Structural Relations Between the Low- and High-Temperature Forms of β-Eucryptite (LiAlSiO₄) and Low and High Quartz. I. Low Temperature form of β-Eucryptite and Low Quartz

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At room temperature β-eucryptite with ordered arrangement of Al, Si and Li atoms has a structure which shows similarities to low quartz. Its framework contains low quartz-like structure elements, which can be considered as dauphinée twinned in an ordered way within the range of the supercell.

1. Introduction

The quartz structure is the base structure of a series of aluminosilicates. A portion of the Si atoms is replaced by Al atoms. The lower charge of Al as compared with Si is compensated by small positive ions, *e.g* Li. The additional ions are located in the structural main channels running parallel to the *c* axis. The X-ray diffraction patterns of most of these 'stuffed derivative quartz structures' (Buerger, 1954) at room-temperature are similar to that of high quartz.

The synthesis of β-eucryptite (LiAlSiO₄) in the form of polycrystalline samples and of single crystals by Winkler (1948) was the first derivation of an alumino-silicate from the quartz structure. Symmetry and extinction of the main reflexions in single-crystal X-ray photographs indicated the high-quartz space group *P*6₂22. Weak superstructure reflexions having the same symmetry as the main reflexions required a doubling of the high-quartz-like *c* axis. Winkler explained the doubling of the *c* axis by an alternating sequence of Si and Al layers perpendicular to the *c* axis. He located the Li atoms in the structure main channels running parallel to *c* in places with the same *z* coordinates as the Al atoms in a fourfold O coordination.

The diffraction pattern of β-eucryptite single crystals grown by Tscherry (1971) showed in addition to the main reflexions, super-structure reflexions, which required a doubling of the high-quartz-like *a* and *c* axes. Symmetry and extinction of the reflexions followed space group *P*6₂22 (Tscherry & Laves, 1970). Average and super structure of these crystals have been investigated (Tscherry, Schulz & Laves, 1972*a,b*). The results are the basis for the following considerations.

The properties of Li⁺ or Mg²⁺ containing alumino-silicate quartz phases have been investigate in detail, mainly by means of polycrystalline samples, due to

their low positive or even negative (β-eucryptite) coefficient of thermal expansion. A summary of these results is given in Tscherry *et al.* (1972), Schulz, Hoffmann & Muchow (1971) and Schulz, Muchow, Hoffmann & Bayer (1971).

2. Average and super structure of β-eucryptite

The space group *P*6₄22 is used for the description of the superstructure, which is schematically represented in Fig. 1. Related to the axes *a*(sub) and *c*(sub) of the high-quartz-like subcell the supercell has the axes *a*(super) = 2*a*(sub) and *c*(super) = 2*c*(sub). This supercell, designated as supercell I, contains four structure main channels running parallel to **c**. The *c* axis of the supercell I coincides with the 6₄ axis and with the axis of one of these four main channels. which is designated as central channel. The remaining three channels are designated as secondary channels. Fig. 1 shows that the (*x*,*y*) coordinates of these channels are: central channel: (0,0), secondary channels: (0·5,0), (0,0·5) and (0·5,0·5). The main features of the superstructure are (Tscherry, Schulz & Laves, 1972*b*):

1. The Si and A atoms are ordered in alternating layers perpendicular to the *c* axis. Each Al atom is surrounded by 4 Si atoms and *vice versa*. This arrangement is in agreement with the Al avoidance rule (Loewenstein, 1954).

2. The Li atoms occupy, in an ordered way, sites coordinated by 4 oxygen atoms. The Li atoms in the central channel have the same *z* coordinates as the Al atoms and the Li atoms in the three secondary channels have the same *z* coordinates as the Si atoms.

Supercell I contains 8 subcells. If these subcells are put together into one subcell, the Li atoms occupy exactly the positions of the special equipoint 3(*a*), the (Si, Al) and the O atoms are spread around 'positions of gravity'. By this 'projection' of the superstructure into a subcell one obtains the high-quartz-like average

structure of β-eucryptite (Tscherry, Schulz & Laves, 1972a). If the superstructure is described in space group $P6_422$, the average structure must be described in space group $P6_222$. The positions of gravity of the framework atoms can be described by the special equipoints 3(c) (Si, Al) and 6(j) (O) (cf. Table 1, last line). The relations between the positions of the Si, Al and O atoms in sub- and supercell is discussed with the aid of Fig. 2. It shows (Si, Al) atoms, and O atoms bonded to them, projected from the supercell into the subcell. The high-quartz-like 'position of gravity' of the O atoms is also given and designated by O(hq). The distance (Si, Al)–O(hq) equals the averaged (Si, Al)–O tetrahedral distance in framework silicates (Jones, 1968). The four O atoms around O(hq) correspond to the so-called split positions and are designated by O(s). Each connexion (Si, Al)–O(s) corresponds either to a Si–O or Al–O bond distance.

For the further considerations it is helpful to look at the different symmetries of the (Si, Al)–O_4 tetrahedra of the average structure and of the SiO_4 and AlO_4 tetrahedra of the superstructure.

In the high-quartz-like subcell the symmetry of the (Si, Al)–O_4 tetrahedra is 222 (cf. Fig. 4). The three twofold axes run parallel to c and parallel and perpendicular to the hexagonal a axis on which the (Si, Al) atoms fall by a projection onto (001). In the supercell the symmetry of the SiO_4 and AlO_4 tetrahedra is reduced to 2. The remaining twofold axes run either parallel or perpendicular to a hexagonal a axis (Fig. 1). The walls of the central channels are only formed by AlO_4 and SiO_4 tetrahedra with twofold axes running parallel to the a axis.

3. Structural relations between low quartz, dauphinée twinned low quartz, and high quartz

Fig. 3 shows the structure of low quartz (Young & Post, 1962; Smith & Alexander, 1963; Zachariasen & Plettinger, 1965) and Fig. 4 shows the structure of high quartz (Bragg & Gibbs, 1925; Young, 1962; Arnold, 1962). For the representation of low and high quartz the space groups $P3_221$ and $P6_221$ have been used. The space group $P3_221$ is a subgroup of $P6_222$. The difference between these space groups can be described by the twofold axis which converts from the 3_2 axis to the 6_2 axis. This twofold axis is the twinning symmetry element of the well known quartz twinning law, the dauphinée law. The situation in dauphinée twinned low quartz is illustrated in Figs. 5 and 6. Figs. 5(a) and 6(a) show the atomic positions in two low quartz structures which are related to one another by a twofold axis running within the c axis. (The c axis coincides with the 3_2 axis in low quartz and with the 6_2 axis in high quartz). These two arrangements of the low quartz structure are called in the following: low quartz arrangement 1 (abbreviated to lq1) and low quartz
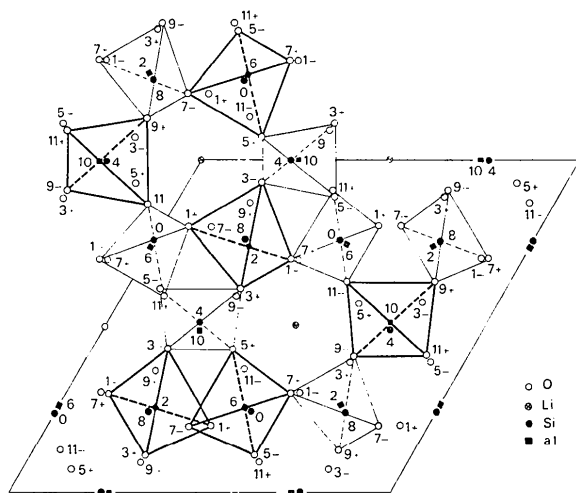

Fig. 1. Schematic representation of the β-eucryptite superstructure. The numbers in the drawing divided by 12 are the exact z coordinates of the Si and Al atoms and the approximate z coordinates of the O atoms. + or − sign after the numbers shows a deviation in the direction of the positive or negative c direction.

Table 1. *Space groups, equipoints and coordinates of low quartz in arrangement* 1 *and* 2, *dauphinée twinned low quartz and high quartz*

	Space group	Si atoms			O atoms		
		Equi-points	Coor-dinates	Approximate values of the variable coordinates	Equi-points	Coor-dinates	Approximate values of the variable coordinates
Low quartz 1	$P3_221$	3(a)	x 0 0	x=0·47	6(c)	x y z	x=0·27 y=0·42 z=0·55
Low quartz 2	$P3_221$	3(a)	x 0 0	x=0·53	6(c)	x y z	x=0·15 y=0·42 z=0·45
Dauphinée-twinned low quartz	$P6_222$	6(g)	x 0 0	x=0·47	12(k)	x y z	x=0·27 y=0·42 z=0·55
High quartz	$P6_222$	3(c)	½ 0 0	–	6(j)	x 2x ½	x=0·21

arrangement 2 (lq2). Fig. 3 may correspond to lq1. If the atoms of lq1 and lq2 are superimposed in one elementary cell as in Figs. 5(a) and 6(a), this atomic arrangement can be described by space group $P6_222$. The space groups, atomic positions, and approximate coordinates of lq1 and lq2 as well as dauphinée twinned low quartz are listed in Table 1. As shown in Figs. 5(a) and 6(a) in this arrangement a Si atom of lq1 and a Si atom of lq2 are always close together. This also holds for the O atoms. They can be linked by split vectors δ which extend from the atoms of lq1 to the corresponding atoms of lq2. A δ vector of the O atoms is shown in Figs. 5(a) and 6(a). As shown in Fig. 6(a), the δ vectors of the O atoms are approximately parallel to the normals on the planes Si–O–Si. The midpoints of the δ vectors are equal to the positions of the Si and O atoms in high quartz [Figs. 5(a) and 6(a)]. In high quartz the Si atoms occupy the special equipoint 3(c) and the O atoms the special equipoint 6(j), which has only one free coordinate (cf. Table 1). Its value is equal to the mean value of x(O) in lq1 and lq2. The relations between high quartz and low quartz are illustrated again in Figs. 5(b)–(d) and 6(b)–(d). A SiO₄ tetrahedron of high quartz is shown in Figs. 5(b) and 6(b), the corresponding tetrahedron of lq1 in Fig. 5(c) and 6(c) and of lq2 in Figs. 5(d) and 6(d). (Of course the tetrahedra of Figs. 5(b) and (c) and 6(b) and (c) are already included in the drawings of the quartz structure of Figs. 3 and 4.)

The SiO₄ tetrahedra of low quartz have the symmetry 2. The twofold axes run parallel to the trigonal a axes, on which the Si atoms fall by projection on (001) (cf. Fig. 3). The symmetry of the SiO₄ tetrahedra is increased to 222 in high quartz. The additional twofold axes run parallel to c and perpendicular to the above mentioned a axes (cf. Fig. 4).

In Figs. 7 and 8 tetrahedra arrangements are shown, which are built up by oxygen atoms of lq1 and lq2. The oxygen atoms are represented in the same manner as in Figs. 5 and 6: oxygen atoms of lq1 and lq2 are marked by circles and squares respectively. These tetrahedra of Figs. 7 and 8 represent a way to connect the lq1 and the lq2 structure. Therefore they are called 'connecting' tetrahedra. There are two sorts of connecting tetrahedra: the first is shown in Figs. 7(a) and (b) and 8(a) and (b); the second is shown in Figs. 7(c) and (d) and 8(c) and (d). The tetrahedra of the first type have the same symmetry as the tetrahedra in high quartz, 222. The tetrahedra of the second type bear some similarities to low quartz: Their symmetry is only 2 in agreement with low quartz, but the direction of this twofold axis is not parallel, as in low quartz, but perpendicular to an a axis.

The quartz structures can be considered as being built up by helices of SiO₄ tetrahedra twisted around the 3_2 axis (low quartz) or 6_2 axis (high quartz). The pitch of such a helix is equal to the doubled c axis of quartz. A second helix runs between the whorls of the first one. The distance between the whorls of the two

helices is equal to the c axis. In high quartz the two helices are transformed in each other by the twofold axis included in the 6_2 axis.
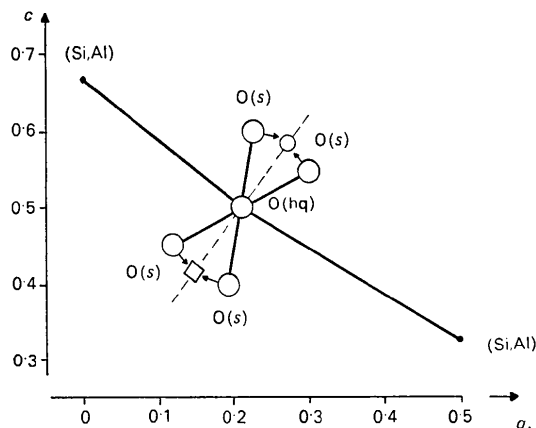

Fig. 2. Relation between oxygen atom positions of the sub-cell, of the supercell and of the idealized arrangement of the framework.
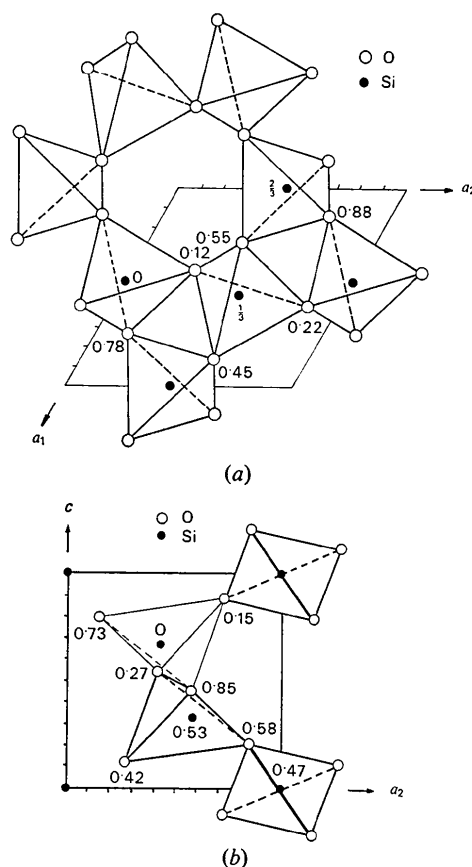

(a)

(b)

Fig. 3. Projections of the low quartz structure. (a) Projection on (001) along the c axis. Numbers are the z coordinates. (b) Projection on (010) along the a_1 axis. Numbers are the x coordinates.
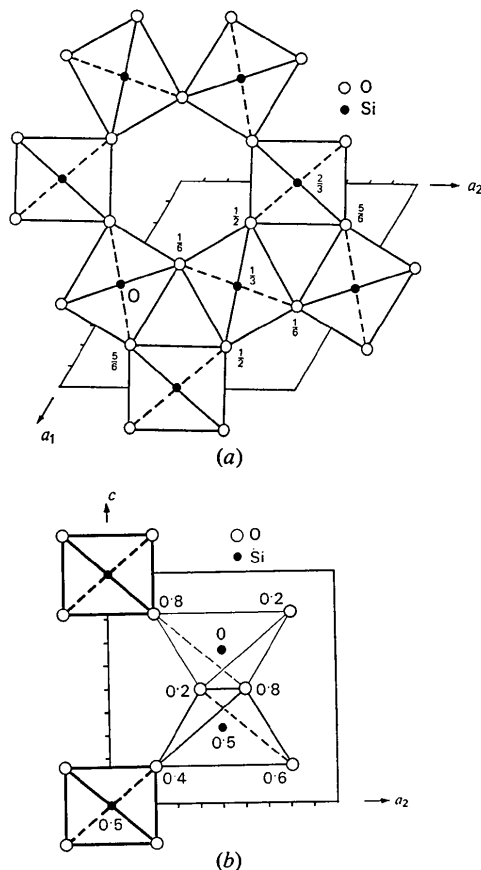
Fig. 4. Projection of the high quartz structure. (a) Projection on (001) along the c axis. Numbers are the z coordinates. (b) Projection on (010) along the a_1 axis. Numbers are the x coordinates.
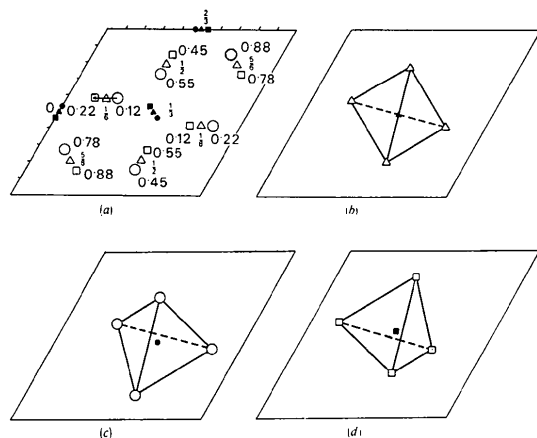

Fig. 5. Relations between dauphinée twinned low quartz and high quartz structures projected on (001) along the c axis. (a) Atomic positions in dauphinée twinned low quartz and high quartz. The numbers are the z coordinates. (b) Tetrahedron of high quartz. (c) Tetrahedron of low quartz in position 1 (lql). (d) Tetrahedron of low quartz in position 2 (lq2). O: O ; low quartz position 1 ; □ low quartz position 2; △ high quartz. Si: ● ; low quartz position 1 ; ■ low quartz position 2; ▲ high quartz.

4. Idealized arrangement of the β-eucryptite framework

4·1. *Generation of the idealized arrangement*

After projection of the β-eucryptite superstructure into the subcell the O atoms occupy four split positions as shown in Fig. 2. Two of these four O atoms are always connected by a line, which runs through the 'position of gravity' O(hq). Suppose there is a rotation of these two connecting lines, so that they coincide with the dashed line. The O atoms now occupy the positions marked by the small circle and small square on the dashed line. The dashed line is approximately perpendicular to the connecting line (Si, Al)–(Si, Al) and approximately parallel to the normal on the (Si, A)–O–(Si, Al) bonding plane. The distances of the (Si, Al) atoms to the two split positions are equal and have the same lengths as the averaged tetrahedral (Si, Al)–O-distances in framework silicates. Therefore the connecting line of the small circle and small square corresponds to a split vector of dauphinée twinned low quartz, the positions marked by a circle and by a square correspond to lq1 and lq2, respectively. The O split positions of Fig. 2 which are related to the small circle are generated by four oxygen atoms of the β-eucryptite superstructure. These four oxygen atoms are now shifted to the idealized O positions and designated by a small circle in Figs. 9 and 10. In the same manner each of the 48 oxygen atoms of the β-eucryptite superstructure is shifted and marked by a small circle or by a small square (Figs. 9 and 10). The shifts of the framework do not alter the features of the diffraction pattern. This means, all groups of superstructure reflexions are preserved, but their intensities may change It should be mentioned once more that the oxygen atom positions of the idealized β-eucryptite framework are related to lq1 or lq2 by shifting the framework, small circles and squares corresponding to lq1 and lq2, respectively.

Owing to the generation of the idealized arrangement of the O atoms the differences between the Si–O and Al–O distances disappear. These distances now correspond to the averaged tetrahedral distances for the ratio Si:Al=1:1. Therefore the Si and Al atoms of the idealized framework must now be considered as (Si, Al) atoms. The (Si, Al) atoms may keep their positions known from superstructure of β-eucryptite, or may move along the twofold axis running through the tetrahedra. By moving along these axis it is possible to generate four equal (Si, Al)–O distances in each tetrahedron. The positions of the (Si, Al) atoms are not shown in Fig. 9 to enable a clear representation of the idealized O arrangement. Their positions can be taken from the schematic representation of the eucryptite superstructure of Fig. 1.

4·2. *Discussion of the idealized arrangement*

As shown in Figs. 9 and 10 there are two types of tetrahedra drawn as white or dashed tetrahedra. The oxygen atoms of the white tetrahedra are marked either

by circles or by squares, the oxygen atoms of the dashed tetrahedra are marked by circles and squares.

From the discussion above follows that the white tetrahedra are low quartz-like, either similar to lq 1 (circles) or similar to lq 2 (squares). Therefore the tetrahedra formed by circles or squares are designated as slq 1 or slq 2, respectively. The dashed tetrahedra are 'connecting tetrahedra' (cf. §3).

Only white tetrahedra (low quartz-like) form the walls of the central channels. As described in §3 the walls of the main channels are built up by two tetrahedra helices running together. In Fig. 9 one of these two helices is shown. The tetrahedra are similar to lq 2
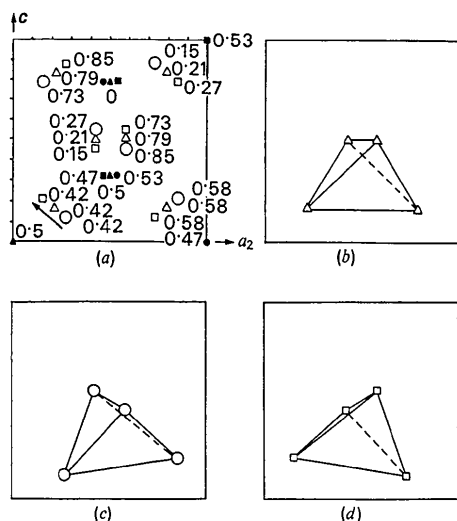
and therefore the helix is similar to lq 2. The similarity can be seen by a comparison of Fig. 3(a) [projection of lq 1 on (001)] and of the helix formed by the white tetrahedra of Fig. 9. The remaining circles are used for the construction of the second helix, which is like lq 1. The two helices are transformed into each other by the twofold axis included in the 6₄ axis of the superstructure. That means, the arrangement of the two tetrahedra helices forming the walls of the central channel can be derived from low quartz. They are transformed

Fig. 6. Relations between dauphinée twinned low quartz and high quartz structures projected on (010) along the a_2 axis. (a) Atomic positions in dauphinée twinned low quartz and high quartz. The numbers are the x coordinates. (b) Tetrahedron of high quartz. (c) Tetrahedron of low quartz in position 1 (lq1). (d) Tetrahedron of low quartz in position 2 (lq2). O: ○; low quartz position 1; □ low quartz position 2; △ high quartz. Si: ●; low quartz position 1; ■ low quartz position 2; ▲ high quartz.
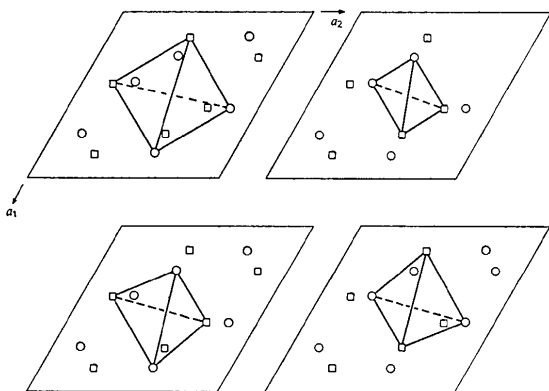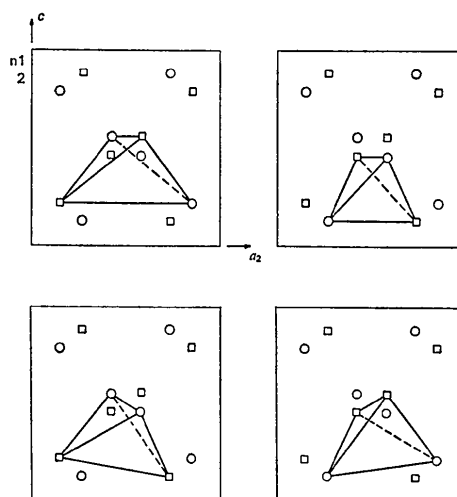

Fig. 7. Arrangement of the 'connecting tetrahedra' projected on (001) along the c axis. ○ low quartz position 1; □ low quartz position 2.

Fig. 8. Arrangement of the 'connecting tetrahedra' projected on (010) along the a_1 axis. ○; low quartz position 1; □ low quartz position 2.

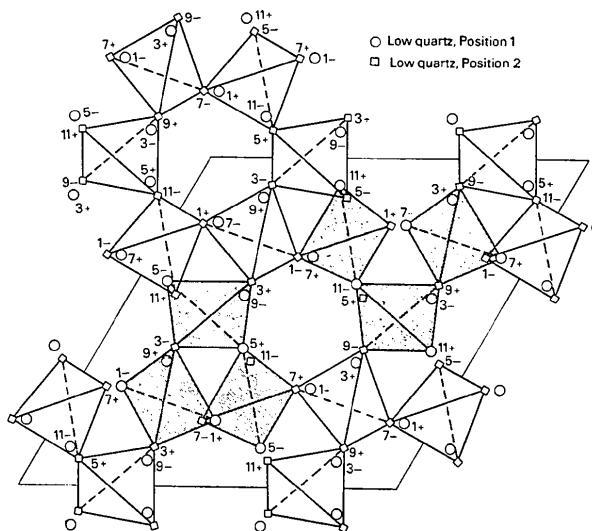Fig. 9. Idealized arrangement of the framework of the β-eucryptite superstructure projected on (001) along the c axis. Numbers divided by 12 are the approximate z coordinates of the O atoms. A + or − sign behind the numbers shows a deviation in the direction of the positive or negative c direction.

in each other by the twinning element of the dauphinée twinning law. In this sense these helices can be considered as low-quartz-like structure elements, which are dauphinée twinned in an ordered way. This is illustrated by the low-quartz-like tetrahedra of Fig. 10. On the right-hand side a part of the helix formed by slq 1 tetrahedra is shown. A comparison of these tetrahedra with Fig. 3(b) shows the similarity to lq 1. On the left-hand side the corresponding parts of the 'dauphinée twinned' helix are drawn.

The quartz-like helices forming the walls at the central channels do not have points of contact with each other, but only with connecting tetrahedra. These tetrahedra, shown as dashed tetrahedra in Figs. 9 and 10, share two corners with other connecting tetrahedra and the remaining two corners with a slq 1 and slq 2 tetrahedra. In this sense one can say these tetrahedra connect the helices running around a central channel. In addition they connect the helices of different central channels, too.
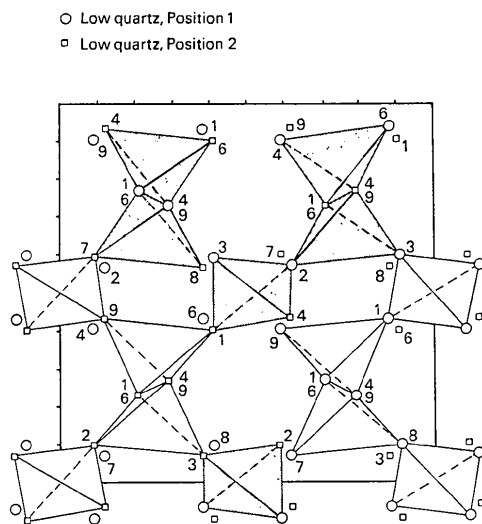
The walls of the secondary channels are formed by both, low quartz-like tetrahedra (slq 1 and slq 2) and connecting tetrahedra (shown as dashed tetrahedra in Figs. 9 and 10).

From the discussion follows that the ordered structure of β-eucryptite at room temperature, usually considered as a 'stuffed derivative of the high quartz structure' is closely related to low quartz. The SiO_4 and AlO_4 tetrahedra have a twofold symmetry and in addition the tetrahedra forming the walls of the central channels are similar to the tetrahedra in low quartz. The β-eucryptite structure at room temperature is related to high quartz only by consideration of the space-group symmetry and average structure but not by consideration of the actual arrangement of the framework.

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O Low quartz, Position 1

□ Low quartz, Position 2

Fig. 10. Idealized arrangement of the framework of the β-eucryptite superstructure projected on (010) along the a_1 axis. Numbers divided by 10 are the approximate x coordinates.