), in other words without *collisions*, the above value is the maximum one allowed, and likewise the above corresponding value of z_1 is the minimum permissible one.