

The Crystal Structure of γ' Sodium Beryllium Tetrafluoride, Na_2BeF_4

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γ' - Na_2BeF_4 is monoclinic, space group $P2_1/n$, with $a=5.5590$ (9), $b=8.0703$ (5), $c=7.9098$ (5) Å, $\beta=99^\circ 21$ (3)', $Z=4$. 989 intensities collected by the θ - 2θ scan technique (Mo $K\alpha$: $\lambda=0.71069$ Å) were used and the structure refined to $R=0.054$. The structure consists of serrated chains of sodium-centered octahedra linked by beryllium tetrahedra. There are two distinct octahedral sites M(1) and M(2), characterized by extreme distortion, the Na-F distances ranging from 2.280 to 2.540 Å in M(1) and 2.272 to 2.469 Å in M(2). The beryllium tetrahedra are severely distorted and have angles (mean: $109^\circ 04'$) consistent with sp^3 hybridization.

Introduction

The polymorphism of sodium beryllium tetrafluoride (Na_2BeF_4) and its isomorphism with a number of calcium and magnesium silicates has been discussed by a number of authors, *e.g.*, Thilo & Liebau (1952); Hahn (1953); Roy, Roy & Osborn (1953). There is agreement that at least four polymorphs exist, namely γ , α_1 , α , and β .

The crystal structure of γ - Na_2BeF_4 (stability range $\approx 20^\circ \rightleftharpoons 187^\circ\text{C}$) was first discussed by O'Daniel & Tscheischwili (1941) and later refined by Hanke (1965) and Deganello (1972*a*), the latter with three-dimensional data. It consists of an array of sodium cations in octahedral coordination with fluorine atoms forming chains aligned along c and linked to one another through beryllium-centered tetrahedra. Such an arrangement is isotypic with the crystal structure of olivine $(\text{MgFe})_2\text{SiO}_4$. No structural information is available for the α_1 phase (stability range $\approx 265 \rightleftharpoons 326^\circ\text{C}$). On the basis of powder data, the α modification (stability range $\approx 326 \rightleftharpoons 578^\circ\text{C}$) has been reported to be hexagonal (O'Daniel & Tscheischwili, 1942) and isotypic with the crystal structure of α - K_2SO_4 . A report on the crystal structure of β - Na_2BeF_4 (stability range $\approx 93 \rightleftharpoons 53^\circ\text{C}$) has been published by Guseinov (1970), although the cell constants used by this author do not agree with values earlier reported by Hahn (1953). The structure, determined from two-dimen-

sional data, consists of chains of distorted sodium-centered octahedra linked by beryllium tetrahedra. The existence of yet another polymorph, γ' , extensively discussed by Thilo & Liebau (1952), has been inconsistently reported in the literature (Toropov & Shchetnikova, 1957) and only lately has been confirmed on the basis of single-crystal data (Deganello, 1972*b*).

In this paper the crystal structure of γ' - Na_2BeF_4 is established as part of a study of the structural relationships between orthofluoroberyllates and their silicate isomorphs.

Experimental

The change $\gamma \rightarrow \gamma'$ was induced by a technique described elsewhere (Deganello, 1972*b*). The opaque, white crystal has a prismatic habit [$\{001\}$, $\{010\}$, $\{100\}$, *etc.*]. Precession photographs were consistent with the cell constants given by Thilo & Liebau (1952) and indicated that the space group† is $P2_1/n$ ($0k0$: $k=2n$; $h0l$: $h+l=2n$). Unit-cell parameters and their estimated errors were determined from a least-squares analysis of fourteen high-angle reflections with a program written by Burnham (1962). The values of 2θ were read at $22(\pm 2)^\circ\text{C}$ on a Picker FACS-1 four-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). The analysis converged to $a=5.5590$ (9), $b=8.0703$ (5), $c=7.9098$ (5) Å, $\beta=99^\circ 21$ (3)'. $D_o=2.477\text{\AA}$ and $D_c=2.48$ for $Z=4$. A prismatic crystal ($0.1 \times 0.06 \times 0.09$ mm) was mounted with its c axis slightly offset from the φ axis of the diffractometer. The θ - 2θ scan technique was used at a scanning rate of $1^\circ/\text{min}$ with 20 sec background counts on the scan limits. 1652 independent reflections

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‡ This figure is only an indicative one since no information is available regarding low-temperature work.

§ Roy, Roy & Osborn (1953) report an upper temperature of $115(\pm 5)^\circ\text{C}$.

‡ In $P2_1/n$ the equivalent positions are: $x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

§ This was determined at 20°C with a pycnometer (Thilo & Liebau, 1952).

$\{[\sin \theta/\lambda]_{\max}=0.807\}$ were collected with the same experimental conditions used for the determination of the lattice parameters. 663 of these intensities (I) were discarded since 86 were systematically absent, 150 exhibited asymmetric background and 427 were less than $2\sigma(I)$. The remaining 989 independent reflections were corrected for Lorentz and polarization effects. Because of the reasonably favorable crystal shape and low value of $\mu(0.5 \text{ cm}^{-1})$, absorption corrections were neglected. No extinction correction was applied.

Determination of the structure and refinement

Four atoms were located from a Patterson synthesis and later confirmed by an E map calculated with the program *MAGIC* (Dewar, 1968). Thirty reflections with the highest E values were manually phased with Sayre's equation prior to the commencement of the automated application of the iterative symbolic addition procedure. Standard Fourier and full-matrix least-squares analyses with the package of computer programs assembled by Frenz (1972) permitted unambiguous determination of the atomic positions. With isotropic values of the temperature factors, the maximum parameter shift was 2.1σ while $R=0.074$ and $R_w=0.067$, where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \left[\frac{\sum w||F_o| - |F_c||^2}{\sum w|F_o|^2} \right]^{1/2}.$$

Table 1. List of observed and computed F values

h	k	l	F_o	F_c	F_o/F_c
0	0	0	100	100	1.00
0	0	1	100	100	1.00
0	0	2	100	100	1.00
0	0	3	100	100	1.00
0	0	4	100	100	1.00
0	1	0	100	100	1.00
0	1	1	100	100	1.00
0	1	2	100	100	1.00
0	1	3	100	100	1.00
0	1	4	100	100	1.00
0	2	0	100	100	1.00
0	2	1	100	100	1.00
0	2	2	100	100	1.00
0	2	3	100	100	1.00
0	2	4	100	100	1.00
0	3	0	100	100	1.00
0	3	1	100	100	1.00
0	3	2	100	100	1.00
0	3	3	100	100	1.00
0	3	4	100	100	1.00
0	4	0	100	100	1.00
0	4	1	100	100	1.00
0	4	2	100	100	1.00
0	4	3	100	100	1.00
0	4	4	100	100	1.00
1	0	0	100	100	1.00
1	0	1	100	100	1.00
1	0	2	100	100	1.00
1	0	3	100	100	1.00
1	0	4	100	100	1.00
1	1	0	100	100	1.00
1	1	1	100	100	1.00
1	1	2	100	100	1.00
1	1	3	100	100	1.00
1	1	4	100	100	1.00
1	2	0	100	100	1.00
1	2	1	100	100	1.00
1	2	2	100	100	1.00
1	2	3	100	100	1.00
1	2	4	100	100	1.00
1	3	0	100	100	1.00
1	3	1	100	100	1.00
1	3	2	100	100	1.00
1	3	3	100	100	1.00
1	3	4	100	100	1.00
1	4	0	100	100	1.00
1	4	1	100	100	1.00
1	4	2	100	100	1.00
1	4	3	100	100	1.00
1	4	4	100	100	1.00
2	0	0	100	100	1.00
2	0	1	100	100	1.00
2	0	2	100	100	1.00
2	0	3	100	100	1.00
2	0	4	100	100	1.00
2	1	0	100	100	1.00
2	1	1	100	100	1.00
2	1	2	100	100	1.00
2	1	3	100	100	1.00
2	1	4	100	100	1.00
2	2	0	100	100	1.00
2	2	1	100	100	1.00
2	2	2	100	100	1.00
2	2	3	100	100	1.00
2	2	4	100	100	1.00
2	3	0	100	100	1.00
2	3	1	100	100	1.00
2	3	2	100	100	1.00
2	3	3	100	100	1.00
2	3	4	100	100	1.00
2	4	0	100	100	1.00
2	4	1	100	100	1.00
2	4	2	100	100	1.00
2	4	3	100	100	1.00
2	4	4	100	100	1.00
3	0	0	100	100	1.00
3	0	1	100	100	1.00
3	0	2	100	100	1.00
3	0	3	100	100	1.00
3	0	4	100	100	1.00
3	1	0	100	100	1.00
3	1	1	100	100	1.00
3	1	2	100	100	1.00
3	1	3	100	100	1.00
3	1	4	100	100	1.00
3	2	0	100	100	1.00
3	2	1	100	100	1.00
3	2	2	100	100	1.00
3	2	3	100	100	1.00
3	2	4	100	100	1.00
3	3	0	100	100	1.00
3	3	1	100	100	1.00
3	3	2	100	100	1.00
3	3	3	100	100	1.00
3	3	4	100	100	1.00
3	4	0	100	100	1.00
3	4	1	100	100	1.00
3	4	2	100	100	1.00
3	4	3	100	100	1.00
3	4	4	100	100	1.00
4	0	0	100	100	1.00
4	0	1	100	100	1.00
4	0	2	100	100	1.00
4	0	3	100	100	1.00
4	0	4	100	100	1.00
4	1	0	100	100	1.00
4	1	1	100	100	1.00
4	1	2	100	100	1.00
4	1	3	100	100	1.00
4	1	4	100	100	1.00
4	2	0	100	100	1.00
4	2	1	100	100	1.00
4	2	2	100	100	1.00
4	2	3	100	100	1.00
4	2	4	100	100	1.00
4	3	0	100	100	1.00
4	3	1	100	100	1.00
4	3	2	100	100	1.00
4	3	3	100	100	1.00
4	3	4	100	100	1.00
4	4	0	100	100	1.00
4	4	1	100	100	1.00
4	4	2	100	100	1.00
4	4	3	100	100	1.00
4	4	4	100	100	1.00

After anisotropic thermal refinement, R and R_w converged respectively to 0.054 and 0.051 while the maximum parameter shift was 2σ . At this stage, a final difference synthesis showed no anomalies.

The atomic scattering factors for Na^+ , Be^{+2} and F^- were taken from *International Tables for X-ray Crystallography* (1968). No anomalous scattering correction was applied. Unit weight was assigned to each observation.

The values of the observed and calculated F 's are reported in Table 1.

Discussion of the structure

The structure consists of an array of close-packed fluorine atoms which coordinate sodium octahedrally and beryllium tetrahedrally. There are two distinct octahedral sites M(1) and M(2) arranged so that chains of octahedra are linked to one another by beryllium-centered tetrahedra, two of which point down while the other two point up. This may be seen in Fig. 1, which is a projection of the tetrahedra down $[100]$. Each tetrahedron shares one edge with an octahedron while the two remaining unshared vertices are linked to three distinct octahedra belonging to chains located in alternate layers. In contrast to this edge and vertex sharing, responsible for knitting chains belonging to

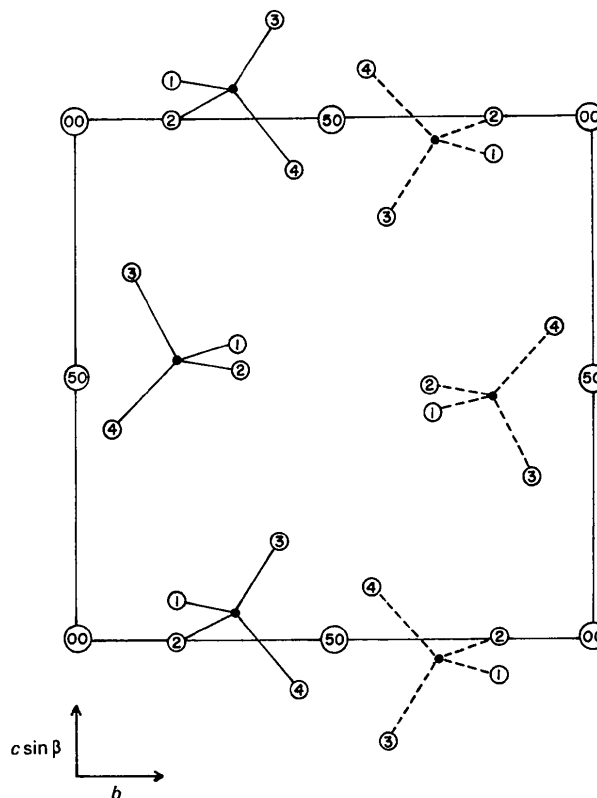


Fig. 1. A projection of the beryllium tetrahedra down $[100]$.

different layers, linking of adjacent layers within each chain is accomplished by vertex sharing. As a consequence, in no instance do any of the octahedra share faces; instead, the octahedron of one chain $M(1)$ shares one edge with the octahedron $M(2)$ of a neighboring chain, thus determining the layering sequence responsible for the magnitude of a . Efficient packing is achieved since each chain lies in the voids created by a neighboring one. This may be seen in Figs. 2 and 3 which show, respectively, a projection of the crystal structure and a portion of a serrated chain down $[010]$.

In both octahedral sites extreme distortion from ideal geometry is present as can be seen in Table 4 which lists the bond lengths obtained from the program *ORFFE* (Busing, Martin & Levy, 1964). Fig. 4 shows the dimensions of the two octahedra. Although $M(2)$ is the less distorted [average value of the sodium-fluorine bonds: 2.338 Å versus 2.398 Å in $M(1)$], its cation-anion distances range from 2.272 to 2.469 Å [2.280 to 2.540 Å in $M(1)$]. Such a variance is quite remarkable in view of the fact that the crystal structure is based on a close-packed arrangement of fluorine atoms. In agreement with electrostatic arguments requiring a shortening of the edges shared between tetra-

hedra and octahedra, it is seen (Table 4) that the distances $F(1)-F(2)$, $F(3)-F(4)$, and $F(1)-F(4)$ are the shortest in both octahedra. Furthermore, edges shared between octahedra [$F(1)-F(3)=2.955$ Å] are longer than those shared between tetrahedra and octahedra.

Both octahedral sites exhibit longer mean values of the cation-anion distances than in the orthorhombic modification (Table 4). However, this is not the case for the tetrahedron. This contraction is reflected in the slightly smaller volume of the monoclinic cell (349.84 Å³) compared with its orthorhombic counterpart (351.22 Å³).

The values of the tetrahedral angles (mean: $109^{\circ}04'$) are consistent with sp^3 hybridization as expected from the small atomic radius, high ionization potential and high sublimation energy of the beryllium atom (Cotton & Wilkinson, 1962). Furthermore, in the severely distorted tetrahedron (Table 4), the short value of the Be-F(3) distance (1.532 Å) would suggest an enhancement in the s character of the related beryllium orbital. However, simple electrostatic arguments suggest that effects of cationic repulsion between Na(1) and Be [Na(1)-Be: 2.92 Å] are likely to be responsible for such a shortening of the Be-F(3)

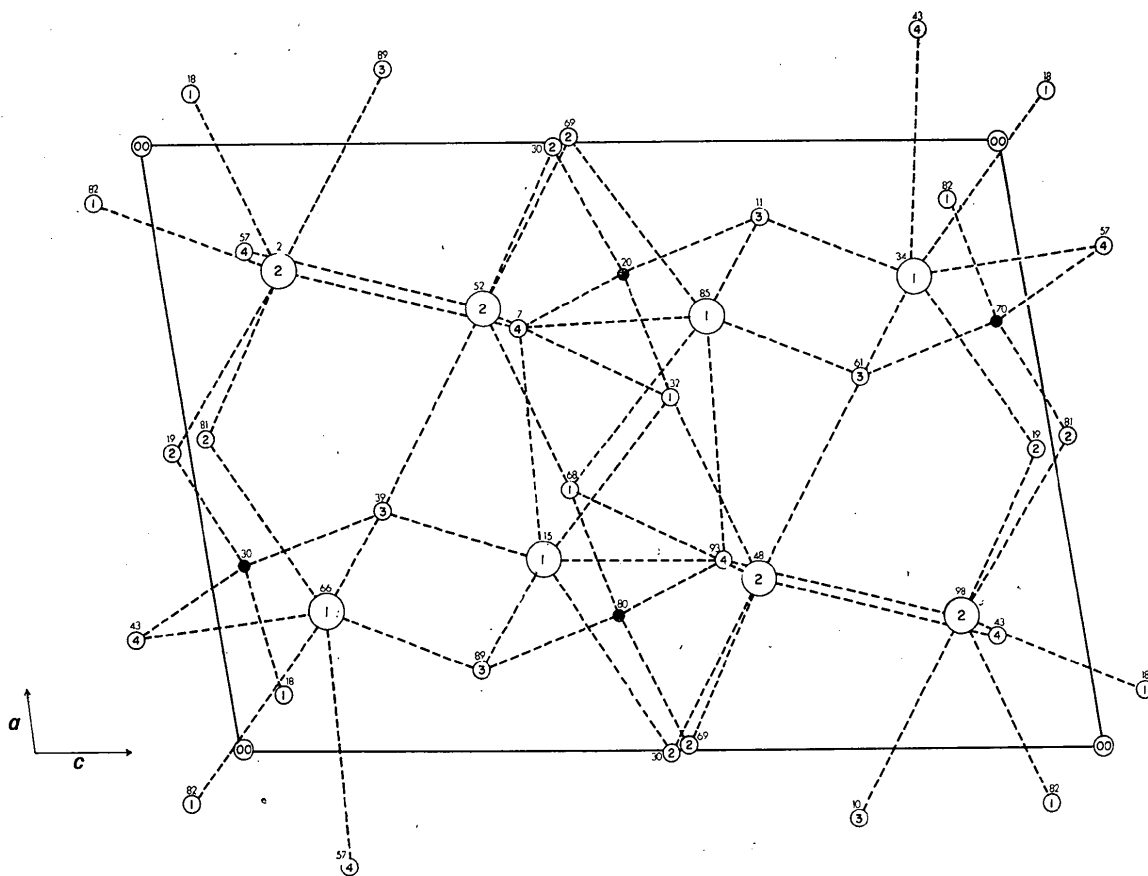


Fig. 2. Projection down $[010]$ showing the unit-cell content. The sodium, beryllium and fluorine atoms are represented by large circles, dots and smaller circles respectively. Positions in percentage of the b repeat are indicated.

distance. Thus, an optimal interrelationship between covalent and ionic forces appears to stabilize the structure in agreement with some of the observations by Birle, Gibbs, Moore & Smith (1968) on the stability of the olivine structure type.

The values of the temperature factors are satisfactory and typical of a close-packed atomic arrangement.

The isotropic values are given in Table 2 and the anisotropic ones in Table 3. Since all the atoms show a preferential direction of thermal vibration along β_{11} , it would be interesting to know if this affects the thermal expansion. Unfortunately, no results on the temperature dependence of the lattice parameters are available.

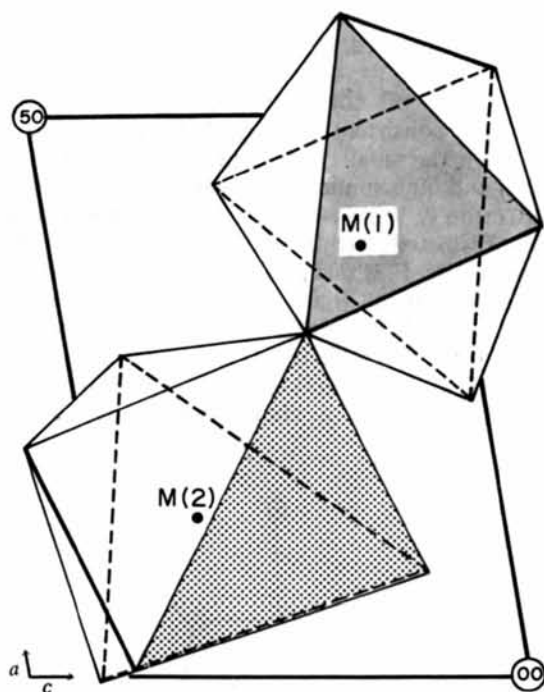


Fig. 3. Projection of a serrated chain down [010].

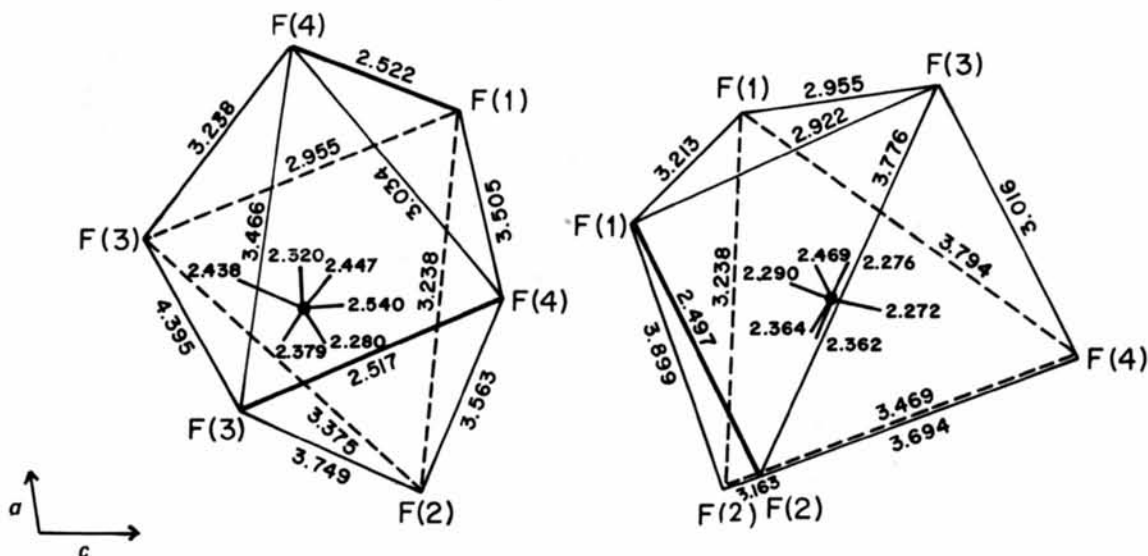


Fig. 4. Dimensions of coordination octahedra around the sodium atoms. Shared edges are shown by thick lines.

Table 2. Fractional atomic coordinates with standard deviations ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> [*] (Å ²)
Na(1)	-0.2847 (2)	-0.1565 (1)	-0.3753 (1)	1.50 (3)
Na(2)	0.2185 (2)	-0.0136 (1)	-0.1369 (1)	1.27 (3)
Be	-0.2926 (6)	-0.3020 (4)	-0.0386 (4)	0.92 (6)
F(1)	-0.0834 (3)	-0.1818 (2)	-0.0686 (2)	1.39 (4)
F(2)	0.4942 (3)	0.1950 (2)	-0.0200 (2)	1.81 (5)
F(3)	-0.3847 (3)	-0.3923 (2)	-0.2070 (2)	1.75 (5)
F(4)	0.1871 (3)	0.4295 (2)	-0.1002 (2)	1.66 (4)

* The thermal parameters are from isotropic refinement.

Table 3. Anisotropic thermal parameters

The thermal parameters are defined as

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})].$$

Standard deviations are given in parentheses. All values have been multiplied by 10^4 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	106 (3)	61 (2)	72 (2)	0	18 (2)	-4 (1)
Na(2)	93 (3)	54 (2)	57 (2)	-4 (2)	12 (2)	0
Be	77 (8)	43 (4)	53 (5)	-6 (4)	21 (5)	0
F(1)	93 (5)	57 (2)	69 (2)	-22 (3)	19 (3)	9 (2)
F(2)	106 (5)	64 (3)	94 (3)	13 (3)	32 (3)	0
F(3)	162 (5)	63 (3)	59 (3)	-24 (3)	-7 (3)	-8 (2)
F(4)	140 (5)	67 (3)	63 (3)	0	19 (3)	18 (2)

Table 4. *Interatomic distances and angles*

	γ' polymorph	γ polymorph
Be tetrahedron		
Be-F(1)	1.562 (4) Å	
Be-F(2)	1.544 (4)	
Be-F(3)	1.532 (4)	
Be-F(4)	1.548 (4)	
Mean	1.546	1.557 Å
F(1)-F(2)	2.497 (2) Å	
F(1)-F(3)	2.509 (3)	
F(1)-F(4)	2.522 (2)	
F(2)-F(3)	2.547 (3)	
F(2)-F(4)	2.558 (3)	
F(3)-F(4)	2.517 (2)	
Mean	2.525	2.551 Å
F(1)-Be-F(2)	107.0 (2)°	
F(1)-Be-F(3)	108.3 (2)	
F(1)-Be-F(4)	108.3 (2)	
F(2)-Be-F(3)	111.7 (2)	
F(2)-Be-F(4)	111.6 (2)	
F(3)-Be-F(4)	109.5 (2)	
Mean	109.4	
M(1) polyhedron		
Na(1)-F(1')	2.447 (1) Å	
Na(1)-F(2)	2.280 (2)	
Na(1)-F(3)	2.438 (2)	
Na(1)-F(3')	2.379 (2)	
Na(1)-F(4)	2.320 (2)	
Na(1)-F(4')	2.540 (2)	
Mean	2.400	2.326 Å
F(1)-F(2)	3.238 (2)	
F(1)-F(3)	2.955 (2)	
F(1')-F(4)	2.522 (2)	
F(1')-F(4')	3.505 (2)	
F(2)-F(3)	3.375 (3)	
F(2)-F(3')	3.749 (3)	
F(2)-F(4')	3.563 (2)	
F(3)-F(3')	4.395 (1)	
F(3)-F(4)	3.226 (3)	
F(3')-F(4)	2.517 (3)	
F(4)-F(4')	3.034 (4)	
M(2) polyhedron		
Na(2)-F(1')	2.290 (2) Å	
Na(2)-F(1)	2.469 (2)	
Na(2)-F(2)	2.364 (2)	
Na(2)-F(2')	2.362 (2)	
Na(2)-F(3)	2.276 (2)	
Na(2)-F(4)	2.272 (2)	
Mean	2.338	2.302 Å
F(1)-F(1')	3.213 (3)	
F(1)-F(3)	2.955 (2)	
F(1')-F(2')	2.497 (2)	
F(1')-F(3)	2.922 (2)	
F(2)-F(2')	3.163 (4)	
F(2)-F(4)	3.469 (3)	
F(2')-F(3)	3.776 (3)	
F(2')-F(4)	3.694 (3)	
F(3)-F(4)	3.016 (2)	

The increasing opacity of γ -Na₂BeF₄ on heating and in particular during the process of phase transition to the monoclinic polymorph γ' is probably related to the reorganization of the beryllium tetrahedra and of the octahedral chains, as anticipated elsewhere (Deganello, 1972a).

In conclusion, it is noted that none of the calcium magnesium silicates reported in the literature and characterized by a stoichiometric ratio of the cationic and anionic species equivalent to that exemplified by Na₂BeF₄ is structurally related to the polymorph γ' .

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