

Structural Relations Between the Low- and High-Temperature Forms of β -Eucryptite (LiAlSiO_4) and Low and High Quartz. II. High-Temperature Form of β -Eucryptite and High Quartz

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At about 400°C the low-temperature form of ordered β -eucryptite changes into a high-temperature form. From the point of view of the framework it is a first-order transition. By displacements an arrangement closely related to high quartz is generated. The ordering of the Li atoms at room temperature is destroyed and probably replaced by a statistical distribution of the Li atoms over all sites of the main channel coordinated by four oxygen atoms.

1. Introduction

As described in part I (Schulz & Tscherry, 1972), §2 the axes of the supercell I are twice the length of the axes of the high-quartz-like subcell. Diffraction patterns of β -eucryptite at room temperature show, in addition to the main reflexions of a high quartz-like subcell, two sorts of superstructure reflexions (*cf.* Tscherry, Schulz & Laves, 1972*b*, §1 and Fig. 1). On the basis of the supercell these different groups of reflexions can be described in the following way:

- | | |
|-------------------------------|-----------------------|
| (1) main reflexions | $h, k, l = 2n$ |
| (2) superstructure reflexions | $l = 2n + 1$ |
| (i) c reflexions | $h, k = 2n$ |
| (ii) a reflexions | $h, k = 2n + 1$ |
| | or $h + k = 2n + 1$; |

c reflexions require only a doubling of the high-quartz-like c axis, a reflexions require a doubling of all three axes of the high-quartz-like subcell.

The intensities of the a reflections decrease with increasing temperature and are zero at about 400°C (Tscherry & Laves, 1970). This is shown by the three precession photographs of Fig. 1 which are taken at different temperatures. With decreasing temperatures the a reflexions appear again. At room temperature they have reached their original intensity. Main and c reflexions are not affected significantly by the heating. This means that from room temperature up to approximately 400°C the supercell is eight times larger, above this temperature it is only twice as large as the high-quartz-like subcell. The supercell at high temperatures (designated at supercell II) is related to the subcell in the following way:

$$\begin{aligned} a(\text{super}) &= a(\text{sub}) \\ c(\text{super}) &= 2c(\text{sub}) \end{aligned}$$

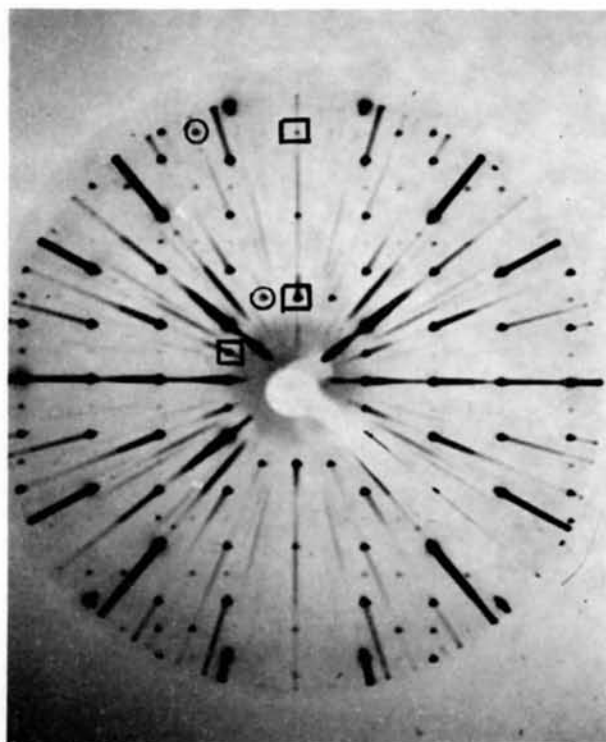
The high temperature form of the β -eucryptite superstructure can be easily derived from the low-temperature form of the superstructure.

2. Derivation of the high-temperature form of the β -eucryptite superstructure

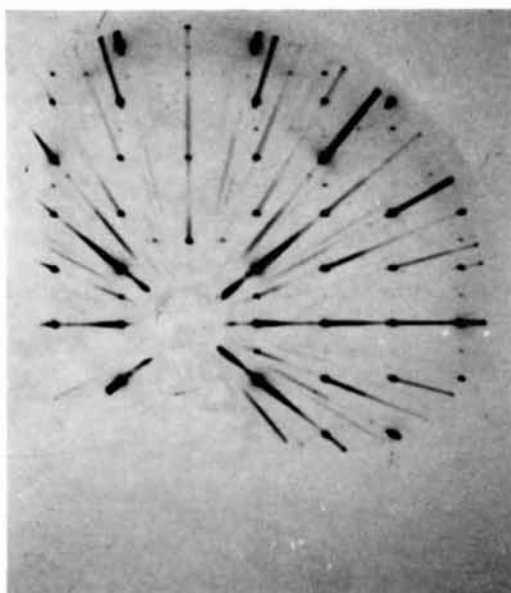
The disappearance of the a reflexions is caused by the generation of a new superstructure built up in the supercell II. Its equipoints and coordinates can be derived by the 'projection' of the superstructure at low temperature from supercell I into supercell II. The meaning of the term 'projection' is described in part I, §2 and in more detail in Tscherry, Schulz & Laves (1972*a*, §3). The projected atoms occupy either the same positions or are spread around positions of gravity. In the latter case the split-positions can be replaced by the corresponding positions of gravity.

Table 1 shows the derivation of the β -eucryptite superstructure at high temperatures from its superstructure at low temperatures (Tscherry, Schulz & Laves, 1972*b*). Through the projection the two Si and the two Al equipoints fall together forming the new equipoints 3(c) for the Si atoms and 3(d) for the Al atoms. From this it follows that in the high-temperature form the Al and Si atoms are also ordered. They are arranged in alternating layers perpendicular to the c axis. Their equipoints do not have variable coordinates.

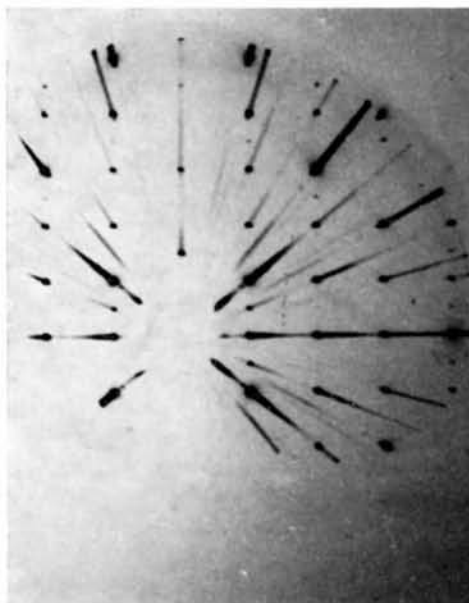
In supercell I the O atoms occupy four different equipoints 12(k). In supercell II, in each case, four projected O atoms are arranged around one position of gravity. Each of these four projected O atoms belongs to a different equipoint in supercell I. Their positions of gravity in supercell II can be described by one general equipoint 12(k). Its coordinates can be calculated by averaging the coordinates of four O split



(a)



(b)



(c)

Fig. 1. β -Eucryptite. Precession photographs of the $(h0l)$ layer taken with filtered Mo $K\alpha$ radiation: \square c reflexions, \circ a reflexions. Note the decreasing intensities of the a reflexions with increasing temperature. (a) Room temperature, (b) 300°C , (c) 480°C .

Table 1. Derivation of the equipoints and atom coordinates of the high-temperature form from the low-temperature form of the β -eucryptite superstructure and their 'refined' values

Supercell I Low-temperature form			Supercell II High-temperature form			'Refined' high-temperature form		
Atom designation	Equipoints	Coordinates x y z	Coordinates after projection from supercell I into supercell II	Atom designation	Equipoints	Coordinates x y z	Atomic parameter	Refined values
Si(1)	6(g)	0.249 0 0	$\pm(0.498$ 0 0)	} Si	3(c)	0.5 0 0	B (\AA^2)	0.35 (2)
Si(2)	6(t)	0.249 2x 0	$\pm(0.498$ 0.996 0)					
Al(1)	6(h)	0.251 0 0.5	$\pm(0.502$ 0 0.5)	} Al	3(d)	0.5 0 0.5	B (\AA^2)	0.36 (3)
Al(2)	6(j)	0.251 2x 0.5	$\pm(0.502$ 1.004 0.5)					
O(1)	12(k)	0.087 0.199 0.242	0.174 0.398 0.242	} O	12(k)	0.199 0.405 0.254	x y z	0.404 (1) 0.255 (1)
O(2)	12(k)	0.604 0.701 0.262	1.208 1.402 0.262					
O(3)	12(k)	0.105 0.708 0.263	0.210 1.416 0.263					
O(4)	12(k)	0.592 0.203 0.250	1.184 0.406 0.250					
			mean value					
Li(1)	3(b)	0 0 0.5	0 0 0.5	} Li(1) Li(2)	3(b)	0.0 0.0 0.5	B (\AA^2)	1.4 (4)
Li(2)	3(c)	0.5 0 0	1.0 0 0					
Li(3)	6(f)	0.5 0 0.324	$\pm(1.0$ 0 0.324)					

atoms belonging to one position of gravity as in Table 1. The arrangement of the Li atoms in the subcell II will be discussed in §5.

By replacing the split atoms by their positions of gravity an ordered arrangement of the framework is generated. The Si-O and Al-O distances have known values. This is shown in Fig. 2. This Figure is closely related to Fig. 2 of part I which deals with the projection of the framework atoms from the supercell I into the high quartz-like subcell. In this case 8 O atoms occupy 4 different split positions. (It may be noted that this is only valid approximately if the coordinates obtained by the refinements are used.) If the O atoms are projected into the supercell II, only 4 O atoms occupy two different split positions, for example the positions shown in Fig. 2. The O atoms of this schematic representation are the O atoms listed in Table 1.

Fig. 2 shows that the positions of gravity of the O atoms in the supercell II [O(h)] and in the subcell [O(hq)] deviate from each other. As discussed in part I, §2 the distances of the Si and Al atom of Fig. 1 to O(hq) are the same. Because of the deviation of O(h) from the O(hq) position the distance Si-O is decreased and the distance Al-O increased, so that the normal Si and Al distances in framework silicates are generated.

3. Discussion of the framework of the high-temperature form of β -eucryptite

As shown in Table 1, the Si and Al atoms occupy the special equipoints 3(c) and 3(d), respectively. The point symmetry of these equipoints and therefore the symmetry of the corresponding SiO_4 and AlO_4 tetrahedra, is equal to 222. These symmetry relations can also be taken from Fig. 3, a schematic representation of the framework of the high temperature form of β -eucryptite. The SiO_4 tetrahedra in high quartz also have the symmetry 222 as discussed in part I, §3. A comparison of Fig. 4(a) of part I and Fig. 3 of part II (this paper) shows the strong relations existing between these

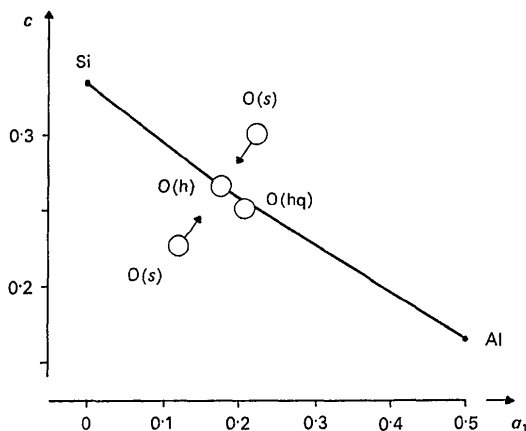


Fig. 2. Relations between oxygen positions in the supercells I and II.

frameworks. Therefore the framework of the high temperature form of β -eucryptite can be considered as high quartz-like with an ordered distribution of the Si and Al atoms. These two Figures would be nearly identical if the framework of the high-temperature form of β -eucryptite were to be changed into an idealized arrangement as in the corresponding low-temperature form (*cf.* part I, §4). This means the Si and Al atoms are replaced by (Si,Al) atoms and the O atoms are shifted such that they occupy the position O(hq) (*cf.* Fig. 2 of part I and Fig. 2 of part II). After this procedure the new framework does not allow for superstructure reflexions but only for high quartz-like main reflexions. This means that the c axis of the supercell II is divided into two and the high quartz-like average structure is generated.

4. 'Refinement' of the high-temperature form of the β -eucryptite superstructure

A structure 'refinement' of the high-temperature form of β -eucryptite was started using only the c reflexions of the low-temperature form of β -eucryptite and the parameters of Table 1. The scaling factor for the least-squares calculations was calculated from the scaling factor of the refinement of the average structure. The final R value was 0.09. The refined parameters (Table 1) do not correspond to the true structure parameters of the high-temperature form, but they can be considered as an estimate of these parameters and as a comparison of the high-temperature structure derived from their low-temperature form. The refined coordinates of the

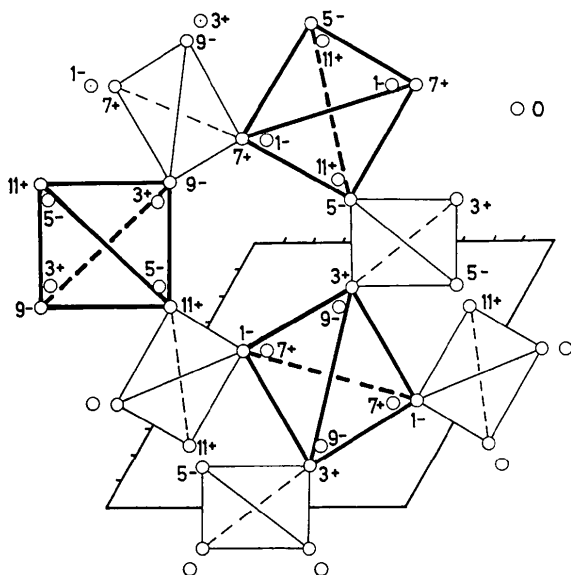


Fig. 3. Schematic representation of the high-temperature form of the superstructure of β -eucryptite. Numbers divided by 12 are the approximate z coordinates of the O atoms. A + or - sign after the numbers shows a deviation in the direction of the positive or negative c direction.

O atoms agree within two standard deviations with the estimated parameters. As expected from the discussion on the relations between superstructure and average structure (*cf.* §2), their isotropic temperature factor (1.21 \AA^2) is close to the one in the average structure (1.21 \AA^2) but deviates significantly from those in the low-temperature form of the superstructure (0.8 \AA^2) (Tscherry, Schulz & Laves, 1972*a,b*). In the average structure the coordinates of the split positions of the projected Si, Al and Li atoms deviate only about 0.006 \AA from their positions of gravity. Therefore it is not surprising that their isotropic temperature factors have nearly the same values in the average structure and in the low- and high-temperature form of the structure (Si and Al: 0.35 to 0.41 \AA^2 ; Li: 1.5 to 1.6 \AA^2).

5. The Li atoms

In the low-temperature structure the Li atoms occupy different sites in the central channel and in the secondary channels (*cf.* part I, §2). With the z coordinates of Table 1 their z values are: $\frac{1}{6}$, $\frac{2}{6}$, $\frac{5}{6}$ in the central channel and 0 , $\frac{1}{3}$, $\frac{2}{3}$ in the secondary channels. The projection of the superstructure of supercell I into supercell II corresponds to a superposition of the secondary channels with the central channel. After superposition the Li atoms occupy places with the z values: 0 , $\frac{1}{6}$, $\frac{2}{6}$, \dots , $\frac{5}{6}$ in the one main channel of supercell II, *i.e.* the Li atoms are statistically distributed on the equipoints 3(*b*) and 3(*a*).

From this discussion follows that in the low-temperature superstructure the Li atoms occupy different positions in central channel and secondary channels and therefore contribute to the intensity of the a reflexion of the low-temperature superstructure. In the high-temperature superstructure, the arrangement of the Li atoms is the same in all main channels. This is a necessary consequence of the disappearance of the a reflexions above 400°C . Therefore the Li atoms must change places, either in the central channel or in the secondary channels or *vice versa*. Then the Li atoms would be arranged again in an ordered manner. But it is more likely that the Li atoms which are able to change places at a certain temperature do not occupy new sites at higher temperatures in an ordered way, but are statistically distributed on the equipoints 3(*b*) and 3(*a*). To decide these questions structure investigations of β -eucryptite at higher temperature are in preparation.

Summary

Ordered β -eucryptite behaves like quartz. A low-temperature form and a high-temperature form exist and their structures show similarities to low and high quartz, respectively. The transition takes place at about 400°C . The transition is caused by displace-

ments of the framework atoms and place changing of the Li atoms.

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The Crystal and Molecular Structure of 1-*p*-Tolyl-3-(α -cyano)benzylidenetriazene, C₁₅H₁₂N₄*

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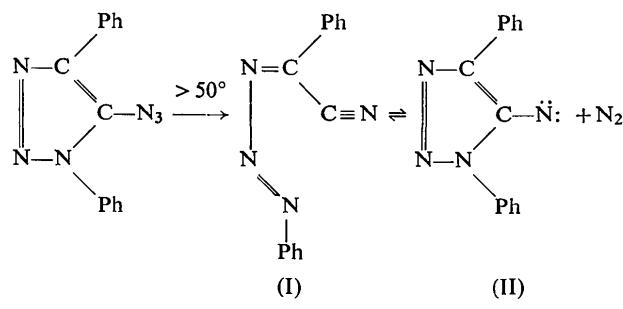
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The compound 1-*p*-tolyl-3-(α -cyano)benzylidenetriazene, C₁₅H₁₂N₄, is a product of the thermal decomposition of 1-*p*-tolyl-4-phenyl-5-azidotriazole, crystallizing from petroleum ether in the monoclinic space group *Pc* with $a = 4.036$ (2), $b = 11.109$ (2), $c = 14.805$ (8) Å, $\beta = 93.57$ (6)°, and two molecules per cell. 1019 reflections were recorded by the integrating oscillation and integrating Weissenberg techniques. The structure was solved by the vector search method from a sharpened Patterson function assuming the existence of the *p*-toluidyl skeleton, C₇N. The final value of $R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}|$ after refinement by full-matrix least-squares methods is 0.077. In previously determined aromatic triazene structures, R₁-N=N-N-(R₂,R₃), the triazene moiety usually displays equivalent N-N bond distances (of about 1.25 Å) when R₂ or R₃ is hydrogen or when the triazenido anion is acting as a bidentate ligand to a transition metal cation; in this structure neither R₂ nor R₃ is hydrogen and the N-N distances are nonequivalent (1.24 and 1.40 Å). This study is inconclusive regarding the hypothesis of Smith, Krbecek & Resemann [*J. Amer. Chem. Soc.* (1964), **86**, 2025] (based on its chemical reactions) that C₁₅H₁₂N₄ occurs in solution in an equilibrium between the title compound and a closed-ring nitrene.

Introduction

A product, C₁₄H₁₀N₄, of unknown structure, obtained from the thermal decomposition of 1,4-diphenyl-5-azidotriazole, was thought to exist in solution as an equilibrium mixture of the open chain triazene (I) and a stable nitrene (II):



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(Smith, Krbecek & Resemann, 1964). The compound crystallizes very readily from a variety of nonpolar solvents in the orthorhombic space group *Pbca* with $a = 27.6$, $b = 11.4$, $c = 7.82$ Å; $Z = 8$.

A structure analysis was undertaken by the vector-search method (Nordman, 1966; Nordman & Schilling, 1970; Schilling, 1970a) upon an analogue, C₁₅H₁₂N₄, the product of 1-*p*-tolyl-4-phenyl-5-azidotriazole. This substance [compound (III), M.W. 248.31] displays the same chemical properties and would suffice to confirm the proposed structure, but since it crystallizes in space group *Pc*, only a one-dimensional determination of fragment location is required (*i.e.* with respect to the glide plane) rather than the three-dimensional location required in space group *Pbca*. The possibilities for the structure of (III) are analogous to (I) and (II) above, and will be designated CH₃-(I) and CH₃-(II).

A variety of possible structures were eliminated by Smith *et al.* on the basis of physical and chemical properties, but the positive evidence for the structure was inconclusive. C₁₄H₁₀N₄ and C₁₅H₁₂N₄ are dark red in color. The infrared spectrum normally exhibits no bands higher than 1600 cm⁻¹, but under certain conditions a weak band at 2200 cm⁻¹ occurs, suggesting the existence of a cyano group. The n.m.r. spectrum of C₁₄H₁₀N₄ shows six aromatic hydrogen atoms and two pairs of hydrogens at 1.75 and 2.1 τ ; the former are