

The low-temperature inversion in sub-potassic nephelines

C. M. B. HENDERSON

*Department of Geology, The University
Manchester M13 9PL, England*

AND ALAN BRUCE THOMPSON

*Institut für Kristallographie und Petrographie, ETH
Zürich CH-8092, Switzerland*

Abstract

Differential scanning calorimetric (DSC) and high-temperature X-ray diffraction studies on seven nephelines belonging to the system $\text{NaAlSiO}_4(\text{Ne})\text{--KAlSiO}_4(\text{Ks})$ show that samples with less than 2.5 mol percent Ks (sub-potassic nephelines) exhibit complex relations. A Type-C nepheline containing 1.6 percent Ks has a single sharp DSC peak near 360 K; this temperature is close to that at which extra X-ray reflections characteristic of an orthorhombic 3c superstructure disappear (365 K) and marks an inversion to hexagonal symmetry. Type-B nephelines containing 0 to 0.36 percent Ks have two DSC peaks below 480 K which are separated by 20° to 40°. The two peaks confirm the existence of two phases in Type-B nephelines and the presence of two inversions. For each sample, the lower-temperature DSC peak coincides with the disappearance of the orthorhombic superstructure (*cf.* Type-C) and the higher-temperature peak with the disappearance of extra X-ray reflections typical of a low-symmetry second phase. Type-B and -C nephelines have DSC scans similar to that for tridymite which suggests that the low-temperature inversions in sub-potassic nephelines are caused by the collapse of the 'tridymite-like' framework about the relatively small Na^+ in the larger cation sites. In contrast, nephelines with more than 2.5 percent Ks are hexagonal at room temperature and show no inversions. Thus a Type-H nepheline containing 27 percent Ks does not have extra X-ray reflections and does not show any peaks on DSC scans between 340 and 520 K.

The heat capacity (C_p) data for A.407 (pure-Na, Type-B) above 500 K show excellent agreement with the C_p equation fitted to the drop calorimetric data of Kelley *et al.* (1953) on synthetic pure Na nepheline between 467 and 1180 K and can be used for thermochemical calculations on Ks-bearing nephelines *above about 500 K.*

Introduction

Although the natural occurrence of nepheline minerals is restricted, they have been the subject of many detailed experimental studies. In particular, the nepheline (NaAlSiO_4 , Ne)–kalsilitite (KAlSiO_4 , Ks) system has served as a useful analogue for modelling activity–composition relations of other immiscible Na–K phases (*e.g.* feldspars, micas, and halides). In addition, nepheline solid solution towards SiO_2 has provided necessary information on defect solid solutions, and the $\text{Na}_6\text{K}_2\text{Al}_8\text{Si}_8\text{O}_{32}$ phase is an excellent example of what may be an ordered compound within a solid-solution series. However, nephelines of

the same composition may crystallize in different space-groups under different conditions and these forms may be related by phase transitions of higher than first-order. Very little is known generally of how such transitions affect phase equilibria in mineral systems, but the large amount of information available for nephelines makes them suitable candidates for such studies.

Henderson and Roux (1977) showed that nephelines synthesized in the system Ne–Ks have different structures, depending upon composition and method of synthesis. At room temperature those with between 25 and 2.5 percent Ks (all compositions are given as mol percent) are hexagonal (Type-H). This

composition range has $x = 2.0$ to 0.2 , where x is the number of K atoms in the unit cell $\text{Na}_{8-x}\text{K}_x\text{Al}_8\text{Si}_8\text{O}_{32}$. All X-ray peaks in this type of nepheline can be unequivocally indexed using the Hahn and Buerger (1955) cell (HBC). In contrast, Henderson and Roux (1977) showed that nephelines with <2.5 percent Ks [sub-potassic nephelines (Donnay *et al.*, 1959)] have extra reflections that cannot be indexed with the HBC, have anomalous pseudohexagonal cell parameters, and show multiple twin lamellae. Nephelines with between 2.5 and ~0.7 percent Ks ($x = 0.2$ to 0.06) were believed to be orthorhombic (Type-C) with $a_h, \sqrt{3}a_h, 3c_h$ superstructures, where a_h and c_h refer to hexagonal cell parameters. Hydrothermally synthesized nephelines with 0 to ~0.7 percent Ks (Type-B) were shown to contain two phases, one with an orthorhombic $3c$ superstructure and a second with even lower symmetry. Pure-Na nephelines synthesized dry from gels at 1 atm were found to be single-phase (Type-A), with a different set of extra reflections from those characterizing pure-Na, Type-B nephelines.

Henderson and Roux (1977) showed that Type-B and -C nephelines inverted to hexagonal symmetry at ≤ 473 K; the inversion temperature decreased as the Ks content increased. The extra reflections and twin lamellae disappeared at the inversion, and the cell parameters became consistent with those expected for nephelines having the HBC structure. The specimens showed $\sim 30^\circ$ hysteresis, with inversion temperatures during cooling being lower than those on heating; however, the effect of cooling rate on the degree of hysteresis was not studied. All pure-Na, Type-B nephelines (A.72, A.88, A.407, and the Schairer sample) showed small steps in the a parameter at the low-temperature inversion with some specimens also having distinct steps in c , and hence discontinuities in volume (see Fig. 6, Henderson and Roux, 1977). A Type-C nepheline (N.233) showed inflections, but no steps in a and c at the inversion; the displacements in a and c were in the opposite sense so that no discontinuity in V was detected. A Type-A specimen (N.10) showed a rather different behavior. Although there was an inflection in a (but no step) at 453 K, and no apparent inflection in c , the extra reflections only disappeared above 873 K. The temperature of 453 K was equated with the low-temperature inversion observed in the other sub-potassic nephelines.

Henderson and Roux (1977) related the differences in the inversion behavior of the samples to varying degrees of collapse of the framework about the small Na cations that must occupy the larger cat-

ion site (Foreman and Peacor, 1970; Dollase, 1970). In addition it was suggested that superstructures observed in natural nephelines could also be related to framework collapse at the low-temperature inversion.

Because the thermal effects of the low-temperature inversion in nepheline are detectable by differential thermal analysis (*e.g.* Cohen and Klement, 1976), the inversion could be further characterized by differential scanning calorimetry (DSC). Because the inversion is *displacive* (in the sense of Buerger, 1951), it is important to correlate the presence or absence of a discontinuity in V , or in the coefficient of thermal expansion at the inversion, with possible changes in heat capacity or its integrated thermodynamic functions.

We have studied at least one sample of Type-A, -B, -C, and -H nephelines by DSC and the results are presented here. DSC measurements on Type-B nephelines show two heat effects at ≤ 473 K, consistent with the presence of two phases, but Henderson and Roux (1977) only identified one inversion at < 473 K in such nephelines. We have, therefore, reconsidered the results of their X-ray experiments and have further studied the low-temperature inversion with several new samples using high-temperature X-ray diffraction methods.

X-ray investigations

Sample preparation and X-ray procedures

Several of the samples are those studied by Henderson and Roux (1976, 1977), namely: A.417, N.4, NE. Schairer, and A.407. Unfortunately, there were insufficient quantities of some of Henderson and Roux' samples for heat capacity measurements, so new samples (NE.12, NE.17, and NE.1289) were synthesized hydrothermally from gels of the appropriate compositions. The compositions and synthesis conditions for the nephelines studied are summarized in Table 1. Because the nepheline type is crucially related to Ks content, the compositions for some of the synthesized samples were confirmed by determination of K_2O by atomic absorption spectrophotometry. The quoted compositions (Table 1) are believed to be accurate to ± 5 percent (relative).

Cell parameters were determined at room temperature (293 K) using a conventional Philips PW 1050 diffractometer with $\text{CuK}\alpha$ radiation ($\text{CuK}\alpha$ 1.54178, $\text{CuK}\alpha'$ 1.54051 Å) and a scanning rate of $0.5^\circ/2\theta/\text{min}$. Si was added as internal standard ($a = 5.43065$ Å) and cell parameters were calculated by least squares.

Cell parameters at elevated temperatures were determined using the method of Henderson and Taylor (1975) in which the Pt sample holder peaks were used for internal standardization. The 2θ values for the peaks were measured with a vernier rule and are reproducible to within $\pm 0.005^\circ 2\theta$.

The room temperature cell parameters (Table 1) for the sub-potassic nephelines refer to a pseudo-hexagonal cell, whereas those for Type-B nephelines are averaged values for the two phases present (Henderson and Roux, 1977, p. 293). This averaging is reflected in the relatively high standard errors for these samples.

The low-temperature inversion was studied with a heating stage mounted on an X-ray diffractometer, using a heating rate of $\sim 3^\circ \text{min}^{-1}$ and a cooling rate of $\sim 5^\circ \text{min}^{-1}$.

X-ray results

The room-temperature X-ray patterns for the three new specimens show that NE.17 (1.6 percent Ks) is Type-C whereas NE.12 (0.36 percent Ks) and NE.1289 (0.30 percent Ks) are clearly Type-B. All three specimens have anomalous cell parameters at room temperature (Table 1) and plot below the 'normal nepheline line' defined in Figure 3 of Henderson and Roux (1977). Note that the average c parameter for the two phases in NE.1289 is substantially smaller than the c parameters for the specimens studied previously.

The inversion in NE.17 was monitored using the extra reflection at $\sim 28.2^\circ 2\theta \text{CuK}\alpha$ which is characteristic of the orthorhombic $3c$ superstructure of Type-C nephelines. The reflection decreased in intensity and eventually disappeared over the temperature range $358\text{--}368\pm 5 \text{ K}$, but it reappeared on cooling with a hysteresis of $\sim 15^\circ$.

Type-B nephelines have split (002) reflections, indicating the presence of two phases. The presence of an extra reflection at $\sim 28.2^\circ 2\theta \text{CuK}\alpha$ confirms that one of the phases has the orthorhombic $3c$ superstructure whereas extra reflections at 22.6° , 29.2° , and $30.2^\circ 2\theta \text{CuK}\alpha$ presumably belong to the lower-symmetry second phase (Henderson and Roux, 1977, p. 293). Thus the inversions in NE.12 and NE.1289 (both Type-B) were monitored using the extra reflections at 28.2° and $30.2^\circ 2\theta$, and the split (002) reflection. On heating NE.12, the $28.2^\circ 2\theta$ reflection decreased and disappeared over the temperature range $413\text{--}428\pm 5 \text{ K}$. The (002) peak was broad and asymmetric at 448 K, showing that two phases were still present. The $30.2^\circ 2\theta$ reflection disappeared over the

Table 1. Synthesis conditions, composition and room temperature (293 K) cell parameters for different types of synthetic nephelines

Specimen	Ks mol %	T, K	P	Time days	a , Å	c , Å	V , Å ³
Type-A N.4*	0	1390	1 atm	1	9.963(1)**	8.341(2)	717.7(2)
Type-B Schairer*+	0	1370 1320	1 atm	{ 5 24	9.969(3)	8.361(4)	719.6(5)
A.407*	0	870	2.5 kbar	50	9.977(2)	8.339(4)	718.9(5)
NE.12	0.36	1170	1 kbar	4	9.931(6)	8.339(9)	719.5(9)
NE.1289	0.30	1240	2 kbar	3	9.995(3)	8.275(6)	715.9(5)
Type-C NE.17	1.6	990	1 kbar	3	9.990(1)	8.329(2)	719.9(2)
Type-H A.417	27	873	2 kbar	40	10.004(2)	8.390(3)	727.2(3)

* Data from Henderson and Roux (1977).

+ Glass starting material; others synthesized from gel.

** Numbers in parentheses are estimated standard deviations of parameters: a , $c \times 10^3$, $V \times 10^3$.

range $428\text{--}468\pm 5 \text{ K}$. On cooling, the extra reflections reappeared at about 15° below these temperatures. On heating NE.1289, the $28.2^\circ 2\theta$ reflection disappeared over the range $413\text{--}428\pm 5 \text{ K}$, (002) was comparatively sharp at 425 K, and the $30.2^\circ 2\theta$ extra reflection disappeared over the range $423\text{--}444\pm 5 \text{ K}$. On cooling, all of the extra reflections reappeared at $\sim 410 \text{ K}$ but broadening of (002) could only be detected at $\sim 365 \text{ K}$.

In NE.12 and NE.1289 the $28.2^\circ 2\theta$ reflection disappeared before there was any major decrease in the intensity of the $30.2^\circ 2\theta$ reflection. Further study of X-ray charts from heating experiments on Type-B nephelines N.1042 (0.2 percent Ks) and N.1040 (0.5 percent Ks) (Henderson and Roux, 1977) also showed that the extra reflections at $\sim 28.2^\circ 2\theta$ disappeared $\sim 10 \text{ K}$ before the $30.2^\circ 2\theta$ reflection began to decrease. The same relationship was reported for the pure-Na, Type-B nephelines (e.g. A.72, Henderson and Roux, 1977, p. 289). The implication is that the two phases present in Type-B nephelines invert to hexagonal symmetry over different temperature ranges (see later discussion).

The X-ray patterns for NE.12, NE.17, and NE.1289 above their respective inversion temperatures are entirely consistent with hexagonal symmetry and can be fully indexed using the HBC. Cell parameters determined above the inversions are: NE.17 (408 K) $a = 9.981 \text{ esd } 0.001$, $c = 8.360 \text{ esd } 0.002$; NE.12 (500 K) $a = 9.992 \text{ esd } 0.001$, $c = 8.366 \text{ esd } 0.002$; NE.1289 (448 K) $a = 9.983 \text{ esd } 0.001$, $c = 8.360 \text{ esd } 0.001\text{Å}$. These values plot close to the 'normal nepheline line' and in this respect the new speci-

Table 2. Change in proportions of the two phases present in Type-B nephelines after annealing near the low-temperature inversion

Specimen	Mol. % Ks	% of phase with lower c parameter	
		Before annealing	After annealing
NE. Schairer	0	30	45
A.407	0	30	30
NE.12	0.36	30	50
NE.1289	0.30	80	50
A.72	0	40	80

mens are similar to other sub-potassic nephelines immediately above their inversion temperatures (Henderson and Roux, 1977, Fig. 3).¹ Note that NE.1289 shows an increase of 0.085 Å in c relative to the room temperature value.

Henderson and Roux (1977, p. 290 and 293) reported that the proportions of the two phases in Type-B nephelines at room temperature changed with thermal treatment. We have attempted to quantify this effect by comparing the peak heights of the split components of the (002) and (004) reflections before and after annealing the samples near the low-temperature inversion for 2 to 3 hours (Table 2). Because the split components substantially overlap, the estimated proportions are not better than ± 20 percent (relative). After thermal treatment, A.72 and NE. Schairer (both pure-Na) and NE.12 (0.36 percent Ks) show *increased* proportions of the phase with the lower c parameter whereas this phase *decreased* in proportion in NE.1289 (0.30 percent Ks). All heat-treated samples show a marked increase in the intensities of the $30.2^\circ 2\theta$ extra reflection; thus it is the low-symmetry second phase that increases in amount. These relations allow the relative c parameters of the two phases in Type-B nephelines to be deduced for all samples except A.407. Thus in A.72, NE. Schairer, and NE.12 the low-symmetry second phase has the lower c parameter while the phase with the orthorhombic $3c$ superstructure has the higher c parameter. In NE.1289 the converse is true. Note that the c parameters for the low-symmetry phases in A.72 and NE.1289, estimated from the split (002) and (004) reflections, are very similar, with values of 8.325 and 8.315 Å, respectively.

Differential scanning calorimetric study

DSC procedures with the Perkin Elmer DSC-2

DSC analysis is a comparative technique involving electrical-thermal balance between a sample sealed in a gold pan against an empty reference gold pan in the twin platinum holders of an adiabatic enclosure (O'Neill, 1966). The temperature scans with the DSC

were performed at a rate of $10^\circ \text{ min}^{-1}$ with an instrument RANGE setting of $5 \text{ mV sec}^{-1} \text{ cm}^{-1}$. Temperature and energy calibrations were made relative to the melting of indium metal (429.8 K) and the α - β quartz inversion (844.0 K) (Table 3). Because of the limited amounts of material available, only one aliquot was studied for some nepheline samples. However, two different aliquots studied for each of NE.12, NE.1289, and NE.17 showed that the DSC scans were reproducible.

Because the voltage displacement on a DSC scan is a function of mass, the weights of empty gold pans, sapphire reference disc, and the powdered nepheline samples in their gold pans were determined with a digital microbalance before and after each scan. Al-

Table 3. Experimental heat capacities of pure-Na, Type-B nepheline A.407 (g.f.w. = 142.055 g) determined by differential scanning calorimetry

Temp.	Heat capacity	Temp.	Heat capacity
T Kelvin	C_p^0 J/(mol. K)	T Kelvin	C_p^0 J/(mol. K)
367.8	135.5	466.8	165.5
372.8	136.3	471.7	157.6
377.7	137.7	476.7	152.9
382.7	138.4	481.6	148.1
387.6	139.6	486.6	147.8
392.6	140.5	496.1	145.2
397.5	141.6	501.1	145.6
402.5	142.2	506.1	148.9
407.4	143.5	511.1	146.7
412.3	144.9	521.1	147.0
417.3	146.3	531.1	147.6
422.2	149.4	541.0	149.1
427.2	150.9	551.0	149.2
432.1	155.2	561.0	150.0
437.1	159.6	571.0	151.0
442.0	161.5	581.0	151.2
447.0	159.0	591.0	152.4
451.9	161.3	601.0	153.1
456.9	169.7	610.0	153.6
461.8	178.0	621.0	154.0
		630.9	154.5
		640.9	154.9
		650.9	155.9
		660.9	156.4
		670.9	157.8
		680.9	158.6
		690.9	159.3
		700.9	160.7

Heat capacity was determined with reference to α -Al₂O₃ (Ditmars and Douglas, 1971) and is believed to be accurate to within 1 percent on the basis of alternate scans on a sapphire disc and α -Al₂O₃ powder.

Temperatures were calibrated against peak onset for indium melting at 429.8 K and the α - β quartz inversion at 844.0 K and have a precision of $\sim 0.2^\circ$.

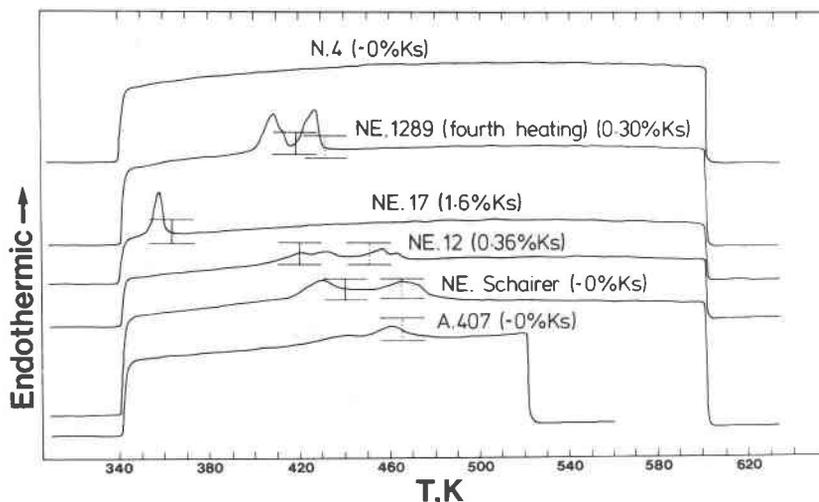


Fig. 1. Tracings of DSC scans for various nepheline samples in the temperature interval 340 to 600 K. Scans were made at 10 K min^{-1} , with a RANGE setting of 5 $\text{mcal sec}^{-1} \text{cm}^{-1}$, chart range 10 mV (= 25 cm) and chart speed 20 mm min^{-1} . The scan for NE.1289 is the fourth heating scan (after the three scans in Fig. 2). Sample weights are between 20 and 30 mg. The solid vertical lines refer to the temperatures (± 10 K) at which the extra X-ray reflections at $\sim 28.2^\circ 2\theta$ $\text{CuK}\alpha$ disappear, and the dotted vertical lines to those (± 10 K) at which the $30.2^\circ 2\theta$ $\text{CuK}\alpha$ extra X-ray reflections disappear. The displacements are a function of sample mass and heat capacity of sample and enclosing gold pans, and are measured relative to the low- and high-temperature isothermals bracketing the scans.

lowance was made for the small amounts of powdered samples that were lost during removal of the gold pans with a vacuum tool. Chart measurements were used as input for a computer program (originally written by K. Krupka, U.S. Geological Survey, Reston, and modified at ETH, Zürich) to make the necessary corrections for temperature calibration, differences in sample pan weights, energy calibration constant for the DSC instrument, and differences in low- and high-temperature isothermal baselines. The program was also used to compute the sample heat capacity relative to corundum (the sapphire reference disc), using data of Ditmars and Douglas (1971).

DSC results

Tracings of the chart recorder output for various nepheline specimens are shown in Figure 1. A scan interval of 340 to 600 K was used for N.4 (pure-Na, Type-A), NE. Schairer (pure-Na, Type-B), NE.1289 and NE.12 (both Type-B, 0.3 and 0.36 percent Ks, respectively), and NE.17 (1.6 percent Ks, Type-C). The scan interval for A.407 (pure-Na, Type-B) was 340–700 K and that for A.417 (27 percent Ks, Type-H) was 340–520 K.

The DSC scans for the Type-A, pure-Na nepheline (N.4) show only a smooth, continuous displacement without peaks over the temperature range 340 to 600 K (Fig. 1); Type-H nepheline (A.417) has a similar behavior between 340 and 520 K. The DSC scan for

the Type-C nepheline (NE.17) has a single peak near 360 K (Fig. 1). The scans for the Type-B nephelines are more complex. NE. Schairer (pure-Na) shows two broad peaks, of approximately equal intensity, near 430 and 470 K; the other pure-Na, Type-B nepheline (A.407) shows a similar overall behavior, but the lower temperature peak is less pronounced. The scan for NE.12 (0.36 percent Ks) also shows two broad double peaks some 5° below those of NE. Schairer. The scan shown in Figure 1 for NE.1289 (0.3 percent Ks) is the fourth successive heating scan for this specimen and shows two distinct peaks near 370 and 390 K, each having a shoulder possibly concealing a second peak.

The nature of the DSC scans is noticeably dependent on temperature cycling, as is well illustrated for Type-B specimen NE.1289 (Fig. 2). The first scan, made without initially cycling between the low- and high-temperature isothermals so that the sample was not annealed, produced a strong split peak near 410 K with a minute irregularity near 425 K. The second heating scan on NE.1289 included cycling the sample across the full temperature interval, thus annealing it, and showed two distinct peaks. The lower-temperature peak contains shoulders corresponding to the split peak of the first scan. The higher-temperature peak, near 425 K, corresponds to the minute irregularity near this temperature observed in the first scan. Note that the combined area under the two peaks of

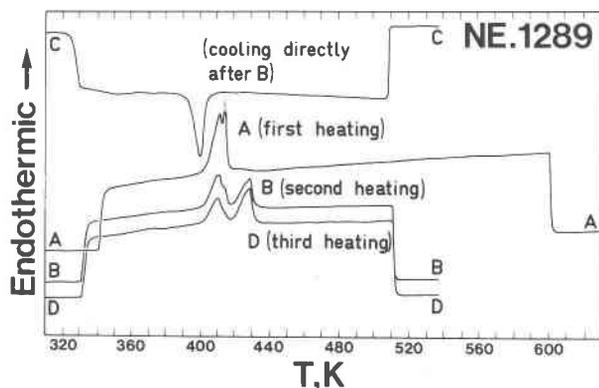


Fig. 2. Traces of DSC scans for Type-B nepheline sample NE.1289, made under the same machine conditions as for Fig. 1. Trace A represents the first heating without cycling the sample through the inversion. Curve B represents the second heating, including cycling the sample through the temperature range to adjust lower and upper isothermals. Curve C represents a cooling scan made directly after B. Curve D represents the third heating, including isothermal adjustments, made after C. See Fig. 1 for the fourth heating trace.

the second scan is similar to that under the single peak of the first scan. A cooling scan from 510 to 330 K was made directly after the second heating scan. This cooling scan revealed a single peak about 10° below and of comparable area to that of the first (unannealed) scan, and a small feature near 355 K. After the cooling scan, a third heating scan (again annealing between the low- and high-temperature isothermals) was performed and also revealed the two peaks. There was an apparent increase in the area under the higher temperature (~ 425 K) peak at the expense of the area under the lower peak (~ 410 K). The fourth heating scan on NE.1289 (Fig. 1) is similar to the third scan (Fig. 2) in terms of peak area and shape.

The presence of peaks in the DSC scans confirms the occurrence of crystallographic inversions in these nephelines, some of which may be lambda transitions (Rao and Rao, 1978, p. 22). However, it is not clear whether the broad DSC peaks in some specimens represent lambda transitions, proceeding more slowly than the α - β quartz inversion, or whether they reflect the superposition of transitions due to different composition domains in chemically zoned crystals (see later discussion). If the temperature scanning rate keeps pace with the rate of the nepheline inversion, the temperatures and areas under the DSC peaks could be used to obtain quantitative values for the heats of transition relative to the α - β quartz inversion and indium melting peaks (see later).

Discussion

Relationship between DSC and X-ray results

The absence of DSC peaks in Type-H nepheline A.417 (27 percent Ks) and the absence of discontinuities in its thermal expansion behavior (Henderson and Roux, 1976) confirm that such nephelines have the normal HBC structure at room temperature.

The absence of DSC peaks in Type-A nepheline (N.4, pure-Na) between 340 and 600 K is significant because an equivalent specimen (N.10) showed an inflection in a at 453 K. Henderson and Roux (1977) correlated this temperature with the low-temperature inversion shown by pure-Na, Type-B nephelines, but the extra X-ray reflections in N.10 did not disappear until above 873 K. The DSC results confirm that Type-A nephelines do not show the same transition near 473 K as the pure-Na, Type-B nephelines.

The single DSC peak near 360 K for Type-C nepheline NE.17 (1.6 percent Ks) can be correlated with the temperature (365 ± 5 K) at which the extra X-ray reflection near $28.2^\circ 2\theta$ disappears (Fig. 1). In addition, Type-C nepheline N.233 (0.3 percent Ks) showed inflections, but not discontinuities, in the thermal expansion of the cell edges close to the temperature at which the $28.2^\circ 2\theta$ peak disappears (Henderson and Roux, 1977, Fig. 6). It seems clear that the single DSC peak is caused by the inversion of the orthorhombic $3c$ superstructure, characteristic of Type-C nephelines, to hexagonal symmetry.

The occurrence of two peaks in the DSC scans for Type-B nephelines is consistent with the presence of two phases, as suggested by the split (002) and (004) X-ray reflections. The temperatures of the lower-temperature DSC peaks in Type-B nephelines are within ~ 10 K of those at which the extra X-ray reflection at $28.2^\circ 2\theta$ disappears (Fig. 1). By analogy with Type-C nephelines, this DSC peak is presumably caused by inversion of one of the phases from orthorhombic ($3c$ superstructure) to hexagonal symmetry. The higher-temperature DSC peaks in Type-B nephelines can be correlated with the temperatures at which the $30.2^\circ 2\theta$ extra X-ray reflection disappears (Fig. 1); this reflection is characteristic of the lower-symmetry phase. Type-B nephelines also show discontinuities in cell volumes at this temperature (e.g. NE. Schairer, Fig. 6, Henderson and Roux, 1977). The higher-temperature DSC peak can, therefore, be correlated with inversion of the low-symmetry (second) phase to hexagonal symmetry.

The assignments of the DSC peaks in Type-B nephelines are consistent with the proportions of the

phases deduced from X-ray and DSC scans for NE.1289. The increase in intensity of the higher-temperature DSC peak for NE.1289 after temperature cycling suggests that the phase producing this peak increased in proportion. This effect is also seen in the high-temperature X-ray results, which show that the phase with the higher c parameter increased in amount during annealing (Table 2). We have already deduced that in NE.1289 the low-symmetry second phase has the higher c parameter and, therefore, the higher-temperature DSC peak can be correlated with the inversion shown by this phase.

The DSC trace obtained on cooling NE.1289 immediately after the second heating (Fig. 1, scan C) shows only a single peak near 400 K. This behavior is consistent with the reappearance of both the 28.2° and $30.2^\circ 2\theta$ extra X-ray reflections at 400 ± 5 K upon cooling. Thus both inversions in NE.1289 appear to be indistinguishable on cooling. In addition, broadening, and ultimately splitting, of the (002) reflection can only be detected at ~ 363 K; this broadening may be correlated with the small feature on the DSC scan near 355 K (Fig. 2, scan C).

Dependence of inversion temperature on composition

The work of Henderson and Roux (1977) and the results of our X-ray and DSC studies demonstrate a clear relationship between increasing Ks content of nepheline and decreasing temperature of the inferred orthorhombic to hexagonal inversion. In Type-B nephelines this inversion has been correlated with the lower DSC peak (Fig. 1). The upper DSC peak also appears to be displaced to lower temperatures with increasing Ks.

The identification of two inversion peaks in the DSC study of Type-B nephelines could imply that the two phases in these samples coexist stably and have different Ks contents. Henderson and Roux (1977) considered this possibility for Ks-bearing Type-B nephelines but pointed out that it could not be the case for the supposed pure-Na, Type-B specimens. They concluded that the two phases in the latter specimens had the same composition, that the orthorhombic $3c$ superstructure was metastable, and that the lower-symmetry phase was the stable low-temperature form. Our results are not inconsistent with this interpretation, but the presence of small amounts of impurity K_2O in the nominally pure-Na nephelines could have an important effect. Partial analyses of A.407 and NE. Schairer gave $<0.005 \pm 0.005$ wt. percent and 0.008 ± 0.005 wt. percent K_2O , respectively, for these specimens (equiva-

lent to maximum values of ~ 0.03 and ~ 0.04 mol. percent Ks). The Schairer nepheline specimen, after annealing, contains approximately equal proportions of the two phases. If we assume that one of these was K-free, the other would contain ~ 0.08 percent Ks, which leads to a downward displacement of only $\sim 8^\circ$ in the inversion temperature for the Ks-bearing phase. In fact, the two DSC peaks in NE. Schairer are $\sim 35^\circ$ apart, suggesting that the existence of the two heat effects in Type-B nephelines cannot be primarily due to the two phases having different Ks contents. It is noteworthy, however, that the two DSC peaks in the Ks-bearing Type-B nephelines NE.12 and NE.1289 both have shoulders or split peaks (Fig. 1). The fine structure of the DSC scans, including split peaks and shoulders, were reproducible in repeated scans on the same sample and in second aliquots taken from NE.1289 and NE.12. These complexities may indicate the presence of phases having slightly different Ks contents in at least these samples. However, in view of the findings of Ishibashi and Takagi (1975), it is not certain whether the complexities are the result of sample configuration and thermal properties rather than due to the presence of two discrete phases.

Although Type-B nephelines NE.12 and NE.1289 have almost identical bulk compositions (0.36 and 0.30 percent Ks, respectively) they show significantly different DSC behavior on both heating and cooling (Figs. 1 and 2). These two nephelines could have different degrees of Na and K ordering between the two cation sites, but the limited amount of ordering possible for such K-poor compositions would be unlikely to cause such different behavior. In addition, both specimens are members of the $NaAlSiO_4$ - $KAlSiO_4$ series and should not contain any excess Si, which precludes the possibility that the samples may have different degrees of vacancy disorder in the larger cation site. The reason for the different behavior of NE.12 and NE.1289 is not fully understood, but it presumably is related to their very different states of framework collapse below the low-temperature inversion (see Table 1, especially the c parameters). One of the factors controlling the state of collapse is believed to be variation in the degree of Si,Al ordering in the framework of the different samples (Henderson and Roux, 1977, p. 296).

The possibility that the coexisting phases in Type-B nephelines could have different bulk Si/Al ratios cannot be excluded, but the reasons adduced by Henderson and Roux (1977, p. 295) against this possibility still seem valid to us. Although the room-tem-

perature c parameters for the orthorhombic $3c$ superstructures in A.72 and NE.1289 differ by as much as 0.12\AA , the lower-symmetry phases, which increase in amount on annealing in both specimens, have almost identical room-temperature c parameters ($8.320\pm 0.005\text{\AA}$, based on HBC-indexing). Thus phases with the orthorhombic $3c$ superstructure occur in very different states of framework collapse. These structures are almost certainly metastable, and the low-symmetry phase therefore appears to be the stable low-temperature form.

Relations between low-temperature inversions in nepheline and tridymite

Henderson and Roux (1977) related the occurrence of the low-temperature inversion in sub-potassic nephelines to the collapse of the 'tridymite-type' framework about the small Na atoms occupying the larger cation sites (Dollase, 1970; Foreman and Peacor, 1970). They also drew attention to the similar behavior of tridymite, which exhibits displacive transformations near 470 K and which forms various lower-symmetry (pseudohexagonal) cells below 470 K (Sato, 1963a,b, 1964; Dollase, 1967; Kihara, 1977; Nukui *et al.*, 1978).

Thompson and Wennemer (1979) measured the heat capacities of synthetic tridymite, cristobalite, and tridymite-cristobalite 'mixed phases' by DSC. Tridymite showed a sharp peak at 390 K and two broad, overlapping peaks in the range 436–470 K. These heat effects were correlated with the monoclinic to low-orthorhombic and low-orthorhombic to intermediate-orthorhombic tridymite inversions of Nukui *et al.* (1978).

The DSC traces for sub-potassic nephelines and tridymite are broadly similar in that DSC peaks occur within similar ranges of temperature. The single DSC peak occurring in Type-C nephelines (NE.17) has a similar form to the 390 K peak in tridymite. The two peaks occurring in Type-B nephelines (*e.g.* A.407) are similar in form and temperature range to the broad heat effects between 436 and 470 K in tridymite. These similarities support the suggestion (Henderson and Roux, 1977) that the low-temperature inversions in sub-potassic nephelines are primarily a property of framework collapse and that the interframework cations play a relatively subordinate role. Further correlation between nepheline and tridymite is not possible because we do not fully understand either the nature of the structures of the stable low-temperature forms or the role of 'structural cavities' (defects) in determining the structure. In addition,

the nature of tridymite-cristobalite 'mixed phases' is not yet known (Thompson and Wennemer, 1979), but their occurrence suggests the possible existence of analogous nepheline-carnegieite 'mixed phases.' If such structural modulations exist as domains in sub-potassic nephelines (*e.g.* in the two-phase Type-B nephelines) the problem of characterizing the stable low-temperature form of nephelines will become even more complex.

Correlation of heat capacity measurements with previous data

Our data for the heat capacity (C_p°) of nepheline A.407 (pure-Na, Type-B) are shown as a function of temperature in Figure 3. Also shown are the low-temperature (50–298 K) adiabatic calorimetric measurements for synthetic nepheline ($\text{NaAlSi}_3\text{O}_8$) and kaliophilite (KAlSi_3O_8) from Kelley *et al.* (1953). (Note that the nepheline sample used by these workers was synthesized by J. F. Schairer and presumably is similar to our specimen NE. Schairer.) Kelley *et al.* also measured the heat contents for the same synthetic nepheline sample from 387 to 1509 K by drop calorimetry and presented three linear equations of C_p° vs. T for the ranges 298–467 K (the low-temperature inversion), 467–1180 K (the high-temperature inversion), and 1180–1525 K. These equations were adopted by Robie *et al.* (1978) in their recent compilation of thermochemical data. The fits for the 298–467 K and 467–1180 K ranges are shown by short-dashed lines in Figure 3. Our C_p° data for A.407 above 500 K agree well with the 467–1180 K equation of Kelley *et al.* (1953, p. 15). However, their equation for the range 298–467 K represents only an average of measurements for sample A.407 because of the complex behavior of C_p° at the inversions. The DSC measurements (summarized in Table 3) suggest that the peaks at 439 K and 462 K may represent lambda-type transitions (see also Kelley *et al.*, 1953, p. 15).

The difficulties in evaluation of $H_T^\circ - H_{298}^\circ$ and $S_T^\circ - S_{298}^\circ$ from heat capacity measurements across broad transitions are well known (see Rao and Rao, 1978). However, the C_p° data obtained for nepheline A.407 (Table 3) have been fitted to polynomial equations covering various temperature ranges. The smoothed values of C_p° and the integrated functions, $H_T^\circ - H_{298}^\circ$ and $S_T^\circ - S_{298}^\circ$ are presented in Table 4. The heat involved in the transition (Fig. 3) for the inversions in A.407 was estimated by subtracting 14229 J mol^{-1} , the area between 400 K and 500 K below the extrapolated 467–1180 K C_p° equation of Kelley *et al.*, from the integrated areas in Table 4 (15397 J mol^{-1}). The

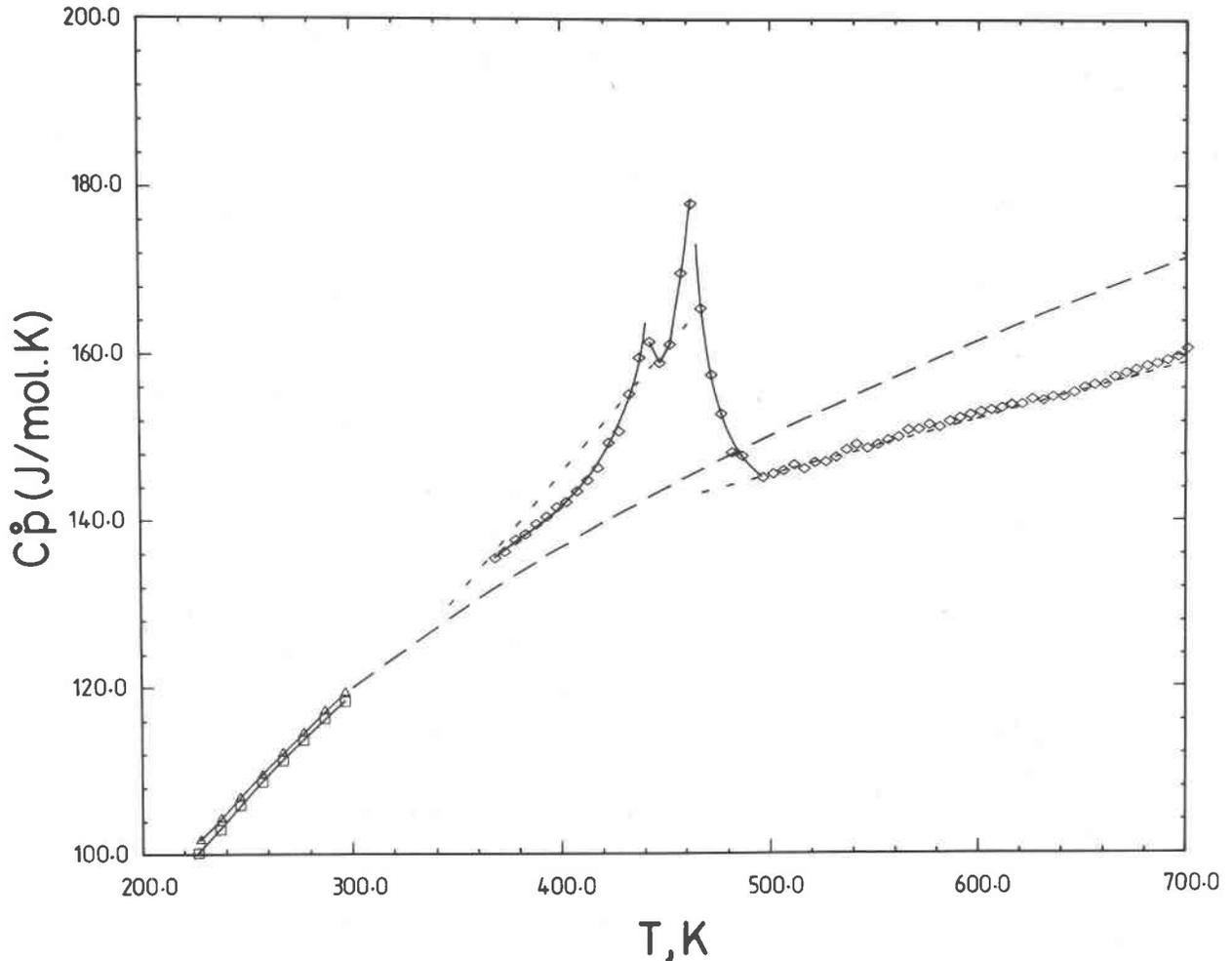


Fig. 3. Heat capacity (C_p°) in joules mol⁻¹ K⁻¹ as a function of temperature for the specimen of pure-Na, Type-B nepheline A.407 measured by DSC (\diamond symbols between 370 and 700 K); note the presence of two peaks near 440 and 460 K. Also shown are data points for synthetic nepheline (\square , NaAlSi₃O₈) and kaliophilite (\triangle , KAlSi₃O₈) to 298 K determined by adiabatic calorimetry (Kelley *et al.*, 1953). The short-dash lines, passing approximately through the transitions to 467 K and from 467 to 700 K, refer to the fits to the drop calorimetric data for NaAlSi₃O₈ (Kelley *et al.*, 1953). The long-dash curve refers to equivalent fits for KAlSi₃O₈ (see Robie *et al.*, 1978, p. 405–416).

resulting value for the heat of transition (1168 J mole⁻¹) is not noticeable on the scale of Figure 4 of Kelley *et al.*, and has not been used to introduce discontinuities into the integrated functions $H_T^\circ - H_{298}^\circ$ and $S_T^\circ - S_{298}^\circ$ presented in Table 4.

Although the 298–467 K C_p° equation of Kelley *et al.* represents an average of our measurements for sample A.407, it will only be valid for nominally pure-Na, Type-B nephelines because the heat capacity relationships for Ks-bearing Type-B and -C nephelines will clearly be different from those for the specimen of Kelley *et al.* (*cf.* NE. Schairer with Ks-bearing nephelines in Fig. 1). In addition, we have shown that Type-H nephelines do not exhibit any

DSC peaks between 340 and 520 K; the only nephelines likely to show such peaks in this temperature range are those with <2.5 percent Ks. The natural nephelines occurring in igneous and metamorphic rocks (*e.g.* Dollase and Thomas, 1978) and meteorites (*e.g.* Allende; Grossman and Steele, 1976) invariably contain more than 2.5 percent Ks and should show smooth curves of C_p° vs. temperature with no discontinuities. Therefore, although the equation of Kelley *et al.* between 467 and 1180 K can be used as a reference in thermochemical calculations applied to *natural* nephelines, the equation below 467 K will normally not be valid. Similar reasoning can be used to justify the extrapolation of the equation of Kelley *et*

Table 4. Smoothed molar thermodynamic properties for nepheline A.407 (NaAlSi₃O₈)

T	C_p^0	$H_T^0 - H_{298}^0$	$S_T^0 - S_{298}^0$
Kelvin	J/(mol. K)	J/(mol.)	J/(mol. K)
298.15	119.2	0	0
300.0	119.7	221	0.7
350.0	131.4	6501	20.1
360.0	133.5	7826	23.8
370.0	135.7	9172	27.5
380.0	137.9	10540	31.2
390.0	140.0	11930	34.8
400.0	142.0	13340	38.3
405.0	142.1	14056	40.1
410.0	142.9	14775	41.9
415.0	144.3	15499	43.6
420.0	146.3	16231	45.9
425.0	149.0	16976	47.1
430.0	152.3	17735	48.9
435.0	156.3	18513	50.7
440.0	160.9	19312	52.5
445.0	158.8	20119	54.4
450.0	160.6	20913	56.1
455.0	166.2	21727	57.9
460.0	174.8	22579	59.8
470.0	160.4	24263	63.4
480.0	150.2	25811	66.7
490.0	145.5	27285	69.7
500.0	145.7	28737	72.7
510.0	146.4	30197	75.5
520.0	147.1	31664	78.4
540.0	148.5	34620	84.0
560.0	149.9	37604	89.4
580.0	151.3	40616	94.7
600.0	152.7	43657	99.8
620.0	154.2	46726	104.9
640.0	155.6	49823	109.8
660.0	157.0	52949	114.6
680.0	158.4	56103	119.3
700.0	159.8	59285	123.9

The low temperature adiabatic data for nepheline (Kelley *et al.*, 1953) was included in the smoothing of the data and thus 298.15 K is the chosen reference temperature. It is, therefore, assumed that no further transitions occur between 298 and 370 K. Note that the integrated functions have not been adjusted for heat or entropy of transition.

al. over the range 467–1180 K to temperatures above 1180 K, because the high-temperature inversion in nepheline only occurs in specimens with <5 wt. percent Ks (Tuttle and Smith, 1958).

Conclusions

Both DSC and X-ray studies indicate that the inversion characteristics of sub-potassic nephelines are dependent upon nepheline type. Type-C nephelines (0.7 to 2.5 percent Ks) have a single, sharp DSC peak between 340 and 600 K. The temperature at which this transition occurs may be correlated with the orthorhombic (3c superstructure)–hexagonal inversion. Type-B nephelines (<0.7 percent Ks) have two DSC peaks below 480 K. The lower-temperature transition may be correlated with the orthorhombic–hexagonal

inversion (*cf.* Type-C) and the upper-temperature transition with the low-symmetry (second phase)–hexagonal inversion. In contrast, Type-H nephelines (>2.5 percent Ks) show no DSC peaks indicative of transitions or inversions between 340 and 520 K; they are hexagonal at room temperature. Type-A nephelines (pure-Na) also have no transitions between 340 and 600 K.

Similarities between the DSC scans of sub-potassic nephelines and tridymite support the suggestion that low-temperature inversions in nepheline are primarily caused by collapse of the framework. The inter-framework cations appear to have only a modifying effect.

In experimental studies of nephelines, the proportions of NaAlSi₃O₈–KAlSi₃O₈–□SiSi₃O₈ (tridymite) and the amount of framework or interframework order–disorder will influence the inversion characteristics and possibly the phase relations, especially if metastable structures occur. These complicating factors should be considered when natural nephelines from igneous and metamorphic rocks are studied. For studies attempting to obtain thermochemical properties for nepheline solid-solutions, the equation of Kelley *et al.* (1953) fitting the heat capacity data for pure-Na nepheline above 467 K can be applied to Ks-bearing nephelines. However, the Kelley *et al.* equation between 298 and 467 K is an averaged fit which, because of complexities introduced by the occurrence of the low-temperature inversions, is specific to pure-Na, Type-B nephelines.

Acknowledgments

We thank Dr. J. Roux for supplying the sample of NE.1289. The differential scanning calorimeter is supported by the ETH Special Project Funds. We also thank K. Krupka for an extremely helpful review of the original manuscript. The work at Manchester was supported by the Natural Environment Research Council.

References

Buerger, M. G. (1951) Crystallographic aspects of phase transformations. In R. Smoluchowski, Ed., *Phase Transformations in Solids*, p. 183–211. Wiley, New York.
 Cohen, L. H. and W. Klement, Jr. (1976) Effect of pressure on reversible solid–solid transitions in nepheline and carnegieite. *Mineral. Mag.*, 40, 487–492.
 Ditmars, D. A. and T. B. Douglas (1971) Measurements of the relative enthalpy of pure α-Al₂O₃ (NBS Heat capacity and enthalpy standard reference material No. 720) from 273 to 1173 K. *J. Res. Natl. Bur. Stands.*, 75A, 401–420.
 Dollase, W. A. (1967) The crystal structure at 220°C of orthorhombic high tridymite from the Steinbach meteorite. *Acta Crystallogr.*, 23, 617–623.
 — (1970) Least-squares refinement of the structure of a plutonic nepheline. *Z. Kristallogr.*, 132, 27–44.

- and W. M. Thomas (1978) The crystal chemistry of silica-rich, alkali-deficient nepheline. *Contrib. Mineral. Petrol.*, **66**, 311–318.
- Donnay, G., J. F. Schairer and J. D. H. Donnay (1959) Nepheline solid solutions. *Mineral. Mag.*, **32**, 93–109.
- Foreman, N. and D. R. Peacor (1970) Refinement of the nepheline structure at several temperatures. *Z. Kristallogr.*, **132**, 45–70.
- Grossman, L. and I. M. Steele (1976) Amoeboid olivine aggregates in the Allende meteorite. *Geochim. Cosmochim. Acta*, **40**, 149–155.
- Hahn, T. and M. J. Buerger (1955) The detailed structure of nepheline $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$. *Z. Kristallogr.*, **106**, 308–338.
- Henderson, C. M. B. and J. Roux (1976) The thermal expansions and crystallographic transformations of some synthetic nephelines. *Prog. Exp. Petrol.*, *N.E.R.C. Rep.* **3**, 60–69.
- and ——— (1977) Inversions in sub-potassic nephelines. *Contrib. Mineral. Petrol.*, **61**, 279–298.
- and D. Taylor (1975) Thermal expansion by X-ray diffraction: the use of the specimen holder as the internal standard and the expansion of MgO (periclase) and MgAl_2O_4 (spinel). *Trans. Brit. Ceram. Soc.*, **74**, 55–57.
- Ishibashi, Y. and Y. Takagi (1975) Comments on specific heat measurements. *Jap. J. Appl. Phys.*, **14**, 637–642.
- Kelley, K. K., S. C. Todd, R. L. Orr, E. G. King and K. R. Bonnickson (1953) Thermodynamic properties of sodium–aluminum and potassium–aluminum silicates. *U.S. Bur. Mines, Rep. Invest.* **4955**.
- Kihara, K. (1977) An orthorhombic superstructure of tridymite coexisting between about 105 and 180°C. *Z. Kristallogr.*, **146**, 185–203.
- Nukui, A., H. Nakazawa and M. Akao (1978) Thermal changes in monoclinic tridymite. *Am. Mineral.*, **63**, 1252–1259.
- O'Neill, M. J. (1966) Measurement of specific heat functions by differential scanning calorimetry. *Anal. Chem.*, **38**, 1331–1336.
- Rao, C. N. R. and K. J. Rao (1978) *Phase Transitions in Solids*. McGraw-Hill, New York.
- Robie, R. A., B. S. Hemingway and J. R. Fisher (1978) Thermodynamic properties of minerals and related substances at 298.15 K and one bar (10^5 pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* **1452**.
- Sato, M. (1963a) X-ray study of tridymite (1). On tridymite M and tridymite S. *Mineral. J. (Japan)*, **4**, 115–130.
- (1963b) X-ray study of tridymite (2). Structure of low tridymite, type M. *Mineral. J. (Japan)*, **4**, 131–146.
- (1964) X-ray study of tridymite (3). Unit cell dimensions and phase transition of tridymite, type S. *Mineral. J. (Japan)*, **4**, 215–225.
- Thompson, A. B. and M. Wennemer (1979) Heat capacities and inversions in tridymite, cristobalite, and tridymite–cristobalite mixed phases. *Am. Mineral.*, **64**, 1018–1026.
- Tuttle, O. F. and J. V. Smith (1958) The nepheline–kalsilite system II. Phase relations. *Am. J. Sci.*, **256**, 571–589.

*Manuscript received, April 2, 1979;
accepted for publication, April 4, 1980.*