Structure of a Potassium-Ion-Exchanged Nepheline Hydrate I Crystal

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A nepheline hydrate I crystal, ion-exchanged using KCl(aq) at 80°C, was found to be orthorhombic, space group $Pnm2_1$, $a = 8.113(3)$, $b = 15.223(2)$, $c = 5.1817(7)$ Å and showed no superlattice X-ray reflections. Structure analysis by means of Fourier and least-squares methods led to the composition $K_{1.1}Na_{1.9}Al_3Si_3O_{12} \cdot H_2O$ ($Z = 2$, $D_c = 2.40$ g cm^{-3}) and the agreement factors: $R = 0.032$ and $R_w = 0.040$. Species assigned to the observed extra framework sites were K(1), K(2), and W(1) in the 8-ring tunnels along c plus Na(1) and Na(2) in the smaller 6-ring voids forming connections in the b direction. The atoms Na(1) and Na(2) coordinated framework oxygens exclusively and were but little affected by the ion-exchange process; K(1) was found near the center of an 8-ring and had five O atoms and two water molecules as closest neighbors, while the weakly occupied K(2) site was near a 6-ring and was found to have a coordination consisting of at least five oxygens and one water. The 10% vacancy of Na(2) is compensated for by an equal amount of K(2), which does not enter the Na(2) site for steric reasons. © 1984 Academic Press, Inc.

Introduction

In the synthetic tektosilicate nepheline hydrate I (NHI), $Na_3Al_3Si_3O_{12} \cdot 2H_2O$, there is a two-dimensional pore system of moderate openness (*1*). The channels in the anionic framework permit the diffusion of cations and water molecules at room temperature. An X-ray crystallographic study of K$^+$-exchanged nepheline hydrate I (KNHI) was made in order to see how the NHI structure accommodates this particular alkali ion. Previously, the Cs$^+$ form (CsNHI) has been shown to contain Na$^+$ ions which were nonexchangeable at 80°C (*2*), a situation which might not be paralleled when a smaller ion like K$^+$ was used. A further point of general interest is the frequent formation of superstructures when

NHI is ion-exchanged. Similar structural phenomena are exhibited by many minerals (*3*), e.g., rock-forming tektosilicates like plagioclase feldspars of intermediate composition, nephelines, cancrinites, and sodalites.

Experimental

Sodium-aluminosilicate glass with a molar ratio of Si/Al ~ 1 was crystallized by treatment with aqueous NaOH at 200°C. This produced NHI crystals in sizes suitable for X-ray work, accompanied by small amounts of a cancrinite phase.

A 0.03-g sample was treated with 10 ml of 0.5 mole liter^{-1} KCl solution in a plastic tube at 80°C for a total duration of 2 weeks. The solution was renewed after 1 week. Af-

Temperature	20°C
Radiation	MoKα (graphite monochromator)
2θ interval	6–70°
ω-2θ scan width, Δ2θ	2.4° + α₁α₂ splitting
Scan rate	1.0–29.3° min⁻¹
Total background time	0.75 × scan time
Linear absorption coefficient, μ	1.04 mm⁻¹
Range of transmission factors	0.91–0.93
Number of reflections measured	1685
Number of reflections with zero weight	647
Number of reflections in final refinement, m	1038
Number of parameters refined, n	121
$R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$	0.032
$R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$	0.040
$S = [\Sigma w(|F_0| - |F_c|)^2/(m - n)]^{1/2}$	1.02

ter the ion exchange some crystals appeared cracked under the microscope.

The KNHI crystals contained K, Na, Al, Si, and small amounts of Fe, all elements were detected by energy-dispersive X-ray analysis in a Philips EM 400 electron microscope. Weissenberg films (CuKα radiation) indicated that the Laue class was still *mmm*. Of the four crystals tested only one showed weak, but distinct, superlattice diffractions which could not be indexed on a cell of approximate size: 8 × 15 × 5 Å. The crystal chosen for data collection on the Nicolet *P3m* diffractometer exhibited no evidence of a superstructure and had the dimensions 0.09 × 0.11 × 0.15 mm. Diffractometer data (28 θ's) gave the orthorhombic cell: a = 8.113(3), b = 15.223(2), c = 5.1817(7) Å, and V = 640.0 Å³. Information on the diffraction experiment and the following data reduction is given in Table I. Since the systematic absences $0kl: k + l = 2n + 1$ were evident in the diffraction material (one octant with all $h,k,l > 0$) it was assumed that the space group of CsNHI, $Pnm2_1$, could be used, see Table IV for equivalent positions. I and $\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects. Only a random

variation of intensity could be detected for the check reflection 2 2 1. Reflections with $I < 3\sigma(I)$ were excluded from the refinements.

Structure Refinement

Initial phasing was obtained by means of the Al, Si, and O atom positions in NHI and the extra-framework electron density was localized by conventional difference Fourier and least-squares methods, using scattering factors and anomalous scattering coefficients for neutral atoms from Ref. (4).

In addition to Na(1) and Na(2), which were situated in their original positions in the small voids, limited by 6-rings, which connect the 8-ring channels running in the c direction, three sites (I–III) were recognized within the 8-ring channels. Sites I and II consisted of two poorly resolved difference Fourier peaks near the center of an 8-ring. Peak I had a maximum density of 6.7 e Å⁻³ and it contained more electrons than the nearby peak II. Site III was located near a 6-ring and had a maximum density of 1.8 e Å⁻³. In order to compensate for the charge of the negative tetrahedral framework, each 8-ring tunnel should contain ∼1K⁺ per unit cell. Since these ions must be placed in a general fourfold position the occupancy factor (g) of K⁺ is not expected to exceed the value 0.5 by any considerable amount. This partial occupancy prevented a straightforward identification of the integrated electron densities and one water molecule (W) could also easily be refined as ∼0.5 K⁺. Further complication arose from the fact that the distances of both K⁺ and W to framework O atoms were expected to be ∼3 Å.

Different occupancy refinements of the channel species gave g = 0.49–0.50 and 0.44–0.45 for Na(1) and Na(2), respectively, which means that there are some vacancies in the Na(2) site. The same refine-

TABLE II

ATOMIC COORDINATES, DISPLACEMENTS, AND
OCCUPANCY FACTORS

Atom	x	y	z	B_{eq} (Å^2)	g
K(1)	0.4511(7)	0.2403(6)	0.938(1)	8.4(2)	0.50
K(2)	0.366(2)	0.3251(9)	0.719(4)	1.3(2)^a	0.05
Na(1)	0.1630(3)	0.00	0.7802(6)	1.29(5)	0.50
Na(2)	0.1805(3)	0.50	0.7832(7)	1.22(6)	0.45
Al(1)	0.4027(2)	0.50	0.2540(8)	0.51(3)	0.50
Al(2)	0.0999(1)	0.14539(6)	0.2440(5)	0.65(2)	1.0
Si(1)	0.3835(2)	0.00	0.25	0.65(2)	0.50
Si(2)	0.1159(1)	0.35757(6)	0.2429(5)	0.73(2)	1.0
O(1)	0.4207(4)	0.00	0.559(1)	1.08(8)	0.50
O(2)	0.4472(4)	0.50	0.5864(9)	0.97(7)	0.50
O(3)	0.2774(3)	0.0854(2)	0.1695(8)	1.42(6)	1.0
O(4)	0.2855(3)	0.4084(2)	0.1723(8)	1.32(6)	1.0
O(5)	0.0259(3)	0.1104(2)	0.5433(8)	1.27(6)	1.0
O(6)	0.0538(3)	0.3873(2)	0.5274(8)	1.24(6)	1.0
O(7)	0.1515(3)	0.2544(2)	0.2225(9)	1.74(5)	1.0
W(1)	0.477(1)	0.2865(7)	0.897(3)	4.6(3)	0.50

^{a} B_{iso}.

finement of this model gave the lowest agreement factors and provided the best coordination for the whole arrangement of extra framework species. With isotropic displacement factors and least-squares minimizing of $\Sigma w(|F_0| - |F_c|)^2$, the refinement reached $R = 0.057$ and $R_w = 0.067$. After introduction of anisotropic displacements for all atoms, except K in site III, and with weights $w^{-1} = \sigma^2(|F_0|) + (0.02|F_0|)^2 + 0.2$, the refinement converged (Table I). Inspection of the final difference map disclosed spurious peaks having a maximum electron density of 0.53 e Å^{-3}. Structural parameters are given in Tables II and III, while distances and angles are presented in Table IV.

ments gave 0.06 K or 0.14–0.15 W in site III, while the g's of sites I and II could not be properly refined, probably due to the fact that they are so close. Trial refinements of several distributions of K and W over the three sites were made. The model finally selected had 0.5 K(1), 0.5 W(1), and 0.05 K(2) in sites I, II, and III, respectively. Re-

Discussion

A projection of the KNHI structure along c is presented in Fig. 1. When the lattice parameters of KNHI are compared with those of the starting material the following changes are found: $\Delta a = -1.2\%$, $\Delta b = +1.4\%$, $\Delta c = -0.8\%$. The overall result is a crystal volume decrease of 0.6% and thus the response of the framework structure to

TABLE III

ANISOTROPIC DISPLACEMENT FACTORS OF THE FORM $\exp(-\beta_{11} \cdot h^2 - \ldots -2\beta_{12} \cdot hk - \ldots)$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0.0226(9)	0.0136(6)	0.063(3)	−0.0075(6)	0.018(1)	−0.010(1)
Na(1)	0.0050(3)	0.00158(8)	0.010(1)	0.0	−0.0005(5)	0.0
Na(2)	0.0041(3)	0.00167(9)	0.009(1)	0.0	−0.0018(5)	0.0
Al(1)	0.0017(1)	0.00076(5)	0.0035(5)	0.0	−0.0002(4)	0.0
Al(2)	0.0033(1)	0.00052(4)	0.0055(4)	0.00015(4)	0.0003(3)	0.0002(2)
Si(1)	0.0024(1)	0.00079(4)	0.0056(5)	0.0	0.0003(4)	0.0
Si(2)	0.0031(1)	0.00067(3)	0.0070(4)	−0.00019(4)	−0.0003(3)	0.0001(1)
O(1)	0.0032(4)	0.0020(2)	0.005(1)	0.0	−0.0012(7)	0.0
O(2)	0.0025(4)	0.0019(2)	0.005(1)	0.0	−0.0010(6)	0.0
O(3)	0.0056(3)	0.0015(1)	0.013(1)	0.0013(2)	0.0020(5)	0.0006(3)
O(4)	0.0049(3)	0.0013(1)	0.014(1)	−0.0013(2)	0.0023(5)	−0.0009(3)
O(5)	0.0053(3)	0.0016(1)	0.009(1)	0.0008(2)	0.0024(6)	0.0005(3)
O(6)	0.0051(3)	0.0018(1)	0.007(1)	−0.0006(2)	0.0003(6)	−0.0008(3)
O(7)	0.0069(3)	0.00060(7)	0.026(1)	0.0001(1)	−0.0002(6)	−0.0001(5)
W(1)	0.009(1)	0.0022(3)	0.087(8)	0.0004(5)	0.020(3)	0.001(1)

TABLE IV

SOME INTERATOMIC DISTANCES (Å) AND ANGLES (°)

(a) Tetrahedral framework

Al(1)–O(4)	1.740(3)	Al(2)–O(7)	1.715(3)
Al(1)–O(4^{vii})	1.740(3)	Al(2)–O(5)	1.746(4)
Al(1)–O(1^{xii})	1.752(5)	Al(2)–O(3)	1.748(3)
Al(1)–O(2)	1.760(6)	Al(2)–O(6^{xiii})	1.750(4)
Mean	1.748	Mean	1.740
O(4)–Al(1)–O(4^{vii})	106.5(2)	O(5)–Al(2)–O(6^{xiii})	103.7(2)
O(1^{xii})–Al(1)–O(4)	107.9(2)	O(3)–Al(2)–O(7)	106.9(1)
O(1^{xii})–Al(1)–O(4^{vii})	107.9(2)	O(3)–Al(2)–O(6^{xiii})	107.3(2)
O(2)–Al(1)–O(4)	110.5(2)	O(3)–Al(2)–O(5)	108.7(2)
O(2)–Al(1)–O(4^{vii})	110.5(2)	O(6^{xiii})–Al(2)–O(7)	114.0(2)
O(1^{xii})–Al(1)–O(2)	113.3(2)	O(5)–Al(2)–O(7)	115.9(2)
Mean	109.4	Mean	109.4
Si(1)–O(3)	1.614(3)	Si(2)–O(7)	1.600(3)
Si(1)–O(3^i)	1.614(3)	Si(2)–O(4)	1.620(3)
Si(1)–O(2^{xiv})	1.614(4)	Si(2)–O(5^{xiii})	1.622(4)
Si(1)–O(1)	1.631(6)	Si(2)–O(6)	1.622(5)
Mean	1.618	Mean	1.616
O(3)–Si(1)–O(3^i)	107.3(2)	O(5^{xiii})–Si(2)–O(6)	106.0(2)
O(2^{xiv})–Si(1)–O(3)	108.6(2)	O(4)–Si(2)–O(7)	107.5(2)
O(2^{xiv})–Si(1)–O(3^i)	108.6(2)	O(4)–Si(2)–O(5^{xiii})	108.4(2)
O(1)–Si(1)–O(3)	110.6(2)	O(4)–Si(2)–O(6)	109.6(2)
O(1)–Si(1)–O(3^i)	110.6(2)	O(5^{xiii})–Si(2)–O(7)	112.4(2)
O(1)–Si(1)–O(2^{xiv})	111.0(2)	O(6)–Si(2)–O(7)	113.0(2)
Mean	109.5	Mean	109.5
Al(1)–O(2)–Si(1^{xv})	133.5(2)		
Al(1^{xvi})–O(1)–Si(1)	135.8(3)		
Al(2)–O(5)–Si(2^{ii})	136.0(2)		
Al(2^{ii})–O(6)–Si(2)	136.4(2)		
Al(1)–O(4)–Si(2)	142.4(3)	Range of distance	3.101(4)–
Al(2)–O(3)–Si(1)	143.4(2)	Al–Si:	3.233(1)
Al(2)–O(7)–Si(2)	154.3(2)	Mean distance	
Mean	141.2	Al–Si:	3.163

(b) NaO$_7$ polyhedra

Na(1)–O(5)	2.360(4)	Na(2)–O(2)	2.392(5)
–O(5^i)	2.360(4)	–O(6)	2.399(4)
–O(1)	2.383(5)	–O(6^{vii})	2.399(4)
–O(3^{iv})	2.573(5)	–O(4^{iv})	2.596(5)
–O(3^{vi})	2.573(5)	–O(4^{viii})	2.596(5)
–O(6^{ii})	2.771(4)	–O(5^{ii})	2.728(4)
–O(6^{ix})	2.771(4)	–O(5^{iii})	2.728(4)

(c) K–O distances shorter than the smallest K–T distance

K(1)–W(1^{xi})	2.48(2)	K(2)–W(1^x)	2.70(2)
–O(3^{xi})	2.851(7)	–O(4^{iv})	2.75(2)
–W(1^x)	2.89(2)	–O(2)	2.83(2)
–O(3^{iv})	2.997(9)	–O(6)	2.88(2)
–O(4^{iv})	3.135(9)	–O(4)	3.17(2)
–O(4^{xi})	3.403(8)	–O(3^{xi})	3.21(1)
–O(7^{xi})	3.413(7)		

(d) Water molecule

W(1)–O(4^{iv})	2.81(1)	O(3^{xi})–W(1)–O(4^{iv})		97.8(3)
–O(3^{xi})	3.03(1)	O(3^{xi})–	–O(7^{iv})	148.7(4)
–O(7^{iv})	3.17(1)	O(3^{xi})–	–O(7^{xi})	52.9(2)
–O(7^{xi})	3.21(1)	O(4^{iv})–	–O(7^{iv})	51.1(2)
		O(4^{iv})–	–O(7^{xi})	142.2(4)
		O(7^{iv})–	–O(7^{xi})	154.4(4)

TABLE IV—Continued

Symmetry code

(None)	x, y, z^a	(ix)	$-x, -\frac{1}{2} + y, \frac{1}{2} + z$
(i)	$x, -y, z^a$	(x)	$1 - x, \frac{1}{2} - y, -\frac{1}{2} + z$
(ii)	$-x, \frac{1}{2} - y, \frac{1}{2} + z^a$	(xi)	$1 - x, \frac{1}{2} - y, \frac{1}{2} + z$
(iii)	$-x, \frac{1}{2} + y, \frac{1}{2} + z^a$	(xii)	$1 - x, \frac{1}{2} + y, -\frac{1}{2} + z$
(iv)	$x, y, 1 + z$	(xiii)	$-x, \frac{1}{2} - y, -\frac{1}{2} + z$
(vi)	$x, -y, 1 + z$	(xiv)	$1 - x, -\frac{1}{2} + y, -\frac{1}{2} + z$
(vii)	$x, 1 - y, z$	(xv)	$1 - x, \frac{1}{2} + y, \frac{1}{2} + z$
(viii)	$x, 1 - y, 1 + z$	(xvi)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} + z$

^{a} Equivalent positions of space group $Pnm2_1$.

the K$^+$ exchange is quite similar to that in the Cs$^+$ case. The T–O distances in Table IVa indicate a nearly complete long-range ordering of Si and Al into adjacent tetrahedra. A small amount of iron, presumably stemming from the steel autoclaves, was detected in the qualitative chemical analysis and it is Fe(III) which is the stable state of oxidation under the conditions of synthesis—high alkalinity and the presence of O$_2$. This ferric ion probably substitutes for tetrahedral Al in KNHI, as in the synthetic pollucite, CsFeSi$_2$O$_6$ (5) and the synthetic microcline, RbFeSi$_3$O$_8$ (6). With an Fe–O distance of 1.88 Å as in Ref. (6), a linear interpolation shows that a minor substitution of Al(III) by, say, 5 at.%, Fe(III) is compatible with the observed (Al,Fe)–O distances in KNHI.

The O atom environments (irregular monocapped trigonal prisms) of Na(1) and
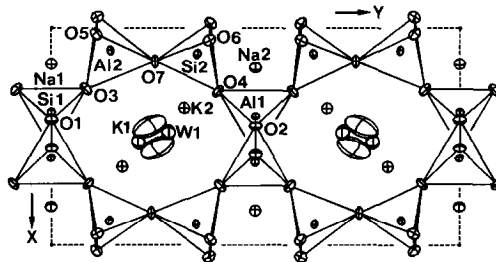

FIG. 1. The structure of K$^+$-exchanged nepheline hydrate I projected on the ab plane. Displacement ellipsoids are drawn at the 50% probability level. Only half of the K(1), K(2), and W(1) sites of an 8-ring tunnel are occupied at any one time.
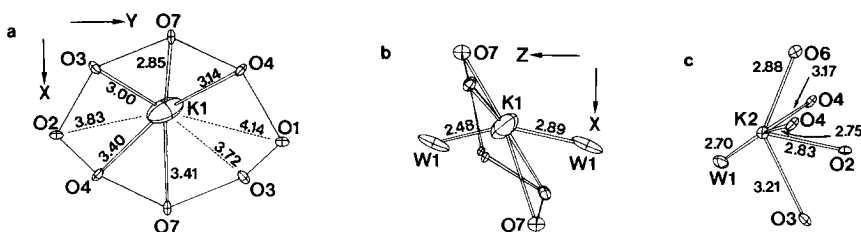
FIG. 2. Environments of K$^+$ with displacement ellipsoids of 50% probability, distances in Ångströms. (a) K(1), *ab* projection, (b) K(1), *ac* projection, (c) K(2), seen approximately along **c**.

Na(2) are nearly identical in KNHI and CsNHI, with differences in the Na–O distances that amount to ~0.02 Å. About 10% of the Na(2) ions have diffused out of the small voids, while the Na(1) ions are still intact, according to the structural calculations.

The assignation of K$^+$ to site I and a water molecule to site II is supported by the difference in electron density at the two sites. K(1) is situated near the center of an elongated ring of eight O atoms (Fig. 2a), of which five are more closely approached. Two water molecules, on either side of the ring, related by a translation of 1*c*, complete the coordination sphere of K$^+$ (Fig. 2b). The K–O distances range from 2.5 Å and upward, i.e., all distances except K(1)–$W(1^{xi})$ are considerably greater than the sum of Pauling radii (2.73 Å). The large displacement ellipsoid of K(1) indicates either thermal vibration or a distribution of individual K atoms over several closely spaced sites, this displacement of the cation could also be the cause of the elongated ellipsoid of $W(1)$. It is, in general, impossible to distinguish between positional and thermal disorder by means of an X-ray diffraction experiment performed at a single temperature. In the case of KNHI the situation is further complicated by the fact that the K(1) and $W(1)$ sites, though not occupied simultaneously, are as close as 0.76 Å, while the experimental resolution is 0.62 Å. As can be seen in Table IVd there are framework O atoms in the environment of

$W(1)$ suitable for hydrogen bonding. A different model with 0.25 K at both sites I and II was refined to $R = 0.035$, but this model was ruled out since it leads to a ring-shaped, flat coordination of K$^+$ which is typical for dehydrated zeolites, e.g., the 8-ring site, K(2), in dehydrated K$^+$-exchanged zeolite A, $K_{12}Al_{12}Si_{12}O_{48}$ (7) or the 8-ring site, KIV in dehydrated K$^+$-exchanged mordenite, $K_8Al_8Si_{40}O_{96}$ (8). Hydrated zeolites usually contain K$^+$ in an irregular polyhedron, with rather undefined limits, consisting of both water molecules and O atoms from the tetrahedral frame. Examples are amicite, $K_4Na_4Al_8Si_8O_{32} \cdot 10H_2O$ with $CN = 7$, $d(K–O) = 2.72–3.07$ Å (9) and phillipsite, $KCaAl_3Si_5O_{16} \cdot 6H_2O$, $CN = 12$, $d(K–O) = 2.94–3.51$ Å (10); while in offretite, $KCaMgAl_5Si_{13}O_{36} \cdot 15H_2O$ (11), there is a K$^+$ ion which coordinates six O atoms at 2.96 Å plus six more at 3.33 Å and *no* water molecules. The opposite extreme is also found in this particular structure, cations which exclusively coordinate water molecules and no framework oxygens. The anhydrous K$^+$ ion in offretite is not easily replaced by ion exchange and this is comparable to Na(1) and Na(2) in NHI. Water-free potassium tektosilicates exhibit K$^+$ environments similar to the hydrated species, for example, sanidine, $KAlSi_3O_8$, which has nine O atoms at 2.71–3.14 Å (12); tetragonal leucite, $KAl Si_2O_6$, that has six O atoms at 2.96 to 3.14 Å (13); and nepheline, $KNa_3Al_4Si_4O_{16}$, with nine oxygens at 2.99–3.04 Å (14).

K(2) in the third site, with low population, coordinates at least five framework O atoms and one water molecule (Fig. 2c). All of these framework oxygens belong to the same 6-ring, except O(3). The occupancy factor of K(2) refines to nearly the same value as $\frac{1}{2} - g(\text{Na}(2))$. This is done without constraints and with a correlation matrix coefficient which has an absolute value of less than 0.5. The absence of Na(2), when K(2) is present in the 8-ring tunnel should be favorable since the distance from K(2) to Na(2) is only 3.08 Å. If site III was instead occupied by water molecules, it would be difficult to explain the low occupancy of this site in the crystal as a whole.

The composition used in the final refinements was $K_{1.1}Na_{1.9}Al_3Si_3O_{12} \cdot H_2O$ ($Z = 2$) and this gave a calculated crystal density of 2.40 g cm^{-3}.

Final Remarks

This study shows that all Na$^+$ ions in the 8-ring channels of NHI are readily replaced by K$^+$ at 80°C. There is also some evidence that it is possible to remove a small fraction of the sodium atoms situated in the smaller 6-ring voids. The K(2) atoms which provide a substitute for the missing Na(2) atoms are situated on the opposite side of the 6-ring of oxygens which form a window between the small void and the 8-ring tunnel. This implies that accommodation of K(2) in the already crowded 8-ring channel is energetically favorable compared with penetration of the 6-ring and the placement of K(2) in the Na(2) site which has a volume suitable for a "dry" Na$^+$ ion.

A possible sequence of species in an 8-ring tunnel along **c** is

/K(1),W(1)/K(1),W(1)/K(1),

K(2)/W(1'),K(1')/W(1'),K(1')/

where the length of **c** is indicated by slashes, and primed and unprimed sites are related by a 2_1 operation. This model gives a rather short K(1)–K(2) distance of 4.13 Å and also suggests that $g(W(1))$ should be equal to $\frac{1}{2} - g(\text{K}(2))$. Comparable arrangements occur in kalsilite, $KAlSiO_4$ (15), where the K$^+$ ions are situated above each other at the center of a 6-ring tunnel, with K–K distances of 4.35 Å; while in sanidine (12) the shortest K–K distances are 4.38 Å.

References

1. S. HANSEN AND L. FÄLTH, Zeolites **2**, 162 (1982).
2. S. HANSEN AND L. FÄLTH, Z. Kristallogr. **164**, 79 (1983).
3. P. R. BUSECK AND J. M. COWLEY, Amer. Mineral. **68**, 18 (1983).
4. "International Tables for X-Ray Crystallography" (J. A. Ibers and W. C. Hamilton Eds.), Vol. 4, Kynoch Press, Birmingham (1974).
5. O. C. KOPP, L. A. HARRIS, G. W. CLARK, AND H. L. YAKEL, Amer. Mineral. **48**, 100 (1963).
6. G. D. BRUNTON, L. A. HARRIS, AND O. C. KOPP, Amer. Mineral. **57**, 1720 (1972).
7. J. J. PLUTH AND J. V. SMITH, J. Phys. Chem. **83**, 741 (1979).
8. W. M. MORTIER, J. J. PLUTH, AND J. V. SMITH, in "Natural Zeolites" (L. B. Sand and F. A. Mumpton, Eds.), p. 53, Pergamon, Oxford (1978).
9. A. ALBERTI AND G. VEZZALINI, Acta Crystallogr. Sect. B **35**, 2866 (1979).
10. R. RINALDI, J. J. PLUTH, AND J. V. SMITH, Acta Crystallogr. Sect. B **30**, 2426 (1974).
11. J. A. GARD AND J. M. TAIT, Acta Crystallogr. Sect. B **28**, 825 (1972).
12. P. H. RIBBE, Acta Crystallogr. **16**, 426 (1963).
13. F. MAZZI, E. GALLI, AND G. GOTTARDI, Amer. Mineral. **61**, 108 (1976).
14. W. B. SIMMONS, JR. AND D. R. PEACOR, Amer. Mineral. **57**, 1711 (1972).
15. A. J. PERROTTA AND J. V. SMITH, Mineral. Mag. **35**, 588 (1965).