

The Structure of Dehydrated Zeolite 3A (Si/Al = 1.01) by Neutron Profile Refinement

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A neutron powder diffraction study of a dehydrated commercially available potassium exchanged zeolite A (Linde 3A) has shown that the diffraction pattern can be indexed in cubic space group $Fm\bar{3}c$. For this sample there is 63% exchange of potassium for sodium ($K^+/Na^+ = 1.69$). Data collected at a neutron wavelength of 2.98 Å shows no evidence of rhombohedral distortion and suggests that the assignment of space group $Fm\bar{3}c$ is correct. The final structural model is closely analogous to that found for dehydrated sodium zeolite A (J. M. Adams, D. A. Haselden, and A. W. Hewat, *J. Solid State Chem.* **44**, 245 (1982); J. J. Pluth and J. V. Smith, *J. Amer. Chem. Soc.* **102**, 4074 (1980). Unusual features of previous refinements of potassium containing zeolite A samples, i.e., "zero coordinate" cations (P. C. W. Leung, M. B. Kunz, K. Seff, and I. E. Maxwell, *J. Phys. Chem.* **83**, 741 (1979)) or potassium inside the β -cage (J. J. Pluth and J. V. Smith, *J. Phys. Chem.* **83**, 741 (1979)) have not been found. Refinements using the same 1.9 Å neutron powder diffraction data were also obtained with the models of Leung *et al.* and Pluth and Smith (1979) as starting points (denoted LKSM and PS, respectively) and comparison is made with these. The final R factors for the three refinements were R_{pw} (A. K. Cheetham and J. C. Taylor, *J. Solid State Chem.* **21**, 253 (1977)) = 10.24% for the model presented here, $R_{pw} = 10.38\%$ (PS model), and $R_{pw} = 10.61\%$ (LKSM model).

Introduction

Over the past three years there has been increasing interest in the detailed structure of zeolite A, which began when Engelhardt *et al.* (6), using ^{29}Si NMR, suggested that each Si atom was surrounded not by four, but by three Al atoms and one Si atom and vice versa. This implied that Al-O-Al bonds were present in the structure in contravention of Loewenstein's rule (7). More recently Thomas *et al.* have published a series of papers (8-11) suggesting possible space groups for zeolite A in the light of their own ^{29}Si NMR, neutron and electron diffraction experiments. They found that their neutron powder diffraction data could

be indexed using a rhombohedral unit cell and the space group that they preferred (which was consistent with the 3:1 Si, Al ordering pattern deduced from ^{29}Si NMR measurements by Thomas *et al.* (11) and Lippmaa *et al.* (12)) was $R\bar{3}$. We have recently repeated the neutron diffraction experiments of Thomas *et al.* (9, 11) on Na zeolite A and have shown that for our sample the symmetry is cubic (13) and that indexing and refinement was possible for space groups $Pm\bar{3}m$ and $Fm\bar{3}c$ (1). Attempts to refine the same data in $Fm\bar{3}$ and $R\bar{3}$ failed (1).

It appears that the issue of Si, Al ordering in zeolite A is now resolved: Thomas *et al.* (14) and Melchior *et al.* (15) have, on the

basis of ^{29}Si NMR studies on the A-type zeolite ZK4, shown that regular Si, Al alteration does indeed occur. In addition a further neutron powder diffraction study on a thallium exchanged zeolite A sample has shown that the material is cubic and space group $Fm\bar{3}c$ appears to be correct (16). However, it is apparent that for some samples of dehydrated Na zeolite A rhombohedral symmetry can still occur (17).

Prior to the present controversy, Seff *et al.* had published a series of papers reporting zero coordinate or near zero coordinate cations in various cation exchanged forms of zeolite A (3, 18–22). Pluth and Smith (2, 4) have repeated some of this work, specifically for Na zeolite A and K zeolite A and have shown that the zero coordinate cations do not exist.

Here we have investigated the structure of a commercial sample of zeolite 3A, since structural information on this widely used molecular sieve is unavailable. Moreover, we wished to study a potassium exchanged sample of zeolite A in order to confirm (or otherwise) the existence of “zero coordinate K⁺”. Additionally, we have obtained further evidence that zeolite A is cubic and we have shown that potassium is not present in the β -cage.

Experimental

The zeolite used for this structure determination was commercially available potassium 3A manufactured by Union Carbide (Linde) and was obtained from BDH. Although this zeolite was originally thought to be completely potassium exchanged, it was found that in this instance the exchanging procedure had been incomplete. Analysis for potassium by flame photometry, for water by thermogravimetric analysis, and for silicon and aluminium by gravimetric procedures (23) yielded a composition of $\text{Na}_{35.4}\text{K}_{60.0}\text{Al}_{95.4}\text{Si}_{96.6}\text{O}_{384} \cdot 160\text{H}_2\text{O}$. The sodium content was found by difference. The

Si/Al ratio was determined as 1.01 (2), i.e., the sample was stoichiometric within our analysis limit. The powder diffraction data were collected using the high-resolution powder diffractometer D1A at the Institut Laue–Langevin, Grenoble (24). A 5 g sample was loaded into a 16 mm diameter vanadium sample can and dehydrated at 350°C for 20 hr at 5.10^{-6} Torr, after which the sample was allowed to cool for 24 hr under vacuum to prevent rehydration. Data ranging from 6.04 to 158.04° (2θ) were collected in 22 hr at a wavelength of 1.909 Å, followed by data ranging from 6.04 to 66.04° (2θ) at a wavelength of 2.98 Å. The background was estimated by linear interpolation from regions where no Bragg peaks occurred and peaks due to contamination were removed from the profile. The refinements of the structure were made using the Rietveld technique of profile refinement (25, 26) with the programs of Hewat (27, 28). The scattering lengths used were obtained from the “International Tables for X-Ray Crystallography” (29).

Structure Refinement

The absence of splitting or asymmetry in the 8.8.0 peak in the data collected at a wavelength of 2.98 Å showed that the structure had no rhombohedral distortion, i.e., it was cubic (Fig. 1). Careful study of the diffraction trace revealed the presence of the 21.9.7 reflexion (24.6 Å cell) in the 1.909 Å data (at $\sim 136^\circ$ (2θ)) indicating that the space group $Fm\bar{3}c$ is correct rather than $Pm\bar{3}m$, the other commonly used space group for zeolite A with a 12.3 Å unit cell. Three structure refinements were performed. The first used the structure determined by Leung *et al.* (3) as the starting model (LKSM model), the second used the coordinates found by Pluth and Smith (4) (PS model), and the third made use of a model analogous to that found recently for dehydrated Na zeolite A (1, 2).

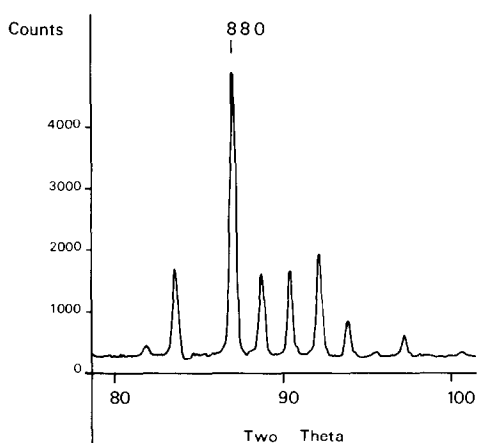


FIG. 1. Observed diffraction profile, using 2.98 Å neutrons, for dehydrated potassium exchanged zeolite A showing the 8.8.0 and 12.0.0 reflections. There is no splitting or asymmetry in the 8.8.0 peak indicative of cubic, rather than rhombohedral, symmetry.

During a preliminary refinement of the aluminosilicate framework in space group $Pm\bar{3}m$ using the LKSM model, Fourier difference peaks were found corresponding to the potassium site in the 8-ring (K(2)) and the "zero coordinate" K(3) site, together with a single peak near the center of the 6-ring at the approximate coordinates of $x = y = z = 0.2$, corresponding to the K(1) site in the LKSM model. However, this site was considered to be too close to the 6-ring to be a purely potassium site on the basis of expected bond lengths. In addition, inspection of a Fourier map showed that the peak at this site was elongated along the $\bar{3}$ axis. Since it was already known from chemical analysis that there had been only partial exchange of Na^+ by K^+ , the peak was considered to be made up of two contributions, one from sodium (Na(1)) and one from potassium (K(1)). Na(1) was initially placed at $x = y = z = 0.198$ and K(1) was placed at $x = y = z = 0.23$ with fixed occupancies derived from the chemical analysis. The coordinates of Na(1) were taken from a recent profile refinement in these laboratories of a

Linde 4A sample and the K(1) coordinate was from Leung *et al.* (3).

As the space group had been shown to be $Fm\bar{3}c$ rather than $Pm\bar{3}m$ the atom coordinates were transformed to $Fm\bar{3}c$. These coordinates were then refined using isotropic temperature factors until refinement ceased with $R_{pw}^1 = 17.9\%$. At this point the oxygen temperature factors were made anisotropic. The magnitude of the anisotropic temperature factors β were calculated from the isotropic temperature factors B using the formula: $\beta = 0.25 a^{*2} B$ and the symmetry dependence of these was obtained from the paper by Peterse and Palm (30). This led to a drop in R_{pw} to 12.4%. Anisotropic refinement of all the atom positions led to a final R_{pw} of 10.61%. However, though the refinement was seemingly complete, large shifts ($\geq \text{ESD}$) in the parameters still occurred. It was also noted that the "zero coordinate" potassium K(3) site had migrated over 1 Å further into the α -cage (to approximately $x = y = z = 0.39$) during the refinement.

As a check on the LKSM model, the K(3) site was deleted from the structure and a Fourier difference map obtained. No peak in the vicinity of the K(3) site was observed, strongly suggesting that the original difference peak had been spurious and had arisen from series termination effects which disappeared as the refinement proceeded.

At this stage, having found that the LKSM model was unsatisfactory, it was decided to try an alternative model proposed by Pluth and Smith (4) for potassium exchanged zeolite A although it was realised that this model was not strictly applicable here since our sample had only partial replacement of Na^+ by K^+ . A preliminary refinement in $Pm\bar{3}m$ was carried out during

¹ $R_{pw} = 100[\sum w(y(\text{obs}) - (1/c)y(\text{calc}))^2 / \sum w(y(\text{obs}))^2]^{1/2}$ where w is the weight at each 2θ step and $y(\text{obs})$ and $y(\text{calc})$ are the observed and calculated intensities at that point.

which peaks corresponding to the K(6) and K(7) sites of the PS model (4) were found (labeled K(3) and K(4) in this work). The cation in the K(3) site is coordinated to the oxygen atoms of the 4-ring and is situated inside the α -cage, whereas the cation in the K(4) site is also coordinated to the 4-ring but occurs inside the β -cage. Refinement in $Pm\bar{3}m$ with Si, Al and O temperature factors anisotropic led to an R_{pw} of 13.84%. Transformation of the coordinates to $Fm\bar{3}c$ together with further refinement led to a drop in R_{pw} to 10.66%. Due to the high correlation between occupancy and temperature factors in the Rietveld method, the occupancies of the K(3) and K(4) sites were refined with their temperature factors fixed. The thermal parameters chosen were thought to be reasonable and were based on values obtained during previous refinements and from structures reported by other authors (e.g., 1-4). Despite these precautions refinement of the K(3) and K(4) occupancies led to values such that there were 2.7 excess cations per unit cell (total

cation content is fixed by the Al occupancy of 95.4 atoms). This meant that one of the other cation sites must only be partially occupied and because of the high temperature factor at the K(2) site ($B \sim 12$) the total potassium occupancy was balanced by removal of potassium from this site. This led to a drop in the B factor for K(2) to 6.0. Anisotropic refinement of Si, Al, O, Na(1), and K(1) led to a final R_{pw} of 10.38%. Attempts to refine K(2) anisotropically caused unstable coordinate shifts for K(2) and therefore the K(2) site was left isotropic. Anisotropic refinement of the K(3) and K(4) sites was not attempted due to their low occupancy.

Although convergence was obtained with this model, its complexity and the presence of potassium inside the β -cage led the authors to check whether the K(4) site was spurious. A Fourier difference map was obtained after deletion of the K(4) site from the model and no peak could be found in the vicinity of the K(4) site. This finding prompted the refinement of the structure in

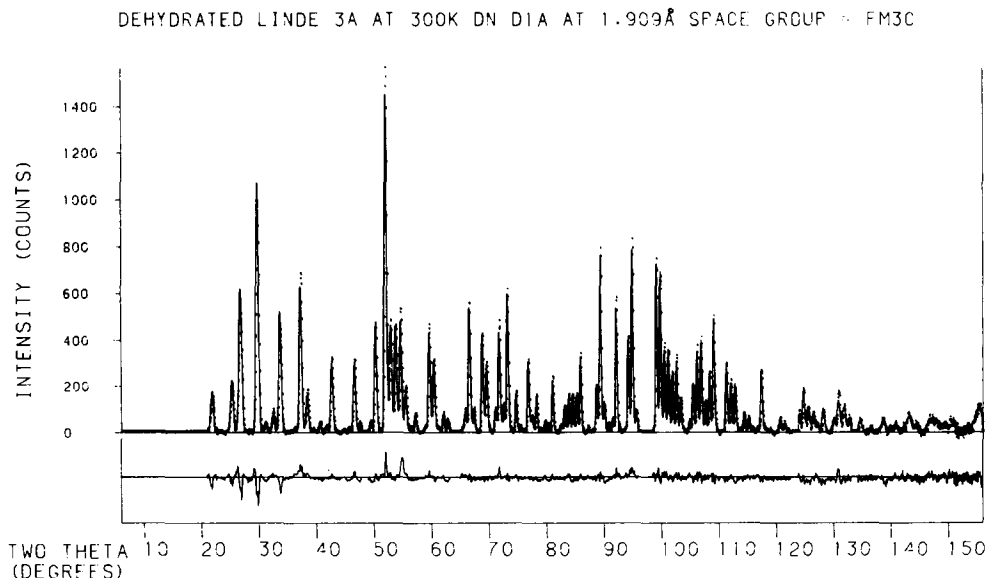


FIG. 2. Observed (\cdots) and calculated (—) neutron diffraction profiles, together with difference plots for dehydrated potassium exchanged zeolite A, in space group $Fm\bar{3}c$.

a much simplified model, closely analogous to that reported recently for sodium zeolite A (1, 2). Only three exchangeable cation sites were used, one adjacent to the 6-ring (K(1)), the second in the 8-ring (K(2)), and the third adjacent to the 4-ring and inside the α -cage (K(3)). In this case the model was slightly complicated by the presence of sodium (Na(1)) in addition to potassium (K(1)) in the structure adjacent to the 6-ring.

The occupancies of the cation sites were obtained using the following evidence. In the case of the Na(1) and K(1) sites, refinement with the site fully occupied (64 atoms in total) led to B factors for Na(1) and K(1) which were closely similar and low. Since a lower occupancy would have manifested itself in the refinement as a higher temperature factor this suggested that the 6-ring site was indeed full. The occupancy of the K(2) site was fixed at 24 cations (this represents full occupancy of this site, on crystal-chem-

ical grounds, to avoid close K-K distances) since Ogawa *et al.* (31) have shown from theoretical electrostatic considerations that potassium, with its large ionic radius, preferentially occupies the 8-ring site. Moreover, after a trial refinement in which the occupancy was increased from 21.3 cations obtained in the PS model to 24 cations the B factor for K(2) remained steady. The remaining 7.44 cations were placed in the K(3) site and refinement led to a satisfactory B factor ($B \sim 5$). Final refinement in $Fm\bar{3}c$ with all the temperature factors anisotropic, except K(3), led to final convergence with $R_{pw} = 10.24\%$.

Figure 2 shows the observed and calculated diffraction traces obtained from the third model. Figure 3 shows plots of nearest neighbor atoms to the four final cation positions. Table I lists the final parameters for this model together with those of Pluth and Smith (4) for comparison and Table II gives bond distances and angles.

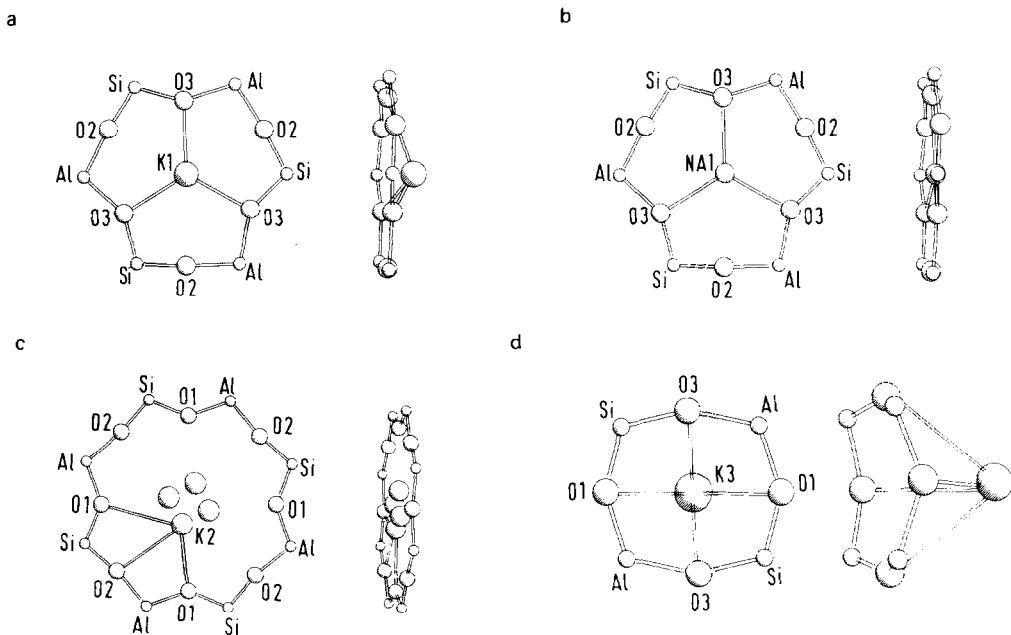


FIG. 3. Plot of nearest neighbor atoms to the four final cation positions: (a) the K(1) site in the 6-ring; (b) the Na(1) site in the 6-ring; (c) the four possible K(2) positions in the 8-ring site; (d) the K(3) site adjacent to the 4-ring.

TABLE I
 ATOMIC COORDINATES, OCCUPANCIES, AND TEMPERATURE FACTORS FOR DEHYDRATED POTASSIUM
 EXCHANGED ZEOLITE A

	Haselden and Adams			Pluth and Smith (4)	
	Si(1)	Si(2)	Al(1)	Si(1)	Al(1)
Position	96(<i>i</i>)	96(<i>i</i>)	96(<i>i</i>)	96(<i>i</i>)	96(<i>i</i>)
Population	96	0.56	95.44(50)	96	96
<i>x</i>	0		0	0	0
<i>y</i>	0.09322(41)		0.18936(44)	0.09460(13)	0.18965(19)
<i>z</i>	0.18591(35)		0.09200(42)	0.18777(17)	0.09152(14)
β_{11}	13(2)		5(2)	5.1(6)	5.9(6)
β_{22}	11(2)		9(2)	5.4(5)	5.6(7)
β_{33}	5(1)		2(1)	3.8(6)	3.9(5)
$\beta_{12,13}$	0		0	0	0
β_{23}	-2(1)		6(1)	0.1(5)	1.5(5)
	O(1)			O(1)	
Position	96(<i>i</i>)			96(<i>i</i>)	
Population	96			96	
<i>x</i>	0			0	
<i>y</i>	0.11641(13)			0.1226(2)	
<i>z</i>	0.24698(35)			0.2455(4)	
β_{11}	17(1)			11.1(8)	
β_{22}	18(1)			3.9(8)	
β_{33}	5(1)			3.4(1.1)	
$\beta_{12,13}$	0			0	
β_{23}	-1(1)			1.6(1.1)	
	O(2)			O(2)	
Position	96(<i>i</i>)			96(<i>i</i>)	
Population	96			96	
<i>x</i>	0			0	
<i>y</i>	0.14335(26)			0.1422(4)	
<i>z</i>	0.14505(25)			0.1419(3)	
β_{11}	20(1)			9.9(7)	
β_{22}	9(1)			10(2)	
β_{33}	7(1)			6(2)	
$\beta_{12,13}$	0			0	
β_{23}	7(1)			2.5(6)	
	O(3)			O(3)	
Position	192(<i>j</i>)			192(<i>j</i>)	
Population	192			192	
<i>x</i>	0.05482(20)			0.0537(2)	
<i>y</i>	0.05830(22)			0.0587(2)	
<i>z</i>	0.17389(8)			0.1795(2)	
β_{11}	9(1)			7.1(1.0)	
β_{22}	14(1)			9.6(1.1)	
β_{33}	16(1)			11.2(6)	
β_{12}	6(1)			2.7(5)	
β_{13}	1(1)			1.1(9)	
β_{23}	1(1)			0.2(9)	

TABLE I—Continued

	Haselden and Adams	Pluth and Smith (4)
	K(1)	K(1)
Position	64(<i>g</i>)	64(<i>g</i>)
Population	28.6(5)	49.9(9)
<i>x, y, z</i>	0.11511(58)	0.11526(10)
$\beta_{11}, \beta_{22}, \beta_{33}$	19(3)	14.7(4)
$\beta_{11}, \beta_{13}, \beta_{23}$	13(3)	7.1(4)
	K(2)	K(2)
Position	96(<i>i</i>)	96(<i>i</i>)
Population	24	24
<i>x</i>	0	0
<i>y</i>	0.24083(477)	0.2356(21)
<i>z</i>	0.21903(116)	6.2391(23)
β_{11}	17(5)	
β_{22}	45(26)	
β_{33}	35(5)	
$\beta_{12,13}$	0	
β_{23}	7(5)	
<i>B</i>		5.0(2)
	Na(1)	K(4,5)
Position	64(<i>g</i>)	64(<i>g</i>)
Population	35.4(5)	12.1(1.0)
<i>x, y, z</i>	0.09866(38)	0.0810(17)
$\beta_{11}, \beta_{22}, \beta_{33}$	17(2)	66(12)
$\beta_{12}, \beta_{13}, \beta_{23}$	5(2)	61(12)
	K(3)	K(6)
Position	96(<i>h</i>)	96(<i>h</i>)
Population	7.44	3.8(8)
<i>x</i>	0.25	0.25
<i>y, z</i>	0.12752(145)	0.119(3)
<i>B</i>	4.889(1.214)	11(4)
		K(7)
Position		48(3)
Population	Not found	1.2(4)
<i>x</i>		0.037(4)
<i>y, z</i>		0
<i>B</i>		3(2)

Discussion

As mentioned previously, the space group of our sample of zeolite A has been shown to be $Fm\bar{3}c$. Three independent observations have been used to reach this conclusion. Firstly, the data collected at a wavelength of 2.98 Å showed no splitting or

asymmetry in the 8.8.0 peak (Fig. 1) showing that the structure had no rhombohedral distortion and indicating that it was cubic. Secondly we have observed (Fig. 2) a reflexion at $\sim 136^\circ$ (2θ) using 1.909 Å radiation which can be indexed as the 21.9.7 reflexion when using a 24.6 Å cell. Space group $Pm\bar{3}m$ cannot therefore be correct

TABLE II
BOND DISTANCES (Å) AND ANGLES (°) FOR PARTIALLY POTASSIUM EXCHANGED DEHYDRATED
Na ZEOLITE A^a

Si(1)–O(2)	1.588(11)	O(1)–Si(1)–O(2)	108.4(6)
Si(1)–O(1)	1.604(12)	O(1)–Si(1)–O(3)	110.9(4)
Si(1)–O(3), O(3 ⁱⁱ)	1.623(7)	O(2)–Si(1)–O(3)	107.1(4)
Al(1)–O(1 ^{vi})	1.675(13)	O(3)–Si(1)–O(3 ⁱⁱⁱ)	112.1(6)
Al(1)–O(2)	1.725(12)	O(1 ^{vi})–Al(1)–O(2)	109.9(6)
Al(1)–O(3 ⁱⁱ), O(3 ^{iv})	1.740(8)	O(1 ^{vi})–Al(1)–O(3)	113.1(4)
K(1)–O(3), O(3 ⁱ), O(3 ⁱⁱ)	2.495(15)	O(3 ⁱⁱ)–Al(1)–O(3 ^{iv})	110.7(6)
K(1)–O(2), O(2 ⁱ), O(2 ⁱⁱ)	3.003(14)	Si(1)–O(1)–Al(1 ^v)	138.2(5)
Na(1)–O(3), O(3 ⁱ), O(3 ⁱⁱ)	2.357(10)	Si(1)–O(2)–Al(1)	170.1(6)
Na(1)–O(2), O(2 ⁱ), O(2 ⁱⁱ)	2.894(10)	Si(1)–O(3)–Al(1 ⁱ)	146.1(5)
K(2)–O(1 ^{vi})	2.538(32)		
K(2)–O(2)	3.005(95)		
K(2)–O(1 ⁱⁱⁱ)	3.132(32)		
K(3)–O(3 ⁱⁱ)	3.094(29)		
K(3)–O(1 ⁱ)	3.145(35)		

Note. Symmetry code for table: (i) z, x, y ; (ii) y, z, x ; (iii) $-x, y, z$; (iv) $-y, z, x$; (v) $-x, z, \frac{1}{2}-y$; (vi) $x, \frac{1}{2}-z, y$.

^a ESD is last figure given in parentheses.

because it is based on a 12.3 Å cell. Finally the bimodal distribution of T–O bond distances (Table II) is indicative of ordering of Si and Al into alternating tetrahedra. Therefore it may be concluded that for this zeolite sample with Si/Al ratio of 1.01(2) the space group is $Fm\bar{3}c$.

The final model we have evolved is simpler, in terms of the cation distribution, than both the LKSM (3) and PS (4) models and confirms Pluth and Smith's results (4) that there are no zero coordinate cations in this zeolite. In addition we have not found any K⁺ cations inside the β -cage as were found by Pluth and Smith (4) (their K(4,5) and K(7) sites). This might possibly be due to the fact that our zeolite sample is not strictly comparable with that of Pluth and Smith (4) because there has been only partial exchange of Na⁺ by K⁺. This is especially true of the LKSM and PS (K(4,5) site(s) which is not occupied in our model presumably due to the full occupancy of the 6-ring by Na(1) and K(1) which would lead to any cations on the K(4,5) site being unreasonably close to either Na(1) or K(1).

The bond distances and angles for the aluminosilicate framework which we have found here are all reasonable. The K(1)–O(3) distances of 2.495(15) Å are shorter than those usually found for K–O, but are comparable with those found in anorthoclase feldspar (32) and are reasonably close to those given by PS. The Na(1)–O(3) bond distances agree within 3 ESD with those found previously for the dehydrated Na zeolite A (1). For K(2) the bonds to framework oxygen are somewhat shorter (by 0.2 Å) than those given by PS, whereas the K(3)–oxygen bonds have been found here to be 0.2 Å longer than those of PS.

Conclusions

The model derived here for the structure of K exchanged zeolite A is simpler than that given by previous workers (3, 4). The exchangeable cations are situated in sites which are reasonable on crystal-chemical grounds. The 6-ring and 8-ring sites are completely filled and the remaining cations which are needed to balance the negative

charge on the framework are situated in a site near the 4-ring (and in the α -cage).

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