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Crystal structure of hexagonal trinepheline—A new synthetic $NaAlSiO_4$ modification

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ABSTRACT

The crystal structure of a synthetic $NaAlSiO_4$ modification has been solved and refined to an R index of 0.020 for 2745 independent reflections. The compound is hexagonal with space group symmetry $P6_1$, a = 9.995(2) Å and c = 24.797(4) Å. The crystal showed twinning by merohedry according to m_{210}, which was accounted for in the calculations. The phase was named trinepheline, following prior studies, because the length of its c lattice parameter is three times the length of the c parameter in nepheline, whereas the a parameter is about 10 Å in both phases. The crystal structure is characterized by layers of six-membered tetrahedral rings of exclusively oval conformation. The rings are built up by regularly alternating AlO_4 and SiO_4 tetrahedra. The stacking of the layers parallel to the c axis results in a three-dimensional network containing channels that are occupied by the Na cations. Although structural similarities with respect to tridymite derivatives can be found, hexagonal trinepheline represents a new type of stuffed tridymite that is not a simple superstructure of nepheline.

INTRODUCTION

Synthetic Na-rich nephelines have been investigated for petrological reasons as well as their interesting properties as solid state ionic conductors (Dollase and Thomas 1978; Gregorkiewitz 1984; Roth 1985); Hippler and Böhm 1989). The composition of these compounds can be represented by the formula $Na_{8-r}Al_{8-r}Si_{8+r}O_{32}$ with $0 \leq r \leq 2$. The basic structure is the same as was reported by Hahn and Bueger (1955) in the space group $P6_3$ for a natural nepheline sample with idealized composition $Na_6K_2Al_8Si_8O_{32}$ and can therefore be considered as a stuffed derivative of the SiO_2 modification of high-tridymite. A slight difference between the natural nephelines and the synthetic pure Na-rich samples results from the substitution of Na cations at the positions of the significantly bigger K ions. The Na ions are too small to occupy the central site of the ditrigonal channels with a diameter of about 4.8 Å and are therefore displaced toward the walls of the channels. The shift for the resulting three split positions is about 0.35 Å away from the 6_3-axis (Hippler and Böhm 1989).

Pure $NaAlSiO_4$ shows complex displacive polymorphic transitions depending on the method of synthesis (Henderson and Roux 1977; Henderson and Thompson 1980). At room temperature two different structures exist: an orthorhombic superstructure with a $\approx a_0$, $b \approx a_0\sqrt{3}$, and $c \approx 3c_0$, where a_0 and c_0 refer to the normal nepheline unit cell and a second phase with even lower symmetry. Henderson and Roux (1977) showed that both room-temperature phases transformed to hexagonal symmetry at about 160 and 200 °C, respectively. A discontinuity in the thermal expansion near 870 °C has been attributed by these authors to a transformation into a high-tridymite structure. At temperatures above 1300 °C, $NaAlSiO_4$ transforms to a carnegieite phase (Schneider et al. 1994).

The orthorhombic phase mentioned above seems to be identical with a hydrothermally synthesized material of composition $NaAlSiO_4$ discussed by Klaska (1974). The space group of the crystals was $Pna2_1$. Although the structure was not refined successfully and no atomic coordinates were given, a structural model for this so-called orthorhombic trinepheline was sketched, wherein all tetrahedral rings have an oval form. A second $NaAlSiO_4$ phase with a beryllonite-type structure was also mentioned (Klaska 1974). Crystals of the pure Na end-member showing hexagonal symmetry in combination with a tripling of the c axis were reported by Jarchow et al. (1966) and Jarchow (1974, unpublished data). Brown et al. (1972) reported the existence of a modification with a hexagonal cell with $a = b \approx a_0\sqrt{3}$, $c = 3\ c_0$. Two monoclinic $NaAlSiO_4$ compounds were prepared by Selker et al. (1985). Table 1 summarizes the structural data for the different $NaAlSiO_4$-phases and for a sodium deficient Na nepheline from the literature.

The aim of the present paper is to determine whether hexagonal trinepheline can be classified as a superstructure of nepheline, with the tripling of the c lattice constant due to minor modifications of the basic nepheline structure. An ordered distribution of the Na-cat-

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TABLE 1. Lattice parameters and space groups for compounds of composition of $NaAlSiO_4$

Space group	*a* (Å)	*b* (Å)	*c* (Å)	β	Reference
$P6_3$	9.958	9.958	8.341		Hippler and Böhm (1989)*
$P2_1$	17.23	25.06	17.23	119.75°	Brown et al. (1972)
$P6_1$	10.046	10.046	25.140		Jarchow (1974)
$Pna2_1$	8.660	14.940	25.140		Klaska (1974)
$P2_1/n$	8.589	8.146	15.033	89.89°	Klaska (1974)
Pn	14.991	8.625	25.110	90.2°	Selker et al. (1985)
$P2_1$	9.990	25.100	9.990	120.0°	Selker et al. (1985)
$P6_1$	9.995(2)	9.995(2)	24.797(4)		This study

* Synthetic Na nepheline with $r = 0.8$. *Note*: $z = 24$; $V(A^3) = 2145.3(7)$.

ions on the threefold split positions in the different subcells together with a coupled relaxation of the framework could be a possible triggering mechanism for the evolution of the superstructure. Despite the fact that the values of the *c* lattice constant differ by about 1.4%, the compound investigated in the present article may be identical with the phase synthesized by Jarchow (1974).

EXPERIMENTAL METHODS

The single crystals investigated in this study were grown in platinum crucibles from a $NaVO_3$-flux in the temperature range between 1100 and 950 °C by slow cooling (Roth 1985). The composition of the crystals obtained was determined with a Cameca Camebax electron microbeam operated at 10 kV (accelerating voltage), a beam current of 6×10^{-8} A and a counting time of 30 s. A defocused beam of 20 μm was used to minimize Na loss. Standards used were albite for Na, corundum for Al, and wollastonite for Si; no other elements were detected. The intensities obtained were corrected for electron scattering, absorption, and fluorescence radiation (ZAF correction). The resulting chemical composition for different specimen did not vary from the ideal stoichiometric composition $Na_8Al_8Si_8O_{32}$.

A fragment of a hexagonal plate with good optical quality was selected for the structural investigations. Precession photographs indicated hexagonal Laue symmetry 6/*m*. The systematic absences (00*l*), $l \neq 6n$ resulted in two possible space groups, $P6_1$ and $P6_5$.

Measurements of the intensities were performed using an Enraf-Nonius CAD-4 four-circle diffractometer of scan type ω-2θ with a graphite monochrometer. For the determination of the lattice constants, 25 reflections with $30° \leq \theta \leq 33°$ were used. Intensity and orientation of three standard reflections were regularly monitored to check for stability and constancy of crystal alignment; no significant change was noted during the data collection. In the range $|h| \leq 15$; $|k| \leq 15$; $l \leq 38$, 16 244 reflections were measured, 15 984 of these have $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization effects using a modified version of the program CORINC (Schollmeier 1991). No corrections were made for absorption because of the low linear absorption coefficient and the nearly constant transmission observed in ψ-scans of selected reflections.

STRUCTURE SOLUTION, REFINEMENT, AND TWINNING

First attempts at the structure determination of hexagonal trinepheline were based on the assumption of a superstructure model. Hence the data set was subdivided into two sets of reflections: the main reflections with $l = 3n$ and the superstructure reflections with $l \neq 3n$. The main reflections define an average structure with space group symmetry $P6_3$, which is a superposition of all three subcells of the actual structure into one subcell. Starting with the structure parameters of a Na nepheline as a model for the average structure, comprehensive least squares refinements were performed with the SHELX76 program (Sheldrick 1976). X-ray scattering factors for the different cations in their respective valence state, together with anomalous dispersion corrections, were taken from the *International Tables for X-ray crystallography* (Ibers and Hamilton 1974); the values for O^{2-} were taken from Hovestreydt (1983). All of the above calculations were completely unsatisfactory regarding the resulting interatomic distances and thermal parameters. Obviously significant differences exist between the true and the assumed average structure.

Second, we tried to determine a model for the whole structure by direct methods without any presumptions, using the program SIR92 (Altomare et al. 1992). Statistical tests on the |E| values indicated the absence of an inversion center. The phase set with the maximum combined figure of merit resulted in an E-map, the most intense peaks of which could be interpreted as atomic positions of a stuffed framework structure. The subsequent refinement calculations were carried out with the SHELXL-93 program (Sheldrick 1993). Although the model seemed to be a reasonable starting point, iterative full-matrix least-squares calculations based on F^2 using isotropic displacement factors converged to an unconvincing unweighted *R*1 index of about 0.16.

Finally, possible twinning of the crystal was considered to explain the difficulties during the refinement. Twinning and especially twinning by merohedry are

features often encountered in tridymite derivatives (Palmer 1994; Hippler and Böhm 1989). For twinning by merohedry, the twin element belongs to the point group of the translation lattice of the crystal (holohedry), but it is not an element of the Laue group of the crystal. It cannot be detected by optical methods, because the optical indicatrix is unaffected. For the specific case, all twelve symmetry elements of the hexagonal holohedry 6/*m* 2/*m* 2/*m* not contained in the Laue group 6/*m* are possible twin elements. The R_{int} values for merging the data in the two hexagonal Laue groups were 0.086 for 6/*m* 2/*m* 2/*m* and 0.0278 for 2745 unique reflections the lower symmetry Laue group 6/*m*. Provided that the hypothesis of twinning by merohedry is true, the significantly higher value for the higher symmetrical Laue group indicates that the volume fraction α of the two twin individuals in the crystal is significantly different from 0.5.

The existence of twinning by merohedry can be verified by a statistical test, assuming $\alpha \neq 0.5$ (Britton 1972). Due to the exact superposition of the reciprocal lattices of the different twin domains the observed net intensity I_n of a reflection is the weighted sum of the intensities I_1 and I_2 of two reflections $(h_1k_1l_1)$ and $(h_2k_2l_2)$ superimposed by the twinning law. The weighting factors are the volume fractions α and 1-α of both twin aggregates, respectively. For every pair of twin-related reflections in the data set, the ratio $k = I_1/(I_1 + I_2)$ can be calculated. According to Britton (1972), the relative frequency distribution of the ratio *k*, *W(k)*, can be evaluated to detect the presence of twinning. In contrast with an untwinned crystal, where all possible values of *k* in the interval $0 \leq k \leq 1$ can occur with a certain probability, the values of $W(k) \neq 0$ for a twinned crystal are restricted to a region $k_1 \leq k \leq k_2$ symmetrical to $k = 0.5$. The values k_1 and k_2 of the discontinuities of *W(k)* correspond to the volume fractions α and 1-α of the two twin individuals.

The function *W(k)* for the actual data set is shown in Figure 1, assuming the mirror plane $m_{2\bar{1}0}$ as the element of twinning. The form of the distribution confirms the hypothesis of the presence of twinning by merohedry. The volume fractions for the two twin-related orientations can be estimated to 0.37 and 0.63, respectively.

The fraction of the twin components with the total fraction restrained to 1.0 and the twinning model described above were therefore introduced into the refinement calculation. The values for *R*1 and *wR*2 (all reflections) dropped to 0.044 and 0.107, respectively; the value α for twin component 1 refined to 0.369(2), in good agreement with the estimated value $\alpha = 0.37$, obtained from the statistical test. The final refinement using anisotropic diplacement parameters converged at *R*1 = 0.021 and *wR*2 = 0.054 for all reflections and at *R*1 = 0.020 and *wR*2 = 0.053 for $F_o > 4\sigma(F_o)$, where $R1 = \Sigma \; ||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/(\sigma^2[(F_o^2) + (aP)^2 + bP]$; and $P = [2F_c^2 + \max(F_o^2,0)]/3$. The largest shift in the final cycle was <0.001. The goodness of fit is 1.036. The final $\Delta\rho_{min}$ is −0.48 e/Å^3 and $\Delta\rho_{max}$ is +0.55 e/Å^3. For $Z = 24$, the volume is 2145.3(7) Å^3, the calculated density is 2.64 g/cm^3, and μ is 8.8 cm^{-1}. Cell parameters are given in Table 1. The refined atomic coordinates, equivalent isotropic and anisotropic displacement parameters, as well as selected interatomic distances and angles are given in Tables 2–5.

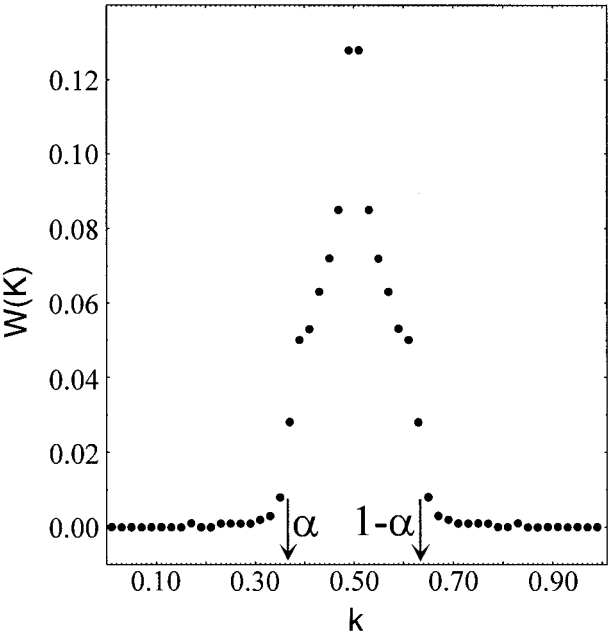

FIGURE 1. Relative frequency distribution *W(k)* for the twinned trinepheline. The arrows indicate the volume ratios of the twin domains.

DESCRIPTION OF THE STRUCTURE

The structure of trinepheline consists of a sequence of tetrahedral layers perpendicular to [001]. Each layer is exclusively composed of oval sixfold rings of SiO_4 and AlO_4 tetrahedra in *UDUDUD*-conformation. Within one layer two different orientations of the oval rings can be distinguished. The long axis of the rings may be parallel to each other or they may lie nearly perpendicular to each other. Figure 2 shows a projection of one of the six tetrahedral sheets that comprise the unit cell of trinepheline along the *c* direction using the computer program STRUPLO90 (Fischer et al. 1991). The equatorial O atoms of the sheets are not strictly coplanar. The tilting angle in the corrugated layers between the plane defined by three basal O atoms of the tetrahedra and the (001) plane varies between 3° and 12°. Subsequent layers are connected by the bridging apical atoms O4, O5, O9, and O14 and their symmetrical equivalents. Using the terminology of Flörke (1967), the relative orientation of one-half of the paired tetrahedra belonging to different adjacent layers can be approximately classified as a cis arrangement. The re-

TABLE 2. Positional parameters in fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq}
Si1	2024(1)	−6964(1)	1279(1)	6(1)
Si2	3637(1)	−2977(1)	−374(1)	8(1)
Si3	9122(1)	−7636(1)	−350(1)	6(1)
Si4	1334(1)	−2218(1)	1358(1)	7(1)
Al1	3266(1)	−9020(1)	864(1)	7(1)
Al2	8807(1)	−7544(1)	917(1)	7(1)
Al3	8111(1)	−2920(1)	954(1)	7(1)
Al4	3308(1)	−3548(1)	906(1)	7(1)
Na1	205(2)	−4352(2)	356(1)	17(1)
Na2	4735(2)	−5579(2)	303(1)	20(1)
Na3	5183(2)	−4426(2)	1864(1)	27(1)
Na4	43(3)	−9851(2)	280(1)	41(1)
O1	3137(2)	−5371(2)	967(1)	13(1)
O2	584(2)	−6637(3)	−741(1)	12(1)
O3	281(2)	−7271(2)	1362(1)	11(1)
O4	2765(2)	−6869(3)	1869(1)	12(1)
O5	581(3)	−2459(2)	1950(1)	16(1)
O6	1918(2)	−8413(2)	955(1)	11(1)
O7	6810(3)	−4652(2)	1264(1)	15(1)
O8	8617(3)	−9457(2)	−394(1)	13(1)
O9	9600(3)	−7096(2)	271(1)	15(1)
O10	7696(3)	−7413(3)	−507(1)	22(1)
O11	1799(2)	−3546(2)	1262(1)	11(1)
O12	5167(2)	−7515(2)	918(1)	14(1)
O13	2881(2)	−533(2)	1303(1)	10(1)
O14	3024(3)	−3226(3)	239(1)	17(1)
O15	45(2)	−2438(2)	920(1)	10(1)
O16	8212(2)	−6234(2)	1086(1)	14(1)

TABLE 3. Anisotropic displacement parameters (Å$^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	6(1)	6(1)	7(1)	0(1)	1(1)	3(1)
Si2	5(1)	7(1)	12(1)	2(1)	1(1)	3(1)
Si3	4(1)	6(1)	8(1)	0(1)	−1(1)	2(1)
Si4	7(1)	6(1)	7(1)	−1(1)	0(1)	3(1)
Al1	7(1)	6(1)	8(1)	0(1)	−1(1)	3(1)
Al2	6(1)	7(1)	8(1)	−1(1)	0(1)	3(1)
Al3	6(1)	5(1)	9(1)	−1(1)	−1(1)	3(1)
Al4	5(1)	5(1)	9(1)	2(1)	1(1)	2(1)
Na1	18(1)	16(1)	18(1)	0(1)	−4(1)	11(1)
Na2	16(1)	20(1)	22(1)	−2(1)	7(1)	7(1)
Na3	19(1)	22(1)	28(1)	−8(1)	6(1)	1(1)
Na4	36(1)	45(1)	37(1)	0(1)	−19(1)	17(1)
O1	11(1)	6(1)	20(1)	4(1)	5(1)	3(1)
O2	7(1)	16(1)	13(1)	4(1)	2(1)	6(1)
O3	7(1)	14(1)	12(1)	−1(1)	−1(1)	6(1)
O4	10(1)	22(1)	8(1)	−2(1)	−1(1)	10(1)
O5	12(1)	16(1)	11(1)	−3(1)	2(1)	0(1)
O6	10(1)	9(1)	16(1)	−5(1)	−2(1)	6(1)
O7	11(1)	7(1)	29(1)	6(1)	7(1)	4(1)
O8	11(1)	6(1)	20(1)	−2(1)	−7(1)	3(1)
O9	15(1)	14(1)	8(1)	0(1)	1(1)	1(1)
O10	16(1)	22(1)	36(2)	−1(1)	−5(1)	15(1)
O11	9(1)	9(1)	17(1)	2(1)	3(1)	5(1)
O12	7(1)	14(1)	15(1)	2(1)	−2(1)	0(1)
O13	9(1)	6(1)	11(1)	2(1)	−3(1)	1(1)
O14	19(1)	26(1)	10(1)	6(1)	3(1)	13(1)
O15	6(1)	12(1)	11(1)	−1(1)	−1(1)	5(1)
O16	7(1)	7(1)	30(1)	0(1)	4(1)	4(1)

maining half adopts the energetically more favorable trans-configuration. The distribution of the Al and Si cations among the tetrahedral sites was analyzed on the basis of averaged T-O bond distances for the tetrahedra listed in Table 4. Two groups of four tetrahedra with significant different mean values of about 1.62 and 1.74 Å can be distinguished. Using the determinative equation given by Jones (1968) the Al content for the two groups was calculated to 0.1 and 0.9, respectively. The sites were therefore labeled as ''Si'' and ''Al.'' Geometrically, the ordering scheme is as expected for an Al:Si ratio of 1:1. The Al-rich tetrahedra share four corners with Si-rich tetrahedra and vice versa, in accord with the aluminum avoidance rule (Loewenstein 1954) producing a polar crystal with all Al-tetrahedra pointing along the negative *c* axis and all Si-tetrahedra pointing along the positive *c* axis. The spread of the individual T-O bonds from the average values is not very pronounced, implying that the tetrahedra are quite regular with regard to distances.

Whereas the average values of the O-T-O angles for all eight tetrahedra are very close to the ideal value of 109.47°, the individual O-T-O angles range from 107.8° to 113.1° for the SiO_4 groups and from 103.7° to 118.0° for the AlO_4 tetrahedra (Table 4). This suggests that the polyhedra deviate from regularity and that the distortion is more clearly recognizable for tetrahedra containing Al. According to Robinson et al. (1971) the distortion can be expressed numerically by means of the angle variance σ^2. The mean value for this parameter for the two sets of SiO_4 and AlO_4 polyhedra has values of 2.65 and 14.75, respectively. The T-O-T angles show a considerable spread between 129.4° and 167.6° with an average of 138.5°. This value is only slightly lower than the value of 142° suggested by Liebau (1985) for an ''unstrained'' Si-O-Al angle.

Charge balance in the structure is achieved by an incorporation of Na ions in the channels of the tetrahedral network running parallel *c* (Fig. 3). Within the

TABLE 4. Selected interatomic distances (Å)

Si1-O6	1.612(2)	Si2-O16	1.620(2)	Si3-O10	1.597(2)
Si1-O4	1.621(2)	Si2-O14	1.612(2)	Si3-O9	1.621(2)
Si1-O1	1.612(2)	Si2-O7	1.623(2)	Si3-O8	1.631(2)
Si1-O3	1.624(2)	Si2-O12	1.616(2)	Si3-O2	1.617(2)
Mean	1.617	Mean	1.618	Mean	1.617
Si4-O5	1.613(2)	Al1-O13	1.742(2)	Al2-O16	1.739(2)
Si4-O15	1.613(2)	Al1-O12	1.741(2)	Al2-O2	1.746(2)
Si4-O11	1.629(2)	Al1-O6	1.747(2)	Al2-O9	1.744(2)
Si4-O13	1.626(2)	Al1-O4	1.733(2)	Al2-O3	1.749(2)
Mean	1.620	Mean	1.741	Mean	1.744
Al3-O8	1.745(2)	Al4-O10	1.716(2)		
Al3-O7	1.740(2)	Al4-O14	1.735(2)		
Al3-O15	1.745(2)	Al4-O11	1.748(2)		
Al3-O5	1.741(2)	Al4-O1	1.749(2)		
Mean	1.743	Mean	1.737		
Na1-O13	2.302(2)	Na2-O1	2.375(3)	Na3-O7	2.297(3)
Na1-O15	2.438(2)	Na2-O11	2.384(2)	Na3-O2	2.385(3)
Na1-O14	2.473(3)	Na2-O3	2.494(3)	Na3-O4	2.430(3)
Na1-O9	2.505(3)	Na2-O12	2.664(3)	Na3-O10	2.777(3)
Na1-O11	2.637(3)	Na2-O5	2.681(3)	Na3-O1	2.844(3)
Na1-O16	2.652(3)	Na2-O16	2.850(3)	Na3-O12	2.932(3)
Mean	2.501	Mean	2.575	Mean	2.611
Na4-O8	2.353(3)	Na4-O4	2.990(3)		
Na4-O6	2.386(3)	Na4-O9	3.000(3)		
Na4-O3	2.902(3)	Na4-O3	3.035(3)		
Na4-O5	2.906(3)	Na4-O16	3.044(3)		

TABLE 5. Selected O-T-O and T-O-T bonding angles (°)

O6-Si1-O4	109.0(1)	O16-Si2-O14	110.8(1)	O10-Si3-O9	108.7(1)
O6-Si1-O1	110.6(1)	O16-Si2-O7	107.9(1)	O10-Si3-O8	109.8(1)
O4-Si1-O1	107.8(1)	O14-Si2-O7	109.1(1)	O9-Si3-O8	108.1(1)
O6-Si1-O3	108.1(1)	O16-Si2-O12	111.8(1)	O10-Si3-O2	111.2(1)
O4-Si1-O3	108.2(1)	O14-Si2-O12	108.6(1)	O9-Si3-O2	109.8(1)
O1-Si1-O3	113.1(1)	O7-Si2-O12	108.6(1)	O8-Si3-O2	109.2(1)
Mean	109.5	Mean	109.5	Mean	109.5
O5-Si4-O15	108.2(1)	O13-Al1-O12	112.0(1)	O16-Al2-O2	109.6(1)
O5-Si4-O11	108.2(1)	O13-Al1-O4	109.8(1)	O16-Al2-O9	108.1(1)
O15-Si4-O11	108.9(1)	O12-Al1-O4	103.7(1)	O2-Al2-O9	109.8(1)
O5-Si4-O13	111.3(1)	O13-Al1-O6	110.3(1)	O16-Al2-O3	108.0(1)
O15-Si4-O13	111.5(1)	O12-Al1-O6	112.8(1)	O2-Al2-O3	113.7(1)
O11-Si4-O13	108.7(1)	O4-Al1-O6	107.9(1)	O9-Al2-O3	107.5(1)
Mean	109.5	Mean	109.4	Mean	109.5
O8-Al3-O7	110.0(1)	O10-Al4-O14	115.1(1)		
O8-Al3-O15	106.7(1)	O10-Al4-O11	114.0(1)		
O7-Al3-O15	118.0(1)	O14-Al4-O11	105.1(1)		
O8-Al3-O5	110.1(1)	O10-Al4-O1	104.1(1)		
O7-Al3-O5	107.3(1)	O14-Al4-O1	109.7(1)		
O15-Al3-O5	104.6(1)	O11-Al4-O1	108.8(1)		
Mean	109.5	Mean	109.5		
Si1-O1-Al4	136.9(1)	Si3-O2-Al2	132.2(1)	Si1-O3-Al2	133.6(1)
Si1-O4-Al1	136.3(1)	Si4-O5-Al3	142.7(1)	Si1-O6-Al1	131.3(1)
Si2-O7-Al3	134.8(1)	Si3-O8-Al3	132.7(1)	Si3-O9-Al2	140.0(1)
Si3-O10-Al4	167.6(2)	Si4-O11-Al4	132.3(1)	Si2-O12-Al1	149.4(2)
Si4-O13-Al1	129.4(1)	Si2-O14-Al4	147.5(2)	Si4-O15-Al3	134.7(2)
Si2-O16-Al2	135.3(1)				

channels, the Na ions are irregularly coordinated. The following two groups can be distinguished: Sodium ions Na1-Na3 located in the less symmetrical tunnels are coordinated by six neighbors at 2.29 to 2.93 Å (average 2.56 Å) in the form of distorted trigonal antiprisms. Na4 occupies the more symmetrical channel containing the 6_1 axis and has two O neighbors at 2.35 and 2.39 Å and six more distant ones between 2.90 and 3.05 Å (average 2.98 Å). Because typical Na-O bond lengths average about 2.5–2.6 Å (Shannon and Prewitt 1969), these six represent weak bonds. Coordination conditions similar to those of Na4 were reported by Klaska (1974) for Na-O distances in beryllonite type $NaXYO_4$ compounds with X:Al,Ga and Y:Si,Ge.

The anisotropic displacement parameters (Table 3) were used to calculate the mean-square displacements of thermal motions and the relation of the principal axes of the thermal ellipsoids to the crystallographic axes. The ellipsoids of thermal motion for the O atoms are prolate and oblate spheroids, the longest axes of which are roughly perpendicular to the T-O vector and the shortest axes nearly parallel to the bonds. From the known high strength of the T-O bonds and from the shape and orientation of the ellipsoids, it seems reasonable to assume that tetrahedra execute a libration motion about the T atom center, as described by Busing and Levy (1964) in their so-called riding model.

The highest values for the displacements were observed for the Na4 atom. The longest principal axis corresponds to a mean displacement of 0.25 Å and is approximately parallel to the direction between this ion and the apical O5 atom. This large magnitude for the

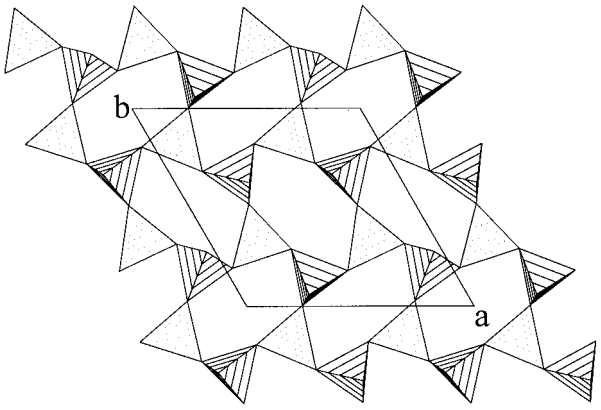

FIGURE 2. Single tetrahedral layer of the trinepheline structure ($0.19 \leq z \leq 0.41$). Hatched and stippled tetrahedra correspond to SiO_4 and AlO_4 groups, respectively.

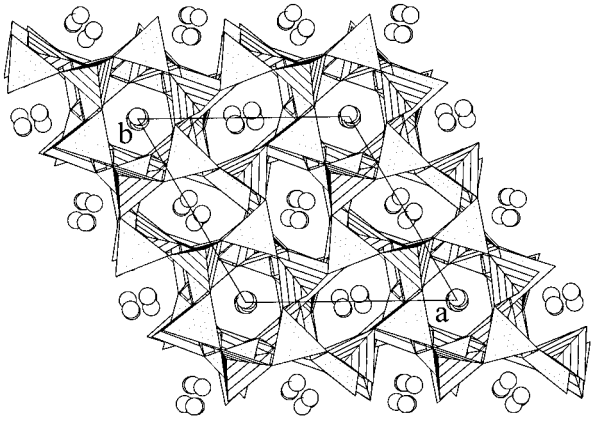

FIGURE 3. Crystal structure of trinepheline as viewed down *c*. Open circles indicate the Na ions.

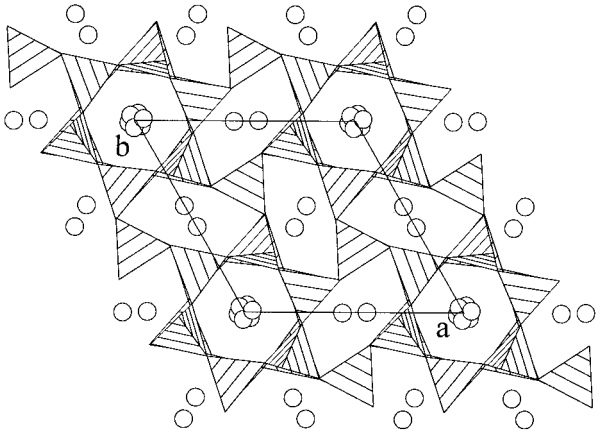

FIGURE 4. Projection of the crystal structure of a Na-deficient nepheline parallel to *c*, based on the data of Hippler and Böhm (1989).

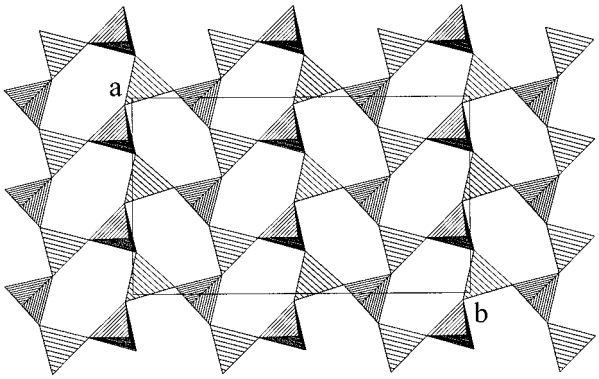

FIGURE 5. Single tetrahedral layer of the so-called *F*1-tridymite (after Konnert and Appleman 1978).

thermal motion indicates that Na4 is disordered. The refined coordinates for the Na4 define an average position, the averaging being either in time (thermal motion interpretation) or in space (static disorder interpretation) or both. To test the static interpretation, the final refinement cycles were repeated using two split positions with isotropic temperature factors for the Na4. The starting values for the coordinates were determined from a difference-Fourier map. Although the temperature factors for the split atoms refined to a more reasonable lower value of 0.029 $Å^2$ and the spread of the Na-O distances for both positions was less pronounced than for the anisotropic approach, the resulting *R* indices were slightly higher. Therefore, the models at this stage cannot be distinguished.

COMPARISON WITH RELATED STRUCTURES

The crystal structures of the known stuffed tridymite derivatives [kalsilite ($KAlSiO_4$), yoshiokaite ($CaAl_2SiO_6$), $CaAl_2O_4$, and nepheline] have been discussed recently in a review paper of Palmer (1994). Hexagonal trinepheline represents a new type of stuffed tridymite.

To some extent trinepheline shows a definite relationship to nepheline. In both structures one quarter of the channels running parallel *c* retain a sixfold symmetry in the projection along this direction, whereas the adjacent ones are distorted to an oval form (compare Fig. 3 and Fig. 4). The diameter of the highly symmetrical channels for nepheline (≈4.8 Å) and trinepheline (≈3.4 Å) deviate considerably from each other. The main difference between the two structures results from the fact that the tetrahedral layers in nepheline consist of both ditrigonal and oval rings, whereas in trinepheline all rings have collapsed to an oval form. The hexagonal shape of the central channels in trinepheline is a result of the stacking of the layers by means of the 6_1 screw axis and is not related to the existence of a highly symmetrical ditrigonal ring system, which is a common structural feature for all the examples mentioned above.

The existence of tetrahedral layers wherein all six-membered rings adopt an oval configuration has been reported for different pure silica polymorphs. A terrestrial tridymite, whose structure has been refined by Konnert and Appleman (1978) in space group *F*1 consists of only oval type rings as does α-cristobalite. In the case of the so-called *F*1-tridymite, a large *c* translation period of 81.86 Å is due the stacking of ten slightly different crystallographic layers consisting of oval rings only. A projection along *c* of one of the sheets that comprise this phase is sketched in Figure 5. The comparison with Figure 2 reveals that the two layers have a high degree of topological similarity. The longest axis of the oval rings as well as the orientations of the rings in terms of the angles between the longest axis of adjacent rings are nearly identical. The differences arise from the relative orientation of the six tetrahedra of the single rings. For reasons of better comparability, a detail of the layers in the form of a single sixfold ring is sketched in Figure 6 for both structures. In the case of *F*1-tridymite, two of the three tetrahedra pointing toward the observer have an identical orientation. A similar configuration of the oval rings was presented by Klaska (1974) for the orthorhombic trinepheline phase mentioned earlier. The orientation between the tetrahedra in the oval ring of hexagonal trinepheline is definitely more complex.

The crystal structure of hexagonal trinepheline is not a simple superstructure of the basic Hahn and Buerger model, as one may be tempted to conclude from the close relationship of the lattice constants. The structure is significantly different from nepheline. Our results confirm the hypothesis of Dollase and Thomas (1978), who predicted appreciable structural modifications for a compound of composition $NaAlSiO_4$ relative to the structures of the Na-deficient nepheline.

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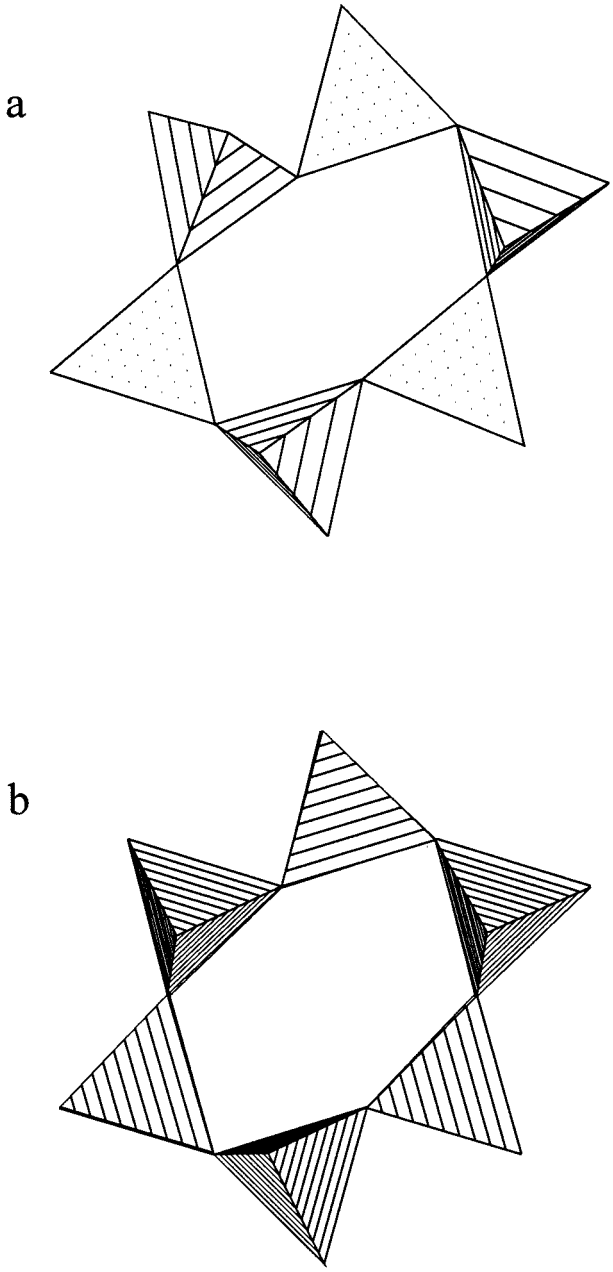

FIGURE 6. Single six-membered rings of (**a**) trinepheline and (**b**) *F*1-tridymite.

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