

On the existence of a Na-deficient monoclinic trinepheline with composition $\text{Na}_{7.85}\text{Al}_{7.85}\text{Si}_{8.15}\text{O}_{32}$

PREDRAG VULIĆ,* VOLKER KAHLBERG, AND JÜRGEN KONZETT

Institute for Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

ABSTRACT

The crystal structure of a new synthetic $\text{Na}_{8-r}\text{Al}_{8-r}\text{Si}_{8+r}\text{O}_{32}$ ($r = 0.15$) modification has been solved by direct methods and refined to an R index of 0.0289 for 11 643 independent reflections and 764 parameters. The compound is monoclinic with space group symmetry $P112_1$, $a = 9.9897(6)$ Å, $b = 9.9622(6)$ Å, $c = 24.979(2)$ Å, and $\gamma = 119.788(4)^\circ$. The twinning of three individuals related by rotation around the c direction for 120° was accounted for in the calculation. The phase was named monoclinic trinepheline because the length of its c lattice parameter is $3\times$ the length of the c parameter in nepheline, whereas the a parameter is almost the same in both structures, similarly to a previously investigated trinepheline of hexagonal symmetry. Actually, the present compound represents an intermediate state between these two phases. The characteristic of the crystal structure are layers of six-membered rings built up of regularly alternating AlO_4 and SiO_4 tetrahedra. The layers are perpendicular to $[001]$ and are connected through apical O atoms. The resulting spatial network contains channels in which the Na cations are situated. The structure of monoclinic trinepheline can be described as a consecutive stacking of basic nepheline like modules (containing two tetrahedral sheets) and one sheet corresponding to those observed in the hexagonal trinepheline structure. The topology of the new compound corresponds to that of tridymite. The coordination sequences are identical for all T atoms in the asymmetric unit: 4-12-25-44-67-96-130-170-214-264. The vertex symbols for the tetrahedral centers are $6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2$. The framework density of the structure is equal to 22.2 T atoms/1000 Å³.

Keywords: Monoclinic trinepheline, $\text{Na}_{7.85}\text{Al}_{7.85}\text{Si}_{8.15}\text{O}_{32}$, flux method, nepheline

INTRODUCTION

The crystal structure of natural nepheline of idealized composition $\text{Na}_6\text{K}_2\text{Al}_8\text{Si}_8\text{O}_{32}$ was reported by Hahn and Buerger (1955) in space group $P6_3$. It can be described as a stuffed derivative of high-tridymite where half of the silicon ions are replaced by aluminum. Charge compensation is achieved by incorporation of alkali cations in the cavities of the structure—75% of the cavities are populated by smaller Na and the remaining 25% by larger potassium cations. No pure Na nephelines are observed in the nature. Synthetically obtained Na-rich nephelines with the same basic structure have been studied by several authors (Dollase and Thomas 1978; Gregorkiewitz 1984; Roth 1985; Hippler and Böhm 1989; Dimitrijević et al. 2004). The investigations were mainly conducted because of nepheline's property to show Na-solid state ionic conductivity. The structural difference between natural samples and synthetic Na nephelines is based on the fact that excess Na in samples containing more than 6 Na apfu (see above) must be accommodated on the large alkali site. Sodium substitution involves either collapse of the hexagonal channels, or an off-centering of Na toward the channel wall (about 0.35 Å). This is due to the fact that ions smaller than potassium cannot establish a regular coordination with the surrounding O atoms, but form bond distances of noticeable different lengths.

According to Henderson and Roux (1977) and Henderson and Thompson (1980) pure NaAlSiO_4 shows complex displacive polymorphic transitions, depending on the method of synthesis. Two different structures can exist at ambient conditions: an orthorhombic superstructure with $a \approx a_0$, $b \approx a_0\sqrt{3}$, and $c \approx 3c_0$, (a_0 and c_0 refer to the normal nepheline unit cell) and a second phase with even lower symmetry. The room-temperature phases transform to hexagonal symmetry at about 160 and 200 °C, respectively (Henderson and Roux 1977). The authors also mention a discontinuity in the thermal expansion near 870 °C and attribute it to a transformation into a high-tridymite-like structure. Dimitrijević et al. (2004) established the presence of a low-carnegieite phase below 850 °C, although nephelines in this work were synthesized by a different method based on thermal treatment of zeolitic material (LTA, FAU, and GIS types). Schneider et al. (1994) reported that single crystals of nepheline (NaAlSiO_4) are stable up to 1300 °C, when they transform to carnegieite.

The orthorhombic structure of Henderson and Roux may be similar to a hydrothermally synthesized phase reported by Klaska (1974). Orthorhombic nepheline crystallizes in space group $Pna2_1$, and, according to Klaska, the structure is composed exclusively of tetrahedral rings of elliptical form, although no atomic coordinates were given. The structure of hexagonal trinepheline (Kahlenberg and Böhm 1998) is also built up of elliptical rings only. NaAlSiO_4 forms showing hexagonal symmetry

* E-mail: Predrag.Vulic@uibk.ac.at

with a tripling of the *c* axis were also reported by Jarchow et al. (1966) and Brown et al. (1972). The latter phase has a hexagonal cell with $a = b \approx a_0\sqrt{3}$, $c = 3c_0$. Selker et al. (1985) reported two monoclinic trinepheline compounds. The first structure is reported to crystallize in space group $P2_1$ with pseudo hexagonal metric symmetry ($a = 9.990 \text{ \AA}$, $b = 25.100 \text{ \AA}$, $c = 9.990 \text{ \AA}$, and $\beta = 120.0^\circ$), while the other structure adopts space group Pn with pseudo orthorhombic symmetry ($a = 14.991 \text{ \AA}$, $b = 8.625 \text{ \AA}$, $c = 25.110 \text{ \AA}$, and $\beta = 90.2^\circ$). Selker (1987) gives detailed graphical description of the both structures without any atomic coordinates. The first structure is composed of ditrigonal and elliptical tetrahedral rings, while the other is composed of exclusively elliptical rings.

The goal of the present investigation is to clarify the structural relationships of the novel synthesized monoclinic trinepheline to already known nepheline-type phases.

EXPERIMENTAL METHODS

As suggested by Roth (1985), the flux technique, using cryolite as high-temperature solvent, was applied for growth of the crystals. The starting materials were Na_2CO_3 (Merck, 99.95%), Al_2O_3 (Fluka, 99.99%), SiO_2 (Alfa Aesar, 99.995%) and natural cryolite Na_3AlF_6 , (obtained from the Ivigtit area of Greenland). The reagents were carefully mixed in an agate mortar. Cryolite was added and the compounds were mixed again. A sample of 1 g with a nutrient-to-flux ratio of 2:5 was placed in a 50 mL platinum crucible with a platinum lid. The mixture was heated from 1073 to 1423 K over a period of 3.5 h in a resistance-heated furnace; it was held at this temperature for 4 h to homogenize the melt, then cooled down to 1323 K at a rate of 6 Kh^{-1} for nepheline to crystallize. Subsequently, it was cooled down to 1073 K by a higher rate of 100 Kh^{-1} and quenched immediately. The only obtained crystal was of pseudo-hexagonal platy habit ($\approx 1 \text{ mm}$ in diameter). It was mechanically removed from the polycrystalline cryolite matrix.

The composition of a crystal fragment was determined with a JEOL JXA 8100 electron microprobe using analytical conditions of 15 kV acceleration voltage and 5 nA beam current. Natural jadeite, natural quartz, and synthetic corundum were chosen as standards with measurement times of 20 s on peaks and 10 s on the backgrounds of the X-ray lines. To minimize beam damage of the sample surface, a rastered electron beam with a size adjusted to the size of the crystal fragment was used for the analyses. Raw counts were corrected using the PRZ correction procedure. X-ray images of the distribution of Na, Al, and Si in the investigated crystal fragment did not show significant spatial changes in composition. The average chemical composition based on six analyzed spots is $\text{Na}_{7.85(1)}\text{Al}_{7.85(1)}\text{Si}_{8.15(1)}\text{O}_{32}$ (Table 1).

Another fragment of the pseudo-hexagonal plate with good optical quality and irregular shape was selected for the structural investigations. X-ray diffraction data collection was performed with a two-circle Stoe IPDS-2 imaging-plate diffractometer at 302 K operated at 50 kV and 40 mA and with crystal-to-detector distance of 100 mm. A full sphere of three-dimensional data were collected using graphite monochromated $\text{MoK}\alpha$ radiation in two consecutive runs ($\phi = 0$ and 90° , respectively) in ω range from 0 to 180° (frame width of 1° and count-time of 5 min per frame). Intensity integration and data reduction was done using the Stoe X-Area (Stoe and Cie GmbH 2005) software. Even though material of the aforementioned chemical composition has a low linear absorption coefficient for Mo-radiation, intensities were corrected for absorption using an analytical numerical absorption correction based on 37 indexed faces precisely describing the morphology of the irregular fragment used for data collection. In the range $|h| \leq 13$; $|k| \leq 13$; $|l| \leq 34$, 39733 reflections were measured, 36564 of these had $I > 4\sigma(I)$. Crystal lattice constants were showing hexagonal metric symmetry, but the highest Laue symmetry with an acceptable R_{int} value of 0.032 corresponds to $112/m$,

while the R_{int} value for Laue symmetry $6/m$ was 0.418. The systematic absences $(00l)$, $l \neq 2n$ resulted in two possible space groups: $P112_1$ or $P112_1/m$ (orientation corresponding to *c* unique).

STRUCTURE SOLUTION, REFINEMENT, AND TWINNING

Determination of a model for the whole structure was done by direct methods, using the program SIR2004 (Burla et al. 2005). *E*-statistics did not clearly indicate the presence of a center of symmetry. Therefore, structure solution was started in both possible space groups. The best solution in space group $P112_1$ (with *R*-value of 0.093) resulted in an *E*-map of which the most intense peaks were describing a stuffed framework structure. The further refinement of the model was carried out with the SHELXL97 program (Sheldrick 1998). X-ray scattering factors for the different cations, and their anomalous dispersion corrections were taken from the *International Tables for Crystallography* (Prince 2004); the values for O^{2-} were taken from Hovestreydt (1983). The starting model seemed to be reasonable, but iterative full-matrix least-squares calculation based on F^2 using isotropic displacement factors converged to an unconvincing unweighted R_1 index of about 0.10. Introduction of anisotropic displacement parameters for all atoms resulted in a slight decrease of R_1 (≈ 0.08). However, almost one fifth of the framework ions had non positive definite values for the principal mean square atomic displacement parameters.

To explain the difficulties during the refinement, a possible twinning was considered. The unit cell is pseudo-hexagonal, with $a \approx b$ and $\gamma \approx 120^\circ$. Twinning of three individuals by rotation around the threefold axis coinciding with *c* is very common in such cases. After the introduction of the corresponding twin law (using TWIN and BASF commands implemented in SHELXL97), the residuals R_1 and wR_2 for the refinement based on F^2 using isotropic displacement for all the reflections dropped to 0.050 and 0.121, respectively. The refined volume fractions for the twin components were 87.9, 7.0, and 5.1%, respectively.

Following the results of the chemical analysis (indicating a Na deficiency), site occupation numbers of three Na atoms were refined. However, a constraint for the total Na content according to the composition derived from the EMP measurement was used. These three sites correspond to the positions of potassium in natural nepheline, and according to Hippler and Böhm (1989) in the case of Na deficiency vacancies are observed on these positions. Indeed, the refinements indicated a depletion of Na on two of these sites.

The final refinement using anisotropic displacement parameters converged at $R_1 = 0.0289$ and $wR_2 = 0.0694$ for all 11643 independent reflections and 764 refined parameters. Experimental details are summarized in Table 2. The refined atomic coordinates, site occupancies, equivalent isotropic and anisotropic displacement parameters, as well as selected bond lengths and angles are given in Tables 3–6.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of monoclinic trinepheline is built up by a sequence of tetrahedral layers perpendicular to the *c* direction. Each layer is composed of different types of sixfold rings made of SiO_4 and AlO_4 tetrahedra. The sequence of directedness of the tetrahedra is *UDUDUD*. Among the six layers corresponding to the translation period along $[001]$ two blocks of 3 sheets can be distinguished, which are related by a 2_1 screw axis. Two layers of each block are composed of two different types of six-membered tetrahedral rings. Of the four crystallographically independent rings comprising these two layers one exhibits a slightly distorted ditrigonal symmetry, while the other three rings are elliptical, and related to each other through a pseudo-threefold axis. This feature results in almost trigonal local layer symmetry. The third sheet situated between the two “trigonal” layers is exclusively composed of elliptical rings. Within this

TABLE 1. Results of the electron microprobe analyses (given as wt% oxides) of the monoclinic trinepheline flux-grown crystal

Oxide	Analysis 1	Analysis 2	Analysis 3	Analysis 4	Analysis 5	Analysis 6	Calculated
Na_2O	21.43	21.38	21.54	21.47	21.35	21.56	21.47
SiO_2	43.14	43.01	43.54	43.01	42.92	43.41	43.21
Al_2O_3	35.32	35.08	35.45	35.25	35.09	35.43	35.32
Σ	99.89	99.47	100.53	99.73	99.36	100.40	100.00
Formula	$\text{Na}_{7.85(1)}\text{Al}_{7.85(1)}\text{Si}_{8.15(1)}\text{O}_{32}$						

TABLE 2. Experimental details

Crystal data	
Chemical formula	Na _{7.85} Al _{7.85} Si _{8.15} O ₃₂
<i>M</i> _r	1133.18
Cell setting, space group	Monoclinic, <i>P</i> 112 ₁ , <i>c</i> unique (no. 4)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.9897(6), 9.9622(6), 24.979(2)
γ (°)	119.788(4)
<i>V</i> (Å ³)	2157.4(2)
<i>Z</i>	3
<i>D</i> _s (Mg/m ³)	2.617
Radiation type	MoKα
No. of reflections for cell parameters	14178
θ range (°)	1.63–29.19
μ (mm ⁻¹)	0.873
Temperature (K)	302(2)
Crystal form, color	irregular, white
Crystal size (mm)	0.23 × 0.2 × 0.17
Data collection	
Diffractometer	Stoe IPDS-2
Data collection method	Rotation method
Absorption correction	Integration
<i>T</i> _{min}	0.871
<i>T</i> _{max}	0.917
No. of measured and independent reflections	39733, 11643, 11519 reflections with <i>I</i> > 4σ(<i>I</i>)
<i>R</i> _{int}	0.032
θ _{max} (°)	29.2
Range of <i>h</i> , <i>k</i> , <i>l</i>	–13 ≤ <i>h</i> ≤ 13 –13 ≤ <i>k</i> ≤ 13 –34 ≤ <i>l</i> ≤ 34
Refinement	
Refinement on	<i>F</i> ²
<i>R</i> ₁ (all), <i>R</i> ₁ [<i>F</i> ² > 4σ(<i>F</i> ²)]	0.029, 0.028
<i>wR</i> ₂ (all), <i>wR</i> ₂ [<i>F</i> ² > 4σ(<i>F</i> ²)]	0.069, 0.069
<i>S</i>	1.084
No. of reflections	11643
No. of parameters	764
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 1.9644P]$ $P = [2F_o^2 + F_c^2]/3$
(Δσ) _{max}	0.089
Δρ _{max} Δρ _{min} (e Å ⁻³)	0.981, –0.835

layer two different orientations of the elliptical rings can be distinguished. The longest axes of the rings may be parallel or perpendicular to each other. Figure 1 shows projections of the three basic tetrahedral sheets of one block (using the computer program STRUPLO91, Fischer et al. 1991). For each of the three layers simplified skeletal representations are given to make the relation of the six-membered rings more obvious.

Connection of the layers is achieved through apical O atoms. The angles between the horizontal (001) and the planes defined by the three basal O atoms of the tetrahedra vary from 5 to 17°. The layers are interconnected by the apical atoms O4a–c, O5a–c, O9a–c, and O14a–c and their symmetrical equivalents. One half of the paired tetrahedra belonging to different adjacent layers can be classified as a *cis* arrangement, whereas the remaining half achieves a *trans* configuration (Flörke 1967). From the T–O bonds in Table 5 it can be seen that two groups of twelve tetrahedra can be distinguished. The first group has mean values for T–O bond lengths of about 1.62, while the second averages of about 1.74 Å. The average Al content for the two groups was calculated to 0.09(3) and 0.84(3), respectively (Jones 1968). This arrangement corresponds to an excess in Si, which is in agreement with the chemical analysis. Al-rich tetrahedra are linked with four Si-rich tetrahedra and vice versa, obeying the aluminum avoidance rule (Loewenstein 1954). This results in a

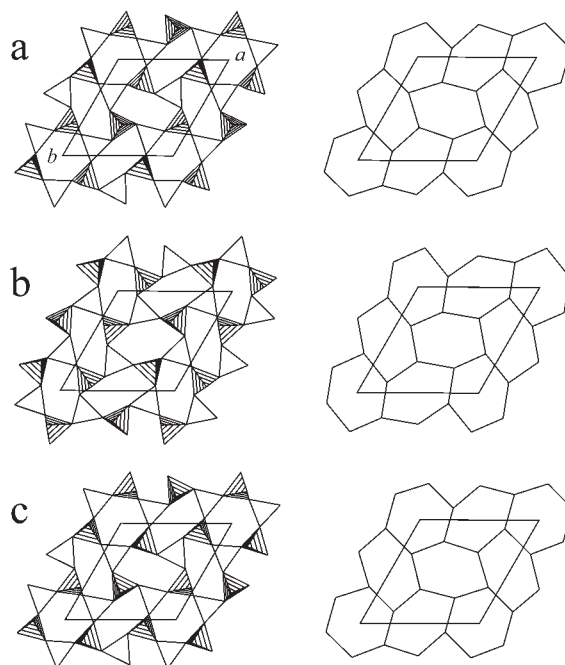


FIGURE 1. The basic three building layers of monoclinic trinepheline. Hatched and white tetrahedra correspond to SiO₄ and AlO₄, respectively. On the right side, skeletal representations are given to outline the positions of tetrahedrally coordinated cations: (a) 0.00 ≤ *z* ≤ 0.24; (b) 0.16 ≤ *z* ≤ 0.40; (c) 0.32 ≤ *z* ≤ 0.56.

polar crystal with all Al- and Si-tetrahedra pointing in different directions along the *c* axis.

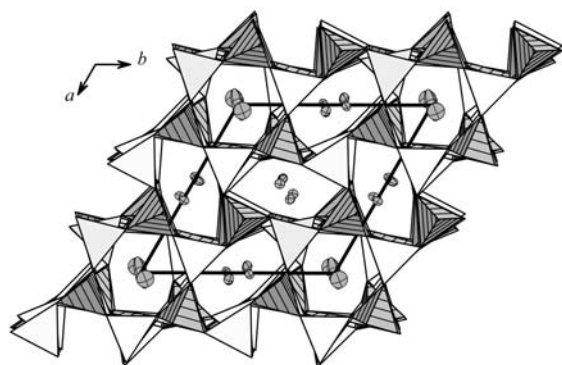
The average values of the O–T–O angles for all 24 tetrahedra are close to the ideal value of 109.47°, but the individual O–T–O angles range from 106.0 to 114.0° for the SiO₄ groups and from 103.5 to 116.8° for the AlO₄ tetrahedra (Table 5). The polyhedral distortion is more obvious for tetrahedra containing Al. The mean tetrahedral angle variance (Robinson et al. 1971) for the SiO₄ and AlO₄ tetrahedra has values of 2.95 and 8.41, respectively. The T–O–T angles vary between 128.9 and 157.0° (average: 139.7°). This value is only slightly lower than the value of 142° suggested by Liebau (1985) for “unstrained” Si–O–Al angles.

The framework density of the present porous crystal structure is 22.2 T atoms/1000 Å³. The connectivity of the T atoms within the framework can be characterized by the so-called coordination sequences, which are identical for all Al/Si-atoms in the asymmetric unit: 4-12-25-44-67-96-130-170-214-264. The vertex symbols for the tetrahedral centers are 6₂·6₂·6₂·6₂·6₂·6₂. In summary, monoclinic trinepheline can be classified as a three-dimensional four-connected net with tridymite topology.

Charge balance in the structure of trinepheline is achieved by incorporation of Na ions located in the channels running parallel *c* [Fig. 2, prepared using the computer program DIAMOND (Crystal Impact 2005)]. Within these tunnels every Na is hosted between two six-membered tetrahedral rings. Regardless of the elliptical or ditrigonal distortion of the rings, Na always occupies an off-centered position, because the dimensions of the cavities are too big for it to take the central position. Therefore, Na atoms are irregularly coordinated. Among them two groups could be

TABLE 3. Fractional coordinates ($\times 10^4$), site occupancies, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	Occ	U_{eq}	Atom	x	y	z	Occ	U_{eq}
Si1a	7561(2)	6722(2)	8687(1)	1.000	10(1)	O3a	9333(4)	7126(4)	8648(2)	1.000	17(1)
Si1b	6497(2)	8996(2)	344(1)	1.000	11(1)	O3b	7122(4)	7785(4)	315(2)	1.000	20(1)
Si1c	981(1)	8031(1)	7077(1)	1.000	10(1)	O3c	2431(4)	9746(3)	7039(2)	1.000	15(1)
Si2a	6691(1)	3381(1)	377(1)	1.000	11(1)	O4a	6978(4)	6869(4)	8096(1)	1.000	16(1)
Si2b	7044(1)	3494(1)	7006(1)	1.000	11(1)	O4b	6666(2)	9723(2)	9750(2)	1.000	19(1)
Si2c	3173(2)	6453(2)	8739(1)	1.000	13(1)	O4c	408(4)	7450(4)	6471(1)	1.000	18(1)
Si3a	836(1)	7548(1)	342(1)	1.000	11(1)	O5a	9613(4)	2582(4)	8025(2)	1.000	18(1)
Si3b	2349(1)	3209(1)	6990(1)	1.000	10(1)	O5b	2391(2)	2594(2)	9741(2)	1.000	21(1)
Si3c	3337(2)	967(1)	8691(1)	1.000	10(1)	O5c	6541(5)	9480(4)	6406(1)	1.000	19(1)
Si4a	8853(1)	2266(1)	8617(1)	1.000	10(1)	O6a	7409(5)	7882(4)	9107(2)	1.000	22(1)
Si4b	7915(1)	6932(1)	5333(1)	1.000	10(1)	O6b	2511(4)	9696(4)	5780(1)	1.000	19(1)
Si4c	6318(1)	8752(1)	7000(1)	1.000	10(1)	O6c	9604(3)	8118(3)	7393(2)	1.000	13(1)
Al1a	6539(2)	9027(2)	9106(1)	1.000	10(1)	O7a	3305(4)	5029(4)	9002(2)	1.000	19(1)
Al1b	1137(2)	7767(2)	5822(1)	1.000	11(1)	O7b	5086(4)	1771(4)	441(2)	1.000	20(1)
Al1c	7631(2)	6809(2)	7456(1)	1.000	10(1)	O7c	8535(4)	3275(4)	7062(2)	1.000	20(1)
Al2a	846(2)	7536(2)	9080(1)	1.000	10(1)	O8a	7786(4)	673(4)	5367(2)	1.000	16(1)
Al2b	2458(2)	3301(2)	5749(1)	1.000	11(1)	O8b	515(4)	1949(4)	7026(2)	1.000	18(1)
Al2c	3704(2)	1290(1)	7440(1)	1.000	10(1)	O8c	2563(5)	2063(4)	8644(2)	1.000	19(1)
Al3a	2082(2)	3054(2)	9106(1)	1.000	12(1)	O9a	172(2)	7179(2)	9739(2)	1.000	23(1)
Al3b	6702(2)	9054(2)	5741(1)	1.000	10(1)	O9b	2993(4)	3136(4)	6399(1)	1.000	16(1)
Al3c	9000(2)	1992(1)	7366(1)	1.000	10(1)	O9c	3568(5)	564(5)	8086(2)	1.000	23(1)
Al4a	6708(2)	3424(2)	9092(1)	1.000	11(1)	O10a	8565(4)	3644(4)	5501(2)	1.000	25(1)
Al4b	6874(2)	3575(2)	5707(1)	1.000	11(1)	O10b	2581(4)	4912(4)	7077(2)	1.000	22(1)
Al4c	2970(2)	6550(2)	7435(1)	1.000	12(1)	O10c	4973(4)	1766(4)	8995(2)	1.000	19(1)
Na1a	9921(1)	4366(1)	9717(1)	1.000	23(1)	O11a	8204(4)	3437(4)	8732(2)	1.000	19(1)
Na1b	5617(3)	5500(3)	6300(1)	1.000	23(1)	O11b	6726(4)	5094(4)	5425(2)	1.000	18(1)
Na1c	5459(3)	9763(3)	8033(1)	1.000	26(1)	O11c	4593(4)	8218(4)	7204(2)	1.000	20(1)
Na2a	5302(1)	5497(1)	9730(1)	1.000	24(1)	O12a	4626(4)	8076(5)	8920(2)	1.000	28(1)
Na2b	4511(3)	147(3)	6410(1)	1.000	25(1)	O12b	8060(4)	3423(4)	743(2)	1.000	17(1)
Na2c	9594(3)	5273(3)	8031(1)	1.000	26(1)	O12c	7285(4)	4934(4)	7375(2)	1.000	22(1)
Na3a	4411(3)	4527(2)	8149(1)	1.000	22(1)	O13a	7442(4)	508(4)	8650(2)	1.000	18(1)
Na3b	4298(1)	9931(1)	9722(1)	1.000	21(1)	O13b	9654(4)	7277(4)	5363(2)	1.000	19(1)
Na3c	353(3)	4702(3)	6401(1)	1.000	27(1)	O13c	6646(4)	7301(4)	6990(1)	1.000	13(1)
Na4a	9637(3)	9596(3)	9723(2)	0.852(5)	57(1)	O14a	7232(2)	3582(2)	9759(2)	1.000	22(1)
Na4b	9828(6)	9842(5)	6433(2)	1.000	91(2)	O14b	6861(5)	3854(5)	6399(2)	1.000	29(1)
Na4c	431(4)	355(4)	7974(2)	0.923(5)	54(1)	O14c	3231(6)	6273(6)	8106(2)	1.000	34(1)
O1a	6450(4)	4956(4)	8904(2)	1.000	20(1)	O15a	144(4)	2527(4)	9060(1)	1.000	16(1)
O1b	4706(4)	8168(4)	524(2)	1.000	23(1)	O15b	7580(4)	7915(4)	5780(1)	1.000	16(1)
O1c	1380(4)	6819(4)	7367(2)	1.000	18(1)	O15c	7510(4)	75(3)	7403(1)	1.000	14(1)
O2a	509(4)	2701(5)	5761(2)	1.000	20(1)	O16a	1571(4)	6340(4)	8917(2)	1.000	24(1)
O2b	3264(4)	2780(4)	7433(2)	1.000	16(1)	O16b	3588(4)	5200(4)	5557(2)	1.000	21(1)
O2c	2198(5)	9464(4)	9038(2)	1.000	24(1)	O16c	5536(4)	1915(4)	7193(2)	1.000	20(1)

**FIGURE 2.** Crystal structure of monoclinic trinepheline viewed parallel to *c*. Sodium ions are represented by thermal ellipsoids (50% probability level).

distinguished. Na1a–Na3c, located in the less symmetrical channels, are surrounded by six or seven O atoms. The interatomic distances are ranging from 2.3 to 2.9 Å. The remaining Na atoms found in the channels created by ditrigonal tetrahedral rings have an even more irregular coordination. Four shorter bonds between 2.3 and 2.7 (close to the typical average bond lengths for Na–O

of 2.5–2.6 Å according to Shannon and Prewitt 1969) could be distinguished from additional three to four interatomic distances ranging from 2.8 to 3.1 Å. This unusual coordination of Na situated in the ditrigonal channels is forced by the geometry of these channels. Pluth and Smith (1980) reported similar coordination environments for Na in the case of dehydrated zeolite A. The very irregular coordination was due to statistical occupation of the positions.

Bond-valence sums (BVS) were calculated based on the parameter set of Brown (1981) using the program IVTON (Balić-Žunić and Vicković 1996). The results are given in the Table 7. For the Si designated sites the BVS values are very close to 4.0 v.u. Al-rich sites have BVS about 3.2 v.u., clearly indicating some excess of silicon in these positions, as it was expected from chemical analysis. The nine Na atoms situated in between elliptical rings only have bond-valence sums ranging from 0.8–1.0 v.u., while for Na4a–c the sums are about 0.5 v.u. A similar BVS value can be observed for Na4 atom in hexagonal trinepheline (Kahlenberg and Böhm 1998) situated in the pseudo hexagonal channels of the structure, as well as for Na2 in pure Na nephelines (Hippler and Böhm 1989) located in the ditrigonal channels. This points to a pronounced underbonding of Na4a–c in this structure.

The mean square displacements for thermal motions were

TABLE 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1a	14(1)	12(1)	9(1)	0(1)	1(1)	9(1)	O3a	17(1)	23(1)	13(1)	-1(1)	-2(1)	12(1)
Si1b	13(1)	9(1)	10(1)	-1(1)	-1(1)	5(1)	O3b	32(2)	23(1)	13(1)	4(1)	2(1)	21(1)
Si1c	9(1)	9(1)	10(1)	0(1)	-1(1)	4(1)	O3c	12(1)	10(1)	19(2)	1(1)	-3(1)	2(1)
Si2a	10(1)	9(1)	13(1)	-1(1)	-1(1)	4(1)	O4a	17(2)	25(2)	10(1)	-1(1)	-1(1)	14(1)
Si2b	10(1)	10(1)	14(1)	-1(1)	0(1)	5(1)	O4b	34(1)	20(1)	12(1)	-1(1)	0(2)	19(1)
Si2c	11(1)	11(1)	18(1)	1(1)	-1(1)	7(1)	O4c	15(1)	20(2)	10(1)	0(1)	1(1)	1(1)
Si3a	9(1)	11(1)	11(1)	0(1)	-1(1)	5(1)	O5a	15(1)	19(2)	12(1)	-4(1)	0(1)	1(1)
Si3b	11(1)	11(1)	10(1)	0(1)	0(1)	7(1)	O5b	30(1)	35(1)	10(1)	-3(2)	-4(2)	25(1)
Si3c	13(1)	9(1)	9(1)	0(1)	-1(1)	6(1)	O5c	33(2)	24(2)	8(1)	0(1)	4(1)	20(1)
Si4a	8(1)	9(1)	9(1)	0(1)	0(1)	2(1)	O6a	40(2)	33(2)	12(1)	-5(1)	-7(1)	32(2)
Si4b	12(1)	12(1)	8(1)	0(1)	-1(1)	7(1)	O6b	22(2)	14(1)	13(1)	1(1)	0(1)	2(1)
Si4c	11(1)	10(1)	10(1)	0(1)	-1(1)	5(1)	O6c	8(1)	10(1)	18(2)	-1(1)	0(1)	2(1)
Al1a	12(1)	9(1)	10(1)	0(1)	0(1)	6(1)	O7a	8(1)	14(1)	33(2)	7(1)	2(1)	4(1)
Al1b	13(1)	12(1)	10(1)	0(1)	1(1)	7(1)	O7b	15(2)	16(2)	29(2)	-1(1)	9(1)	8(1)
Al1c	11(1)	11(1)	9(1)	0(1)	0(1)	6(1)	O7c	16(1)	17(1)	30(2)	11(1)	6(1)	9(1)
Al2a	10(1)	9(1)	10(1)	0(1)	-1(1)	4(1)	O8a	19(1)	10(1)	16(1)	2(1)	2(1)	4(1)
Al2b	10(1)	11(1)	10(1)	0(1)	0(1)	5(1)	O8b	14(1)	26(2)	15(2)	-5(1)	3(1)	11(1)
Al2c	11(1)	12(1)	8(1)	-1(1)	0(1)	6(1)	O8c	29(2)	22(2)	11(1)	-1(1)	0(1)	17(1)
Al3a	14(1)	14(1)	10(1)	0(1)	2(1)	8(1)	O9a	17(1)	24(1)	12(1)	2(2)	4(2)	-1(1)
Al3b	10(1)	10(1)	10(1)	0(1)	0(1)	4(1)	O9b	14(1)	22(2)	11(1)	1(1)	0(1)	9(1)
Al3c	9(1)	9(1)	11(1)	1(1)	2(1)	4(1)	O9c	47(2)	28(2)	11(1)	0(1)	-2(1)	32(2)
Al4a	9(1)	11(1)	11(1)	1(1)	0(1)	5(1)	O10a	13(1)	17(2)	44(2)	-1(2)	3(1)	7(1)
Al4b	10(1)	11(1)	11(1)	-1(1)	-1(1)	4(1)	O10b	29(2)	15(1)	24(2)	-3(1)	1(1)	14(1)
Al4c	13(1)	12(1)	12(1)	-1(1)	-3(1)	8(1)	O10c	13(1)	14(1)	22(2)	4(1)	-1(1)	1(1)
Na1a	23(1)	23(1)	26(1)	0(1)	0(1)	14(1)	O11a	16(1)	16(2)	24(2)	3(1)	4(1)	9(1)
Na1b	26(1)	24(1)	19(1)	-7(1)	-3(1)	11(1)	O11b	23(2)	14(1)	19(2)	-2(1)	-4(1)	11(1)
Na1c	22(1)	38(1)	18(1)	-7(1)	-4(1)	16(1)	O11c	10(1)	12(1)	34(2)	-3(1)	1(1)	3(1)
Na2a	24(1)	28(1)	19(1)	-3(1)	-1(1)	12(1)	O12a	11(2)	18(2)	51(3)	-4(2)	-1(2)	5(1)
Na2b	22(1)	40(1)	20(1)	-2(1)	-2(1)	20(1)	O12b	18(1)	16(2)	22(2)	-5(1)	-6(1)	12(1)
Na2c	31(1)	24(1)	24(1)	12(1)	9(1)	15(1)	O12c	23(2)	11(1)	28(2)	-1(1)	-2(1)	6(1)
Na3a	21(1)	14(1)	24(1)	-2(1)	2(1)	4(1)	O13a	22(2)	10(1)	14(1)	0(1)	1(1)	3(1)
Na3b	21(1)	27(1)	17(1)	-1(1)	-2(1)	13(1)	O13b	17(1)	26(2)	16(1)	-3(1)	-2(1)	11(1)
Na3c	29(1)	23(1)	25(1)	3(1)	9(1)	10(1)	O13c	16(1)	16(1)	9(1)	-2(1)	-5(1)	9(1)
Na4a	66(1)	67(1)	37(1)	-2(2)	0(3)	32(1)	O14a	21(1)	23(1)	13(1)	0(1)	-1(1)	5(1)
Na4b	174(4)	95(3)	62(2)	-51(2)	-53(2)	111(3)	O14b	40(2)	39(2)	16(2)	-1(1)	-5(1)	25(2)
Na4c	50(1)	74(2)	54(2)	-36(2)	-30(1)	43(1)	O14c	46(2)	63(3)	6(1)	-2(1)	-6(1)	36(2)
O1a	18(2)	17(1)	29(2)	7(1)	5(1)	12(1)	O15a	9(1)	24(2)	12(1)	1(1)	-2(1)	6(1)
O1b	17(2)	14(2)	33(2)	4(1)	8(2)	5(1)	O15b	25(2)	21(2)	11(1)	-1(1)	-2(1)	19(1)
O1c	8(1)	15(1)	32(2)	3(1)	1(1)	5(1)	O15c	16(1)	10(1)	11(1)	0(1)	1(1)	3(1)
O2a	10(1)	28(2)	19(2)	5(1)	0(1)	7(1)	O16a	13(2)	12(2)	47(2)	-2(1)	5(1)	6(1)
O2b	22(2)	20(1)	13(1)	-3(1)	-3(1)	15(1)	O16b	13(2)	16(1)	32(2)	5(1)	4(1)	8(1)
O2c	19(2)	16(1)	26(2)	0(1)	0(1)	1(1)	O16c	11(1)	11(1)	36(2)	-3(1)	5(1)	5(1)

calculated from the anisotropic displacement parameters (Table 4). Most of oxygen thermal motion ellipsoids are prolate with the longest axes perpendicular to the T-O direction and the shortest axes nearly parallel to the bonds. It is reasonable to assume that tetrahedra execute a librational motion about the T ion center (Busing and Levy 1964).

The apical O atoms O14b and O14c show a deviation from this general rule. Their anisotropic displacement parameters are considerably higher than the rest of the O atoms. They connect "trigonal" and "elliptical" layers and correspond to the statistical triple split position O1 in the model of Hahn and Buerger (1955) for natural nepheline. O14a connects two "trigonal" layers and shows no deviation with regard to the displacement parameters of the other oxygen atoms in the structure.

The strongly underbonded Na ions Na4a-c also have the highest values for the atomic displacements observed, as is often observed for guest ions in tunnel-like host structures. The lengths of principal axis for these atoms range from 0.15 to 0.46 Å and lead to the conclusion that Na4a-c sodium ions are disordered. The thermal ellipsoid for Na4b exhibits the most pronounced elongation. This Na is located 0.18 Å away from the center of the channel, unlike the other two ions that are off-centered for 0.38 Å. Assuming that these positions represent an average in space and time, refinement with two split ions with isotropic thermal

parameters was implemented. The results indicated two separate, but also differently populated positions. However, the obtained *R*-values were clearly higher, so we concluded that at this level of investigation it is not possible to make a final conclusion about the nature of disorder of the Na ions.

The crystal structure of monoclinic trinepheline (Fig. 1) can be described as a simple stacking of the basic Hahn and Buerger model for natural nepheline composed of two layers (Fig. 3) and one layer (Fig. 4) corresponding to those observed in the hexagonal trinepheline model (Kahlenberg and Böhm 1998). This sequence is further transformed by the means of the 2_1 screw axis, to form an additional three layers, giving a complete set of six layers fully defining the structure of monoclinic trinepheline. With this respect it is interesting to note that in hexagonal trinepheline a six-layer stacking sequence is realized preserving the hexagonal symmetry although the layers exclusively contain elliptical rings. The present structure can be understood as a "frozen" between classical nepheline and hexagonal trinepheline. It should be underlined that monoclinic trinepheline is in that sense closer to natural nepheline.

It is also important to note that the structure described in this paper is very similar to monoclinic trinepheline reported by Selker et al. (1985) and later by Selker (1987). However, as already stated in the introduction, Selker (1987) gave only a

TABLE 5. Selected bond lengths (Å)

Si1a-O3a	1.611(4)	Si1b-O6b ⁱ	1.607(4)	Si1c-O3c	1.603(3)
Si1a-O4a	1.620(4)	Si1b-O3b	1.612(4)	Si1c-O1c	1.619(4)
Si1a-O6a	1.622(4)	Si1b-O1b	1.618(4)	Si1c-O4c	1.620(4)
Si1a-O1a	1.637(4)	Si1b-O4b ⁱⁱ	1.623(5)	Si1c-O6c ⁱⁱⁱ	1.625(3)
Mean	1.623	Mean	1.615	Mean	1.617
Si2a-O14a ^{iv}	1.616(5)	Si2b-O14b	1.591(4)	Si2c-O14c	1.596(4)
Si2a-O7b	1.617(4)	Si2b-O16c	1.614(4)	Si2c-O12a	1.610(4)
Si2a-O12b	1.628(4)	Si2b-O7c	1.616(4)	Si2c-O16a	1.611(4)
Si2a-O16b ^{iv}	1.634(4)	Si2b-O12c	1.618(4)	Si2c-O7a	1.628(4)
Mean	1.624	Mean	1.610	Mean	1.611
Si3a-O9a ⁱⁱ	1.613(5)	Si3b-O10b	1.608(3)	Si3c-O10c	1.608(4)
Si3a-O8a ^{iv}	1.617(4)	Si3b-O2b	1.624(4)	Si3c-O9c	1.609(4)
Si3a-O2a ^v	1.622(4)	Si3b-O9b	1.626(4)	Si3c-O2c ^{vi}	1.610(4)
Si3a-O10a ^{iv}	1.623(4)	Si3b-O8b	1.630(3)	Si3c-O8c	1.626(4)
Mean	1.619	Mean	1.622	Mean	1.614
Si4a-O13a	1.615(4)	Si4b-O13b	1.597(4)	Si4c-O11c	1.612(4)
Si4a-O11a	1.616(4)	Si4b-O15b	1.626(4)	Si4c-O15c ^{viii}	1.616(4)
Si4a-O15a ^{viii}	1.620(4)	Si4b-O5b ^{iv}	1.626(5)	Si4c-O5c	1.618(4)
Si4a-O5a	1.621(4)	Si4b-O11b	1.630(4)	Si4c-O13c	1.633(3)
Mean	1.618	Mean	1.620	Mean	1.620
Al1a-O12a	1.722(4)	Al1b-O6b	1.722(4)	Al1c-O12c	1.735(4)
Al1a-O13a ^{viii}	1.722(4)	Al1b-O4c	1.739(4)	Al1c-O4a	1.739(4)
Al1a-O4b	1.732(5)	Al1b-O13b ⁱⁱⁱ	1.741(4)	Al1c-O13c	1.744(4)
Al1a-O6a	1.745(4)	Al1b-O12b ^x	1.741(4)	Al1c-O6c	1.749(3)
Mean	1.730	Mean	1.736	Mean	1.741
Al2a-O2c	1.716(4)	Al2b-O16b	1.721(4)	Al2c-O16c	1.728(4)
Al2a-O16a	1.722(4)	Al2b-O3b ^{ix}	1.725(4)	Al2c-O3c ^{vi}	1.743(4)
Al2a-O3a ⁱⁱⁱ	1.732(4)	Al2b-O2a	1.730(4)	Al2c-O2b	1.745(3)
Al2a-O9a	1.749(5)	Al2b-O9b	1.740(4)	Al2c-O9c	1.746(4)
Mean	1.730	Mean	1.729	Mean	1.741
Al3a-O5b	1.723(5)	Al3b-O8a ^{viii}	1.707(4)	Al3c-O7c	1.737(4)
Al3a-O8c	1.734(4)	Al3b-O7b ^{ix}	1.724(4)	Al3c-O15c	1.745(3)
Al3a-O15a	1.739(4)	Al3b-O5c	1.741(4)	Al3c-O5a	1.753(4)
Al3a-O7a	1.744(4)	Al3b-O15b	1.748(4)	Al3c-O8b ^{vii}	1.755(3)
Mean	1.735	Mean	1.740	Mean	1.747
Al4a-O10c	1.717(4)	Al4b-O1b ^x	1.729(4)	Al4c-O10b	1.727(4)
Al4a-O14a	1.730(5)	Al4b-O10a	1.734(4)	Al4c-O14c	1.740(4)
Al4a-O1a	1.734(4)	Al4b-O11b	1.740(4)	Al4c-O1c	1.745(3)
Al4a-O11a	1.739(4)	Al4b-O14b	1.752(4)	Al4c-O11c	1.745(4)
Mean	1.730	Mean	1.739	Mean	1.739
Na1a-O14a	2.399(2)	Na1b-O13c	2.327(4)	Na1c-O13a ^{viii}	2.321(4)
Na1a-O13b ^t	2.480(5)	Na1b-O14b	2.514(5)	Na1c-O9c ^{viii}	2.392(4)
Na1a-O15a ^{vii}	2.550(4)	Na1b-O9b	2.519(4)	Na1c-O11c	2.647(5)
Na1a-O10a ^t	2.660(5)	Na1b-O11b	2.572(4)	Na1c-O15c ^{viii}	2.477(4)
Na1a-O9a ^{vii}	2.687(2)	Na1b-O15b	2.575(5)	Na1c-O12a	2.654(6)
Na1a-O16a ^{vii}	2.712(5)	Na1b-O16b	2.653(5)	Na1c-O16c ^{viii}	2.973(5)
Na1a-O11a	2.878(5)	Mean	2.527	Mean	2.547
Mean	2.624				
Na2a-O11b ^{ix}	2.506(4)	Na2b-O6b ^{vi}	2.403(4)	Na2c-O1c ^{vii}	2.362(4)
Na2a-O1a	2.544(5)	Na2b-O5c ^{vi}	2.428(4)	Na2c-O11a	2.411(4)
Na2a-O3b ^{vi}	2.552(4)	Na2b-O3c ^{vi}	2.474(4)	Na2c-O3a	2.516(4)
Na2a-O7a	2.564(4)	Na2b-O16c	2.486(5)	Na2c-O5a	2.690(4)
Na2a-O16b ^{ix}	2.597(5)	Na2b-O1b ^{ix}	2.649(5)	Na2c-O12c	2.711(5)
Na2a-O6a	2.744(5)	Na2b-O11c ^{vi}	2.791(4)	Na2c-O16a ^{vii}	2.801(5)
Na2a-O5b	2.909(2)	Mean	2.539	Na2c-O7c	2.974(5)
Mean	2.631			Mean	2.638
Na3a-O2b	2.357(4)	Na3b-O7b ^{viii}	2.403(5)	Na3c-O7c ^{viii}	2.342(4)
Na3a-O4a	2.469(4)	Na3b-O10c ^{viii}	2.423(4)	Na3c-O12b ^{ix}	2.399(4)
Na3a-O8c	2.541(5)	Na3b-O8a ^{ix}	2.460(4)	Na3c-O2a	2.620(5)
Na3a-O14c	2.542(5)	Na3b-O4b	2.476(2)	Na3c-O4c	2.716(4)
Na3a-O7a	2.562(5)	Na3b-O2c	2.563(5)	Na3c-O10b	2.718(5)
Na3a-O1a	2.651(5)	Na3b-O1b ^{vi}	2.824(5)	Na3c-O10a ⁱⁱⁱ	2.735(5)
Mean	2.520	Mean	2.851(5)	Mean	2.588
		Mean	2.572		
Na4a-O6a	2.541(6)	Na4b-O8b ^{viii}	2.373(5)	Na4c-O6c ^{xiv}	2.434(5)
Na4a-O3b ^{vi}	2.693(5)	Na4b-O15b	2.666(5)	Na4c-O8c	2.576(5)
Na4a-O9a ^{vii}	2.714(3)	Na4b-O4c ^{vii}	2.720(5)	Na4c-O5a ⁱⁱⁱ	2.722(5)
Na4a-O5b ^{viii}	2.886(3)	Na4b-O6c	2.891(6)	Na4c-O8b	2.829(6)
Na4a-O4b	3.034(4)	Na4b-O3c ^{vii}	3.051(7)	Na4c-O2b	2.979(6)
Na4a-O2c ^{vii}	3.135(6)	Na4b-O2a ^{xiii}	3.078(7)	Na4c-O9c	3.049(7)
Na4a-O8a ^x	3.158(6)	Na4b-O5c	3.121(8)	Na4c-O15c ⁱⁱⁱ	3.133(6)
Na4a-O15a ^{viii}	3.171(6)	Mean	2.843	Mean	2.817
Mean	2.916				

Notes: Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 2, z - 1/2$; (ii) $x, y, z - 1$; (iii) $x - 1, y, z$; (iv) $-x + 1, -y + 1, z - 1/2$; (v) $-x, -y + 1, z - 1/2$; (vi) $x, y - 1, z$; (vii) $x + 1, y, z$; (viii) $x + 1, y + 1, z$; (ix) $-x + 1, -y + 1, z + 1/2$; (x) $-x - 2, -y + 1, z + 1/2$; (xi) $x, y, z + 1$; (xii) $x, y + 1, z + 1$; (xiii) $x + 1, y + 1, z$; (xiv) $x - 1, y - 1, z$; (xv) $-x, -y + 1, z + 1/2$; (xvi) $-x + 1, -y + 2, z + 1/2$.

graphical description of the structure. The reported value of R_1 was 0.117, which is significantly higher than the value for our structure refinement.

As was mentioned in the introduction, several authors reported the existence of phase transitions occurring in nepheline-type materials at elevated temperatures. For the near future single-crystal diffraction experiments are planned to investigate the high temperature behavior of monoclinic trinepheline in detail.

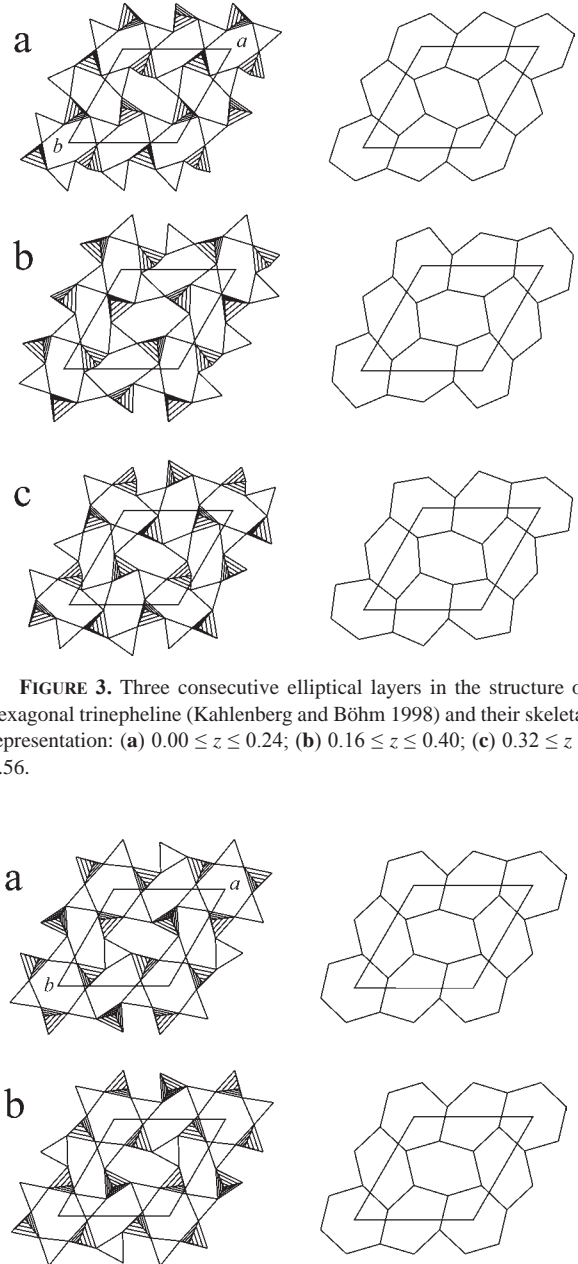


FIGURE 3. Three consecutive elliptical layers in the structure of hexagonal trinepheline (Kahlenberg and Böhm 1998) and their skeletal representation: (a) $0.00 \leq z \leq 0.24$; (b) $0.16 \leq z \leq 0.40$; (c) $0.32 \leq z \leq 0.56$.

FIGURE 4. The two layers building the unit cell in the structure of natural nepheline (Hahn and Buerger 1955), together with the skeletal representations: (a) $-0.05 \leq z \leq 0.55$; (b) $0.45 \leq z \leq 1.05$.

TABLE 6. Selected angles (°)

O3a-Si1a-O4a	108.8(2)	O6b ⁱ -Si1b-O3b	109.0(2)	O3c-Si1c-O1c	113.2(2)
O3a-Si1a-O6a	109.9(2)	O6b ⁱ -Si1b-O1b	107.8(2)	O3c-Si1c-O4c	107.3(2)
O4a-Si1a-O6a	111.1(2)	O3b-Si1b-O1b	111.9(2)	O1c-Si1c-O4c	109.1(2)
O3a-Si1a-O1a	111.3(2)	O6b ⁱ -Si1b-O4b ⁱⁱ	111.8(2)	O3c-Si1c-O6c ⁱⁱⁱ	108.2(2)
O4a-Si1a-O1a	108.5(2)	O3b-Si1b-O4b ⁱⁱ	107.4(2)	O1c-Si1c-O6c ⁱⁱⁱ	110.6(2)
O6a-Si1a-O1a	107.4(2)	O1b-Si1b-O4b ⁱⁱ	109.0(2)	O4c-Si1c-O6c ⁱⁱⁱ	108.3(2)
Mean	109.5	Mean	109.5	Mean	109.4
O14a ^{iv} -Si2a-O7b	108.8(2)	O14b-Si2b-O16c	109.8(2)	O14c-Si2c-O12a	109.1(3)
O14a ^{iv} -Si2a-O12b	108.0(2)	O14b-Si2b-O7c	109.3(2)	O14c-Si2c-O16a	110.8(2)
O7b-Si2a-O12b	112.1(2)	O16c-Si2b-O7c	108.7(2)	O12a-Si2c-O16a	111.2(2)
O14a ^{iv} -Si2a-O16b ^{iv}	110.2(2)	O14b-Si2b-O12c	109.0(2)	O14c-Si2c-O7a	106.2(2)
O7b-Si2a-O16b ^{iv}	108.7(2)	O16c-Si2b-O12c	110.8(2)	O12a-Si2c-O7a	109.8(2)
O12b-Si2a-O16b ^{iv}	109.0(2)	O7c-Si2b-O12c	109.2(2)	O16a-Si2c-O7a	109.6(2)
Mean	109.5	Mean	109.5	Mean	109.4
O9a ^{iv} -Si3a-O8a ^{iv}	108.4(2)	O10b-Si3b-O2b	112.3(2)	O10c-Si3c-O9c	109.3(2)
O9a ^{iv} -Si3a-O2a ^v	110.5(2)	O10b-Si3b-O9b	108.5(2)	O10c-Si3c-O2c ^{vi}	106.4(2)
O8a ^{iv} -Si3a-O2a ^v	109.4(2)	O2b-Si3b-O9b	108.7(2)	O9c-Si3c-O2c ^{vi}	113.3(2)
O9a ^{iv} -Si3a-O10a ^{iv}	108.8(2)	O10b-Si3b-O8b	108.9(2)	O10c-Si3c-O8c	114.0(2)
O8a ^{iv} -Si3a-O10a ^{iv}	111.7(2)	O2b-Si3b-O8b	108.9(2)	O9c-Si3c-O8c	106.0(2)
O2a ^v -Si3a-O10a ^{iv}	108.0(2)	O9b-Si3b-O8b	109.5(2)	O2c ^{vi} -Si3c-O8c	108.1(2)
Mean	109.5	Mean	109.5	Mean	109.5
O13a-Si4a-O11a	109.1(2)	O13b-Si4b-O15b	111.4(2)	O11c-Si4c-O15c ^{viii}	107.8(2)
O13a-Si4a-O15a ^{viii}	109.6(2)	O13b-Si4b-O5b ^{iv}	108.8(2)	O11c-Si4c-O5c	108.9(2)
O11a-Si4a-O15a ^{viii}	109.7(2)	O15b-Si4b-O5b ^{iv}	109.0(2)	O15c ^{viii} -Si4c-O5c	109.0(2)
O13a-Si4a-O5a	109.2(2)	O13b-Si4b-O11b	110.0(2)	O11c-Si4c-O13c	111.3(2)
O11a-Si4a-O5a	109.8(2)	O15b-Si4b-O11b	109.1(2)	O15c ^{viii} -Si4c-O13c	109.9(2)
O15a ^{viii} -Si4a-O5a	109.5(2)	O5b ^{iv} -Si4b-O11b	108.5(2)	O5c-Si4c-O13c	109.9(2)
Mean	109.5	Mean	109.5	Mean	109.5
O12a-Al1a-O13a ^{viii}	105.0(2)	O6b-Al1b-O4c	106.8(2)	O12c-Al1c-O4a	105.5(2)
O12a-Al1a-O4b	108.1(2)	O6b-Al1b-O13b ⁱⁱⁱ	111.6(2)	O12c-Al1c-O13c	112.7(2)
O13a ^{viii} -Al1a-O4b	111.7(2)	O4c-Al1b-O13b ⁱⁱⁱ	110.0(2)	O4a-Al1c-O13c	109.3(2)
O12a-Al1a-O6a	114.7(2)	O6b-Al1b-O12b ^{ix}	111.8(2)	O12c-Al1c-O6c	109.9(2)
O13a ^{viii} -Al1a-O6a	110.0(2)	O4c-Al1b-O12b ^{ix}	105.9(2)	O4a-Al1c-O6c	111.1(2)
O4b-Al1a-O6a	107.4(2)	O13b ⁱⁱⁱ -Al1b-O12b ^{ix}	110.5(2)	O13c-Al1c-O6c	108.3(2)
Mean	109.5	Mean	109.4	Mean	109.5
O2c-Al2a-O16a	113.1(2)	O16b-Al2b-O3b ^{ix}	106.4(2)	O16c-Al2c-O3c ^{vi}	106.9(2)
O2c-Al2a-O3a ⁱⁱⁱ	109.6(2)	O16b-Al2b-O2a	113.3(2)	O16c-Al2c-O2b	111.0(2)
O16a-Al2a-O3a ⁱⁱⁱ	107.9(2)	O3b ^{ix} -Al2b-O2a	112.1(2)	O3c ^{vi} -Al2c-O2b	111.3(2)
O2c-Al2a-O9a	107.2(2)	O16b-Al2b-O9b	107.4(2)	O16c-Al2c-O9c	109.3(2)
O16a-Al2a-O9a	109.4(2)	O3b ^{ix} -Al2b-O9b	110.2(2)	O3c ^{vi} -Al2c-O9c	107.0(2)
O3a ⁱⁱⁱ -Al2a-O9a	109.6(2)	O2a-Al2b-O9b	107.3(2)	O2b-Al2c-O9c	111.1(2)
Mean	109.5	Mean	109.4	Mean	109.4
O5b-Al3a-O8c	108.9(2)	O8a ^{viii} -Al3b-O7b ^{ix}	103.5(2)	O7c-Al3c-O15c	115.7(2)
O5b-Al3a-O15a	107.4(2)	O8a ^{viii} -Al3b-O5c	112.6(2)	O7c-Al3c-O5a	109.9(2)
O8c-Al3a-O15a	111.5(2)	O7b ^{ix} -Al3b-O5c	109.4(2)	O15c-Al3c-O5a	106.5(2)
O5b-Al3a-O7a	108.6(2)	O8a ^{viii} -Al3b-O15b	110.9(2)	O7c-Al3c-O8b ^{vii}	110.8(2)
O8c-Al3a-O7a	107.8(2)	O7b ^{ix} -Al3b-O15b	116.8(2)	O15c-Al3c-O8b ^{vii}	106.0(2)
O15a-Al3a-O7a	112.5(2)	O5c-Al3b-O15b	104.0(2)	O5a-Al3c-O8b ^{vii}	107.5(2)
Mean	109.4	Mean	109.5	Mean	109.4
O10c-Al4a-O14a	109.8(2)	O1b ^{ix} -Al4b-O10a	110.3(2)	O10b-Al4c-O14c	109.3(2)
O10c-Al4a-O1a	106.7(2)	O1b ^{ix} -Al4b-O11b	109.7(2)	O10b-Al4c-O1c	107.5(2)
O14a-Al4a-O1a	110.5(2)	O10a-Al4b-O11b	110.3(2)	O14c-Al4c-O1c	109.7(2)
O10c-Al4a-O11a	112.8(2)	O1b ^{ix} -Al4b-O14b	110.2(2)	O10b-Al4c-O11c	113.2(2)
O14a-Al4a-O11a	106.1(2)	O10a-Al4b-O14b	111.7(2)	O14c-Al4c-O11c	109.2(2)
O1a-Al4a-O11a	110.9(2)	O11b-Al4b-O14b	104.5(2)	O1c-Al4c-O11c	107.9(2)
Mean	109.5	Mean	109.4	Mean	109.5
Si1a-O1a-Al4a	135.9(2)	Si3a ^{xv} -O2a-Al2b	138.4(3)	Si1a-O3a-Al2a ^{vii}	138.0(3)
Si1b-O1b-Al4b ^{iv}	144.2(3)	Si3b-O2b-Al2c	130.0(2)	Si1b-O3b-Al2b ^{iv}	138.2(3)
Si1c-O1c-Al4c	137.6(2)	Si3c ^{viii} -O2c-Al2a	150.8(3)	Si1c-O3c-Al2c ^{viii}	141.6(3)
Si1a-O4a-Al1c	132.6(2)	Si4a-O5a-Al3c	137.7(2)	Si1a-O6a-Al1a	135.9(2)
Si1b ^{vi} -O4b-Al1a	134.5(1)	Si4b ^{ix} -O5b-Al3a	132.5(1)	Si1b ^{vii} -O6b-Al1b	140.8(2)
Si1c-O4c-Al1b	139.8(2)	Si4c-O5c-Al3b	140.8(2)	Si1c ^{viii} -O6c-Al1c	132.4(2)
Si2c-O7a-Al3a	136.7(2)	Si3a ^{ix} -O8a-Al3b ^{vi}	148.4(3)	Si3a ^{ix} -O9a-Al2a	139.5(1)
Si2a-O7b-Al3b ^{iv}	142.9(2)	Si3b-O8b-Al3c ⁱⁱ	131.4(2)	Si3b-O9b-Al2b	134.0(2)
Si2b-O7c-Al3c	137.6(2)	Si3c-O8c-Al3a	133.9(2)	Si3c-O9c-Al2c	139.1(2)
Si3a ^{ix} -O10a-Al4b	138.5(2)	Si4a-O11a-Al4a	137.5(2)	Si2c-O12a-Al1a	145.9(3)
Si3b-O10b-Al4c	156.0(3)	Si4b-O11b-Al4b	134.8(2)	Si2a-O12b-Al1b ^{iv}	135.4(2)
Si3c-O10c-Al4a	146.6(3)	Si4c-O11c-Al4c	138.9(2)	Si2b-O12c-Al1c	152.1(3)
Si4a-O13a-Al1a ^{vi}	139.9(2)	Si2a ^{xii} -O14a-Al4a	147.4(1)	Si4a ^{xiii} -O15a-Al3a	140.4(2)
Si4b-O13b-Al1b ^{vii}	140.8(3)	Si2b-O14b-Al4b	153.5(3)	Si4b-O15b-Al3b	132.2(2)
Si4c-O13c-Al1c	128.9(2)	Si2c-O14c-Al4c	157.0(3)	Si4c ^{xiv} -O15c-Al3c	137.9(2)
Si2c-O16a-Al2a	139.6(2)				
Si2a ^{ix} -O16b-Al2b	136.6(2)				
Si2b-O16c-Al2c	139.7(2)				

Notes: Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 2, z - 1/2$; (ii) $x, y, z - 1$; (iii) $x - 1, y, z$; (iv) $-x + 1, -y + 1, z - 1/2$; (v) $-x, -y + 1, z - 1/2$; (vi) $x, y - 1, z$; (vii) $x + 1, y, z$; (viii) $x, y + 1, z$; (ix) $-x + 1, -y + 1, z + 1/2$; (x) $-x + 2, -y + 1, z + 1/2$; (xi) $x, y, z + 1$; (xii) $x, y + 1, z + 1$; (xiii) $x + 1, y + 1, z$; (xiv) $x - 1, y - 1, z$; (xv) $-x, -y + 1, z + 1/2$; (xvi) $-x + 1, -y + 2, z + 1/2$.

TABLE 7. Bond-valence ranges for cations and bond-valence sums for all atoms in the structure of the monoclinic trinepheline

Atom	B. V. S	B. V. range	Atom	B. V. S	B. V. range	Atom	B. V. S	B.V. range
Si1a	4.02	0.97–1.03	Al1a	3.23	0.78–0.83	Na1a	0.82	0.05–0.20
Si1b	4.10	1.00–1.05	Al1b	3.18	0.78–0.83	Na1b	0.88	0.10–0.24
Si1c	4.09	1.00–1.06	Al1c	3.13	0.77–0.80	Na1c	0.91	0.04–0.25
Si2a	4.00	0.98–1.02	Al2a	3.24	0.77–0.84	Na2a	0.78	0.05–0.15
Si2b	4.16	1.01–1.09	Al2b	3.24	0.78–0.83	Na2b	0.87	0.07–0.20
Si2c	4.15	0.99–1.08	Al2c	3.14	0.77–0.81	Na2c	0.84	0.04–0.22
Si3a	4.06	1.01–1.03	Al3a	3.19	0.78–0.83	Na3a	0.88	0.10–0.22
Si3b	4.02	0.99–1.04	Al3b	3.24	0.77–0.86	Na3b	0.96	0.06–0.20
Si3c	4.12	1.00–1.04	Al3c	3.08	0.76–0.79	Na3c	0.79	0.08–0.23
Si4a	4.06	1.01–1.03	Al4a	3.23	0.79–0.84	Na4a	0.48	0.03–0.14
Si4b	4.05	0.99–1.08	Al4b	3.16	0.76–0.81	Na4b	0.54	0.03–0.21
Si4c	4.05	0.98–1.03	Al4c	3.15	0.77–0.81	Na4c	0.55	0.03–0.18
O1a	-2.00		O6b	-2.07		O11c	-2.04	
O1b	-1.99		O6c	-2.00		O12a	-2.02	
O1c	-2.01		O7a	-2.02		O12b	-1.97	
O2a	-1.95		O7b	-2.04		O12c	-1.90	
O2b	-2.04		O7c	-2.09		O13a	-2.10	
O2c	-2.03		O8a	-2.07		O13b	-2.02	
O3a	-1.98		O8b	-2.02		O13c	-1.99	
O3b	-2.07		O8c	-2.05		O14a	-2.03	
O3c	-2.04		O9a	-1.98		O14b	-2.00	
O4a	-1.96		O9b	-1.92		O14c	-2.00	
O4b	-2.00		O9c	-2.05		O15a	-1.96	
O4c	-1.97		O10a	-1.98		O15b	-1.98	
O5a	-1.94		O10b	-1.94		O15c	-1.99	
O5b	-1.92		O10c	-2.06		O16a	-2.01	
O5c	-2.01		O11a	-2.05		O16b	-2.02	
O6a	-1.99		O11b	-2.05		O16c	-2.04	

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the European Science Foundation EuroMinSci program and the Austrian Science Fund (FWF) under the grant I62-N10. We are also indebted to Bernhard Sartory for help with the EMPA experiments.

REFERENCES CITED

- Balić-Žunić, T. and Vicković, I. (1996) IVTON—A program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. *Journal of Applied Crystallography*, 29, 305–306.
- Brown, I.D. (1981) The bond-valence method: an empirical approach to crystal structure and bonding. In M. O'Keefe and A. Navrotsky, Eds., *Structure and Bonding in Crystals II*, p. 1–30. Academic Press, New York.
- Brown, W.L., Cesbron, F., and Dupont, G. (1972) Trinepheline; a new synthetic modification in the nepheline group. *Zeitschrift für Kristallographie*, 136, 468–470.
- Burla, M.C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G.L., De Caro, L., Giacovazzo, C., Polidori, G., and Spagna, R. (2005) SIR2004: An improved tool for crystal structure determination and refinement. *Journal of Applied Crystallography*, 38, 381–388.
- Busing, W.R. and Levy, H.A. (1964) The effect of thermal motion on the estimation of bond lengths from diffraction measurements. *Acta Crystallographica*, 17, 142–146.
- Crystal Impact (2005) DIAMOND 3.1a, Visual Crystal Structure Information System. Crystal Impact, Bonn, Germany.
- Dimitrijević, R., Dondur, V., Vulić, P., Marković, S., and Macura, S. (2004) Structural characterization of pure Na-nephelines synthesized by zeolite conversion route. *Journal of Physics and Chemistry of Solids*, 65, 1623–1633.
- Dollase, W.A. and Thomas, W.M. (1978) The crystal chemistry of silica rich, alkali-deficient nepheline. *Contributions to Mineralogy and Petrology*, 66, 311–318.
- Fischer, R.X., LeLirzin, A., Kassner, D., and Rüdinger, B. (1991) STRUPLO91, eine neue Version des Fortranprogramms zur Darstellung von Kristallstrukturen. *Zeitschrift für Kristallographie, Supplemental Issue*, 3, 75.
- Flörke, O.W. (1967) Die Modifikationen des SiO₂. *Fortschritte der Mineralogie*, 44, 181–230.
- Gregorkiewicz, M. (1984) Crystal structure and Al/Si-ordering of a synthetic nepheline. *Bulletin Minéralogique*, 107, 499–507.
- Hahn, T. and Buerger, M.J. (1955) The detailed structure of nepheline KNa₃Al₄Si₆O₁₆. *Zeitschrift für Kristallographie*, 106, 308–338.
- Henderson, C.M.B. and Roux, J. (1977) Inversion in sub-potassic nephelines. *Contributions to Mineralogy and Petrology*, 61, 279–298.
- Henderson, C.M.B. and Thompson, A.B. (1980) The low-temperature inversion in sub-potassic nephelines. *American Mineralogist*, 65, 970–980.
- Hippler, B. and Böhm, H. (1989) Structure investigation on sodium nephelines. *Zeitschrift für Kristallographie*, 187, 39–53.
- Hovestreydt, E. (1983) On the atomic scattering factor for O²⁻. *Acta Crystallographica*, A39, 268–269.
- Jarchow, O., Reese, H.H., and Saalfeld, H. (1966) Hydrothermalsynthesen von Zeolithen der Sodalith- und Cancrinitgruppe. *Neues Jahrbuch für Mineralogie Monatshefte*, 10, 289–297.
- Jones, J.B. (1968) Al-O and Si-O tetrahedral distances in aluminosilicate framework structures. *Acta Crystallographica*, B24, 355–358.
- Kahlenberg, V. and Böhm, H. (1998) Crystal structure of hexagonal trinepheline—A new synthetic NaAlSiO₄ modification. *American Mineralogist*, 83, 631–637.
- Klaska, K.H. (1974) Strukturuntersuchungen an Tridymitabkömmlingen. Ph.D. thesis, Fachbereich Geowissenschaften, Universität Hamburg, Germany.
- Liebau, F. (1985) Structural chemistry of silicates. Springer Verlag, Berlin.
- Loewenstein, W. (1954) The distribution of Al in tetrahedra of silicates and aluminates. *American Mineralogist*, 39, 92–96.
- Pluth, J.J. and Smith, J.V. (1980) Accurate redetermination of crystal structure of dehydrated zeolite A. Absence of near zero coordination of sodium. Refinement of Si, Al-ordered superstructure. *Journal of the American Chemical Society*, 102, 4704–4708.
- Prince, E. (2004) *International Tables for Crystallography*, vol. C. Dordrecht, The Netherlands.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: A quantitative measure of distortion in polyhedra. *Science*, 171, 567–570.
- Roth, G. (1985) Zum Zusammenhang zwischen Ionenleitung und Kristallstruktur von Festkörperelektrolyten: Theoretische Modelle sowie experimentelle Untersuchungen an Phasen des Nephelin Typs. Ph.D. thesis, Universität Münster, Germany.
- Schneider, H., Flörke, O.W., and Stoeck, R. (1994) The NaAlSiO₄ nepheline-carnegieite solid-state transformation. *Zeitschrift für Kristallographie*, 209, 113–117.
- Selker, P. (1987) Hydrothermalsynthesen und Strukturuntersuchungen von zwei Trinephelin-Modifikationen der Zusammensetzung NaAlSiO₄. Ph.D. thesis, Ruhr-Universität Bochum, Germany.
- Selker, P., Bartsch, H.H., and Klaska, R. (1985) Struktur und Hydrothermalsynthesen von NaAlSiO₄ Modifikationen. *Zeitschrift für Kristallographie*, 170, 175–176.
- Shannon, R.D. and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallographica*, B25, 925–946.
- Sheldrick, G.M. (1998) SHELXL97—Program for crystal structure analysis (Release 97–2). Universität Göttingen, Germany.
- Stoe and Cie GmbH (2005) X-Area program. Darmstadt, Germany.

MANUSCRIPT RECEIVED MAY 24, 2007

MANUSCRIPT ACCEPTED JANUARY 30, 2008

MANUSCRIPT HANDLED BY SERGEY KRIVOVICHEV