

# Reinvestigation of the Crystal Structure of Dehydrated Sodium Zeolite X

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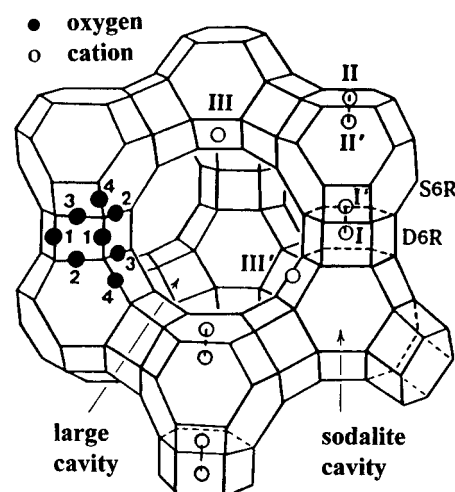
Received: June 3, 1999; In Final Form: August 18, 1999

The structure of a single crystal of dehydrated zeolite Na–X selected from a batch grown by Petranovskii in Russia, of composition  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  per unit cell, was determined by X-ray diffraction methods in the cubic space group  $Fd\bar{3}$ ;  $a = 25.077(4)$  Å at 21 °C.  $R_1 = 0.054$  for the 320 reflections for which  $F_o > 4\sigma(F_o)$ ;  $wR_2$  based on  $F^2$  and all data is 0.140.  $\text{Na}^+$  ions are found at four crystallographic sites. Sites I' and II are fully occupied with 32  $\text{Na}^+$  ions each. The remaining 28  $\text{Na}^+$  ions partially occupy two 12-ring (site III') positions with 10(4) near an O–Al–O sequence and 18(4) near an O–Si–O sequence. These results differ from those of the two previous investigations of dehydrated Na–X, which, in turn, disagree substantially with each other. The near energy equivalence of two (or more) III' sites, the presence of an impurity cation in one determination, and a consideration of the differing qualities of the diffraction data are sufficient to reconcile all results. The substitution of four silicon atoms per unit cell into the aluminum equipoint necessarily has a complicating effect. Considerations involving the ordering of these substituted silicon atoms are not needed.

## 1. Introduction

**1.1. Description of Zeolite X.** Zeolite X is an aluminum-rich synthetic analogue of the naturally occurring mineral faujasite (see Figure 1). The cuboctahedron ( $8 + 6 = 14$ -hedron with  $8 \times 3 = 24$  vertexes) known as the sodalite cavity or  $\beta$ -cage may be viewed as its principal building block. These sodalite units are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal prisms) and, concomitantly, an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertexes of these polyhedra. The oxygen atoms lie approximately midway between each pair of Si and Al atoms but are displaced from those points to give near-tetrahedral angles about Si and Al. Single six-rings (S6R's) are shared by sodalite and supercages and may be viewed as the entrances to the sodalite units. Each unit cell has eight sodalite units, eight supercages, 16 D6R's, 16 12-rings, and 32 S6R's.

If  $\text{Si}/\text{Al} = 1.00$ , the Si and Al atoms alternate in obedience of Loewenstein's rule (–Al–O–Al– sequences are forbidden).<sup>1</sup> The space group is then  $Fd\bar{3}$ ; one 96(g) equipoint, Si, contains only Si atoms, another 96(g) equipoint, Al, contains only Al atoms, and Si–O bond lengths are correctly seen crystallographically to be shorter than Al–O. Usually, however,  $\text{Si}/\text{Al} > 1.00$  in samples of zeolite X. If the Si equipoint remains pure or relatively so, enough long-range order is retained for the space group to remain  $Fd\bar{3}$  with Si/Al disorder at the Al position and for the mean Si–O and Al–O distances to remain different. Arguments have been presented for such Si substitution into the Al position in zeolite A,<sup>2</sup> and a simulated annealing study of zeolite X has shown that there is essentially no Al at the Si equipoint.<sup>3</sup> However, when zeolite X is subjected to harsh structure-threatening chemical treatment, usually intrazeolitic acidity, especially at elevated temperatures, long-range order



**Figure 1.** Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections except that Si substitutes for Al at about 4% of the Al positions in the crystal studied. Extraframework cation positions are labeled with Roman numerals.

is lost, the space group becomes  $Fd\bar{3}m$ , and the mean Si–O and Al–O distances converge to become indistinguishable.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites shown in Figure 1: site I at the center of the D6R, site I' in the sodalite cavity on the opposite side of either of the D6R's six-rings from site I, site II' inside the sodalite cavity near a S6R, site II at the center of the S6R or displaced from this point into a supercage, site III in the supercage on a 2-fold axis opposite a four-ring between two 12-rings, and various III' sites somewhat or substantially distant from III but otherwise near the inner walls of the supercages or the edges of 12-rings. Exchangeable cations select sites within the zeolite that best balance its charge with

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conventional cation-to-oxygen bond lengths. In addition, cations with specific coordination requirements will seek to satisfy them.

As Si/Al increases from 1.0, many nonequivalencies arise in local geometry and charge. This surely affects the cation placement (the number of cation positions, their coordinates, and their occupancies), which should become more complex. It may be possible to learn something about the Si/Al ordering within the zeolite framework from the cation placement.

**1.2. Structure of Dehydrated Na-X.** Zeolite X is usually synthesized in its Na<sup>+</sup> form. Na-X is, in that sense, the initial member of the series ion-exchanged or modified zeolite X. (Zeolite X with Si/Al  $\approx$  1.0 is synthesized in the Na,K system.) To avoid the complication of locating the many water molecules in that structure, dehydrated Na-X may be viewed as the much simplified, minimally modified, initial member of that series.

The structure of dehydrated Na-X has been reported twice before.<sup>4,5</sup> The positions and site distributions of the Na<sup>+</sup> ions differ in these studies. In a precise study of a single crystal of reported unit cell composition Na<sub>88</sub>Si<sub>104</sub>Al<sub>38</sub>O<sub>384</sub> grown by Charnell, Olson<sup>4</sup> found Na<sup>+</sup> ions at sites I, I', II, and III'; furthermore, sites I' and III' show fine structure; there are two very similar site I' positions and three very similar site III' positions to give a total of seven Na<sup>+</sup> equipoints. Cheetham et al.<sup>5</sup> synthesized Na-X powder (Si/Al = 1.2) and determined its low-temperature (5 K) structure. They found Na<sup>+</sup> ions at only three crystallographic sites, I', II, and III'; III' was near an O(1)-Al-O(4) segment of a 12-ring. They did computer simulations (Si/Al = 1) that supported their crystallographic result and that also showed a lesser Na<sup>+</sup> population close to an O(1)-Si-O(4) sequence, another III' site.

**1.3. Reasons for Differences. Irreproducibility.** Several possible reasons for the differences between Olson's and Cheetham's results come to mind. The samples used were synthesized by different workers using different methods. Accordingly, their framework compositions are somewhat different, and the Si/Al ordering<sup>6-9</sup> in their zeolite frameworks may be different. Even if the Si equipoint contains no Al atoms, as could be the case for space group *Fd* $\bar{3}$ , the Si atoms that must be in the Al equipoint may be arranged differently (various styles or degrees of ordering). Alternatively, the differences in structure could be due simply to the precision of Olson's work and the low temperature of Cheetham's.

Unfortunately, this system is particularly sensitive to three possible experimental errors. Some samples may not have been entirely in the Na<sup>+</sup> form; H<sup>+</sup> ions may be present. Simply washing freshly synthesized zeolite with water replaces many Na<sup>+</sup> ions per unit cell with H<sub>3</sub>O<sup>+</sup>.<sup>10-13</sup> Similarly, the zeolite may selectively concentrate impurity cations from any wash or exchange solutions used; this is particularly important when the solution to sample volume ratio is very high, as is often the case for a small sample such as a single crystal. Finally, some samples may not be fully dehydrated; even if fully dehydrated at one stage, this excellent desiccant may be given an opportunity to sorb water upon cooling and subsequent handling.

Problems such as these are not unique to Na-X. They plague much of zeolite science and contribute to its high incidence of irreproducibility.<sup>14</sup> This laboratory is familiar with these errors because it has often seen them crystallographically in its own preparations. The details given in Sample Preparation (section 2.1.) describe the efforts that have been made to avoid them in this work. One must be suspicious of all reports whose authors have indicated their unawareness of these problems by failing to describe their experimental procedures fully.

**1.4. Dehydrated Thallium Zeolite X.** Tl<sub>92</sub>-X<sup>15</sup> is selected for comparison with Na-X because of the very high X-ray scattering power of Tl<sup>+</sup> and the resulting reliability of the Tl<sup>+</sup> positions. Also, the crystal used in that work<sup>15</sup> and the one used here were from the same synthesis batch, grown by Petranovskii.<sup>16</sup> Fully dehydrated Tl<sub>92</sub>-X had been prepared and its structure determined in part for the same purpose, to observe the cation positions and to seek to explain them.

In fully dehydrated fully Tl<sup>+</sup>-exchanged zeolite X, two III' sites are occupied by Tl<sup>+</sup> ions.<sup>15</sup> This was contrary to the expectation that these 28 ions (the remainder after sites I' and II are filled) would simply partially occupy the single lowest-energy 96-fold site III' (or 48-fold site III) equipoint. No explanation for this was offered as "most likely."<sup>15</sup> The two sites may be very close in energy, the four Si atoms at the Al position may somehow be involved, and the ordering of the Si and Al atoms, such as the possible arrangements of the four Si atoms in the Al equipoint, may be important. A simple explanation involving the minimization of intercationic repulsion energy was not apparent.

**1.5. Reasons for This Work.** The positions that the extraframework cations occupy in zeolites directly affect the chemical and physical properties of this important class of materials. The electrostatic fields present within the zeolite channels and cavities are partly responsible for these properties, and these fields depend on the nature and positions of the exchangeable cations. Also very important are the chemical natures of the cations, their accessibility to sorbed molecules, and the amount of window-blocking that they cause.

This work was done to determine the positions of the Na<sup>+</sup> ions in dehydrated zeolite X prepared by Petranovskii working under the supervision of Bogomolov in Leningrad, now St. Petersburg, Russia.<sup>16</sup> It was hoped that something more could be learned about the Si/Al ordering within these crystals; they have been used in many investigations in this and other laboratories. Perhaps sharp differences in Si/Al ordering make various zeolite X samples fundamentally nonequivalent so that work completed on these crystals would not be generally applicable to all zeolite X samples of similar composition. This work shows that there is no evidence for that proposition.

## 2. Experimental Section

**2.1. Sample Preparation.** Large single crystals of sodium zeolite X of stoichiometry Na<sub>92</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub> were prepared in Russia.<sup>16</sup> One of these, a colorless octahedron about 0.15 mm in cross section, was lodged in a fine Pyrex capillary. The crystal was washed for 24 h at 20(1) °C in a flowing stream of 0.1 M aqueous NaCl (Alfa, ACS grade, 99.0% min (assay), Ba 0.001%, Ca/Mg/R<sub>2</sub>O<sub>3</sub> ppt 0.005%, heavy metals as Pb 5 ppm, Fe 2 ppm, K 0.005%) (pH adjusted from 6 to 11 by dropwise addition of NaOH (Aldrich, 99.99%)) to generate a crystal with no H<sub>3</sub>O<sup>+</sup> ions, only Na<sup>+</sup> ions to balance the charge of the zeolite framework. It was then dehydrated at 400 °C and 1  $\times$  10<sup>-5</sup> Torr for 48 h. While these conditions were maintained, the hot contiguous downstream lengths of the vacuum system, including a sequential U-tube of zeolite 5A beads fully activated in situ, were cooled to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystal. Still under vacuum in its capillary, the crystal was then allowed to cool and was sealed in its capillary and removed from the vacuum line by torch. The crystal had remained colorless.

**2.2. Crystallographic Work.** The reflection conditions (*hkl*: *h* + *k*, *k* + *l*, *l* + *h* = 2*n*; 0*kl*: *k* + *l* = 4*n*) indicate that

TABLE 1: Positional, Thermal, and Occupancy Parameters<sup>a</sup>

atom	Wyckoff position	site	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	occupancy	
												varied	fixed
Si	96(g)		-545(1)	1257(1)	353(1)	26(2)	21(1)	20(1)	4(1)	1(1)	-1(1)		96
Al	96(g)		-553(1)	360(1)	1246(1)	20(1)	13(1)	19(1)	1(1)	1(1)	-5(1)		96
O(1)	96(g)		-1098(4)	-1(2)	1068(2)	37(3)	42(3)	32(3)	-7(3)	1(3)	-7(3)		96
O(2)	96(g)		-14(2)	-24(2)	1413(2)	27(3)	24(3)	32(3)	14(2)	8(3)	10(2)		96
O(3)	96(g)		-349(2)	750(2)	724(2)	45(3)	29(2)	23(3)	6(3)	6(2)	7(2)		96
O(4)	96(g)		-697(2)	716(2)	1797(2)	31(3)	25(3)	29(3)	-3(3)	11(3)	-22(3)		96
Na(I')	32(e)	I'	475(2)	475(2)	475(2)	50(4)	50(4)	50(4)	9(3)	9(3)	9(3)	29.5(8)	32
Na(II)	32(e)	II	2298(2)	2298(2)	2298(2)	36(2)	36(2)	36(2)	14(3)	14(3)	14(3)	35.2(7)	32
Na(III')	96(g)	III'	334(71)	675(44)	4138(42)	151(74)	138(86)	122(75)	-50(71)	-8(69)	-62(57)	10(4)	
Na(III'')	96(g)	III''	692(32)	407(41)	4073(13)	129(52)	363(111)	134(24)	40(72)	2(23)	-64(37)	18(4)	

<sup>a</sup> Positional parameters are  $\times 10^4$ . Thermal parameters have the units  $\text{\AA}^2 \times 10^3$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor is  $\exp[-2\pi^2 a^{-2}(h^2 U_{11} + k^2 U_{22} + l^2 U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$ . Occupancy factors are given as the number of atoms or ions per unit cell.

the space group is either  $Fd\bar{3}$  or  $Fd\bar{3}m$ .  $Fd\bar{3}$  was chosen because (a) the low Si/Al ratio requires, at least in the short range, alternation of Si and Al,<sup>1</sup> (b) this crystal, like about 85% of the crystals from the same batch that have been studied, does not have intensity symmetry across (110) (this can be seen in the Supporting Information) and therefore lacks that mirror plane, and (c) the diffraction data from such crystals refine successfully to error indexes lower than with  $Fd\bar{3}m$ , with Si–O distances reasonably less than Al–O.<sup>17,18</sup>

Diffraction data were collected at 20(1) °C with an automated Siemens P3 four-circle computer-controlled diffractometer equipped with a pulse-height analyzer and a graphite monochromator. Molybdenum radiation ( $K\alpha_1 \lambda = 0.709\,30\,\text{\AA}$ ;  $K\alpha_2 \lambda = 0.713\,59\,\text{\AA}$ ) was used. The unit cell constant,  $25.077(4)\,\text{\AA}$ , was determined by least-squares refinement of 30 intense reflections for which  $14^\circ < 2\theta < 28^\circ$ . The  $\theta$ – $2\theta$  scan technique was used for data collection. All reflections in the positive octant of reciprocal space for which  $4^\circ < 2\theta < 50^\circ$  were scanned at a constant rate of  $3.0^\circ \text{ min}^{-1}$  in  $\omega$  from  $1.0^\circ$  below the  $K\alpha_1$  peak to  $1.0^\circ$  above the  $K\alpha_2$  maximum. Background intensity was counted at each end of a scan range for a time equal to one-half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded every 97 reflections to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were observed.

Standard deviations were assigned to individual reflections by  $\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$  where CT is the total integrated count,  $B_1$  and  $B_2$  are the background counts, and  $I$  is the intensity. In the final refinement of the structure,  $p$  converged to 0.0027, a small value. The intensities were corrected for Lorentz and polarization effects; the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. Because the crystal was a small regular octahedron with no heavy atoms, it was decided that an absorption correction was unnecessary. Of the 3757 reflections gathered, 1178 were independent (merging  $R(\text{intensity}) = 0.227$ ).

### 3. Structure Determination

Full-matrix least-squares refinement<sup>19</sup> was done on  $F^2$  using all data. It was initiated using the framework coordinates from a previous structural study of dehydrated Na–X.<sup>4</sup> These positions when refined isotropically yielded  $R_1 = 0.24$  and  $wR_2 = 0.61$ .  $R_1 = \sum |F_o - |F_c|| / \sum F_o$  and is calculated using the 320 reflections with  $F_o > 4\sigma(F_o)$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$  is based on  $F^2$  and is calculated using all 1178 unique reflections measured.

A Fourier difference electron density function yielded two strong peaks at (0.047, 0.047, 0.047) and (0.230, 0.230, 0.230), positions near framework oxygens normally occupied by cations. Isotropic refinement of framework atoms with  $\text{Na}^+$  ions at these two positions converged to  $R_1 = 0.072$  and  $wR_2 = 0.233$ . The occupancies at these two positions refined to 30.3(9) at Na(I') and 32.6(8) at Na(II), respectively. Both were then fixed at 32 per unit cell, the maximum value allowed by symmetry.

An ensuing Fourier function revealed two more peaks at (0.035, 0.072, 0.411) and (0.069, 0.037, 0.409), both III' sites. They refined to 10(4) ions at Na(III') and 18(4) ions at Na(III''), respectively. The four largest least-squares correlations, 0.80–0.92 (absolute values), involved these two positions; the correlation coefficient between their occupancies was  $-0.92$ , hence their high individual esd's and a much smaller esd for their sum, 28(1). The error indexes converged at  $R_1 = 0.065$  and  $wR_2 = 0.215$ .

Attempts to resolve Na(III'') into two separate site III' positions (because its thermal ellipsoid is elongated; see Table 1 and Figure 3) were unsuccessful; least-squares refinement was not stable.

At this stage the occupancies at Na(I') and Na(II) were allowed to refine. They converged at 29.5(8) and 35.2(7), respectively. Each was reset to 32 as before.

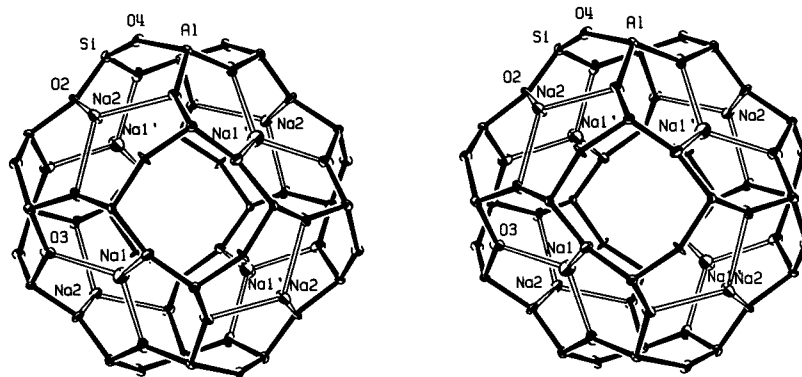
At no time was a peak seen at site I on difference electron density functions. Attempts to refine  $\text{Na}^+$  at this position gave an occupancy of 0.1 with an esd of 0.3  $\text{Na}^+$  ions per unit cell.

Finally, least-squares refinement of all positional and anisotropic thermal parameters converged to the error indexes  $R_1 = 0.054$  and  $wR_2 = 0.140$ . The goodness-of-fit,  $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ , is 0.74; the number of observations,  $m$ , is 1178 (of these 320 had  $F_o > 4\sigma(F_o)$ ), and the number of parameters,  $s$ , is 82. The largest maximum/minimum in the final difference function is  $1.5/-0.3\,\text{e}\,\text{\AA}^{-3}$ . The largest peak refined to an insignificant occupancy. Atomic scattering factors for Si, Al, O, and Na were used.<sup>20</sup> All scattering factors were modified to account for anomalous dispersion.<sup>21,22</sup> The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2.

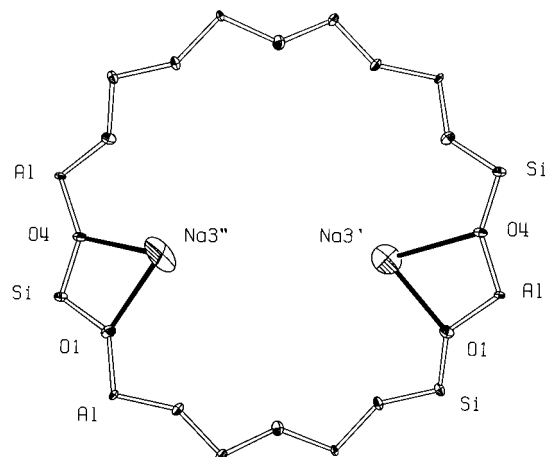
### 4. Results and Discussion

**4.1.  $\text{Na}_{92}$ –X.** In this structure, sodium ions are found at four crystallographic sites, in disagreement with both previous reports.<sup>4,5</sup> Both sites I' and II are fully occupied with 32  $\text{Na}^+$  ions each per unit cell (see Figure 2). The remaining 28  $\text{Na}^+$  ions are found at two different site III' positions (see Figure 3). Each  $\text{Na}^+$  ion at site I' bonds to three framework O(3)'s at





**Figure 2.** Stereoview of a sodalite unit. Both sites I' and II are fully occupied. Ellipsoids of 20% probability are shown.



**Figure 3.** A 12-ring showing the Na(III') and Na(III'') positions. Ellipsoids of 20% probability are shown.

**TABLE 2: Selected Interatomic Distances and Angles**

bond distances (Å)		bond angles (deg)	
Si—O(1)	1.630(8)	O(1)—Si—O(2)	113.2(4)
Si—O(2)	1.643(8)	O(1)—Si—O(3)	111.0(4)
Si—O(3)	1.650(8)	O(1)—Si—O(4)	107.5(4)
Si—O(4)	1.633(7)	O(2)—Si—O(3)	105.2(4)
mean Si—O	1.639	O(2)—Si—O(4)	107.1(4)
Al—O(1)	1.700(7)	O(3)—Si—O(4)	112.9(4)
Al—O(2)	1.713(8)	O(1)—Al—O(2)	113.5(4)
Al—O(3)	1.713(8)	O(1)—Al—O(3)	110.1(4)
Al—O(4)	1.682(7)	O(1)—Al—O(4)	109.1(4)
mean Al—O	1.702	O(2)—Al—O(3)	105.2(4)
Na(I')—O(3)	2.266(7)	O(2)—Al—O(4)	105.6(4)
Na(I')—O(2)	2.932(7)	O(3)—Al—O(4)	112.8(4)
Na(II)—O(2)	2.355(6)	O(3)—Na(I')—O(3)	116.42(18)
Na(II)—O(4)	2.885(6)	O(2)—Na(II)—O(2)	112.89(21)
Na(III')—O(1)	2.44(10)	O(1)—Na(III')—O(4)	66.8(24)
Na(III')—O(4)	2.56(14)	O(1)—Na(III'')—O(4)	67.1(13)
Na(III')—Al	3.07(10)		
Na(III')—Si	3.69(17), 3.72(12)		
Na(III')—Na(II)	4.78(10)		
Na(III'')—O(4)	2.33(5)		
Na(III'')—O(1)	2.43(9)		
Na(III'')—Si	2.95(5)		
Na(III'')—Al	3.43(8), 3.80(10)		
Na(III'')—Na(II)	4.65(4)		

2.266(7) Å. Each Na<sup>+</sup> ion at site II bonds to three O(2)'s at 2.355(6) Å. These distances are similar to those previously reported.<sup>4,5</sup>

Cheetham et al. also found site I' to be full with 32 Na<sup>+</sup> ions,<sup>5</sup> but Olson found only about 26–28 Na<sup>+</sup> ions there with three or two Na<sup>+</sup> ions, respectively, per unit cell at site I.<sup>4</sup> (The relationship  $(n_I/2) + n_I \leq 16$  must be obeyed to avoid a too short distance.) No Na<sup>+</sup> ions were found at site I in Cheetham's

work or in this work. All three reports agree that site II is full<sup>4,5</sup> (see Table 3).

About 10 Na<sup>+</sup> ions are found at a site III' position; about 18 Na<sup>+</sup> ions are found at another III' position, hereafter called III'' (see Figures 3 and 4). Each occupancy has a high esd of four Na<sup>+</sup> ions. Na(III') is close to the side of a 12-ring near an O(1)—Al—O(4) sequence and is essentially identical to one of the three site III' positions, Na(6'), reported by Olson<sup>4</sup> and the single III' position found by Cheetham et al.<sup>5</sup> (see Table 3). Na(III'') is also close to the side of the 12-ring but near an O(1)—Si—O(4) sequence. Its thermal ellipsoid is elongated, and it seems to represent the other two site III' positions, Na(5) and Na(6), reported by Olson (see parts a and b of Figure 5). The sum of the occupancies at Na(5) and Na(6) in Olson's work, 10.6(10) + 10.6(10) = 21.2(14), is similar to the occupancy at Na(III'') in this work, 18(4). Perhaps Olson was able to resolve Na(5) and Na(6) because his data set was relatively large: 536 reflections with  $I > 3\sigma(I)$ .

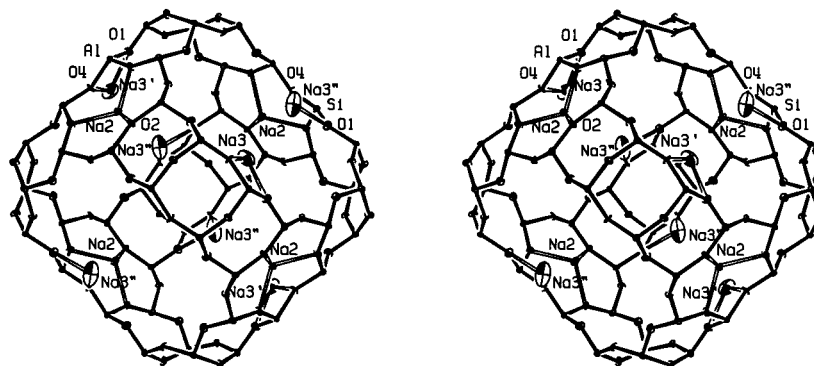
The crystal structure of Na—X at 5 K was determined by Cheetham et al.;<sup>5</sup> all site III' Na<sup>+</sup> ions were found at a single equipoint near O(1)—Al—O(4) sequences, like Na(III') in this work. Their Monte Carlo calculation (on Na—LSX, Si/Al = 1) supports their result by showing that the most stable structure has 82% of its Na<sup>+</sup> ions at site III' positions facing O(1)—Al—O(4) sequences with the remainder at site III'' near O(1)—Si—O(4) sequences. When higher energy configurations were considered, the distribution of Na<sup>+</sup> ions among sites III' and III'' became more even. Qualitatively, these calculations are in agreement with the two single-crystal structures (Olson's<sup>4</sup> and this work) determined at ambient temperature. At 5 K the occupancy at Na(III'') might be zero or negligible; this would be expected if the energy at III' is just a little lower than that at III''. In addition, a low occupancy of Na<sup>+</sup> ions at III'' might not have been observable using powder diffraction data, although the authors were careful to check. This result indicates that the III' and III'' sites are similar in energy and that further justification based on Si substitution into the Al position or Si ordering within the Al position is not needed.

In Figure 5a, all of the III', III'', and III''' positions within a 12-ring in Olson's structure<sup>4</sup> are plotted. Remember, these positions are sparsely occupied with 28 ions distributed among 16 12-rings, so no more than two Na<sup>+</sup> ions need to be placed in any 12-ring; all obvious too-short contacts can easily be avoided. Figure 5b shows the positions found in this work. If the III' sites (III', III'', and III''') are close in energy, these figures suggest that the 12-ring Na<sup>+</sup> ions should have a very low barrier for migration among them. At ambient temperatures, these ions may move about in their 12-rings from III' to III'' to another III', etc., perhaps moving in a circular path on the inner surface

**TABLE 3: Comparison of the Dehydrated Structures of Na–X and Tl–X**

	Na <sub>88</sub> –X <sup>a</sup>	Na <sub>92</sub> –X <sup>b,c</sup>	Na <sub>ca. 87</sub> –X <sup>d</sup>	Tl <sub>92</sub> –X <sup>c,e</sup>	maximum
Occupancy <sup>f</sup>					
site I	2.9(5)				16
site I'	21.1(19), 8.0(19)	29.5(8) <sup>g</sup>	32	31.8(4) <sup>g</sup>	32
site II	31.0(3)	35.2(7) <sup>g</sup>	32	32.1(4) <sup>g</sup>	32
site III'	8.6(10)	10(4)	24(2)	16.3(5)	96
site III''	10.6(10)	18(4)		10.6(6)	96
site III'''	10.6(10)				96
M <sup>+</sup> –Framework Distances (Å)					
M(I')–O(3)	2.242(7), 2.36(3)	2.266(7)	2.241(8)	2.59(1)	
M(II)–O(2)	2.36(3)	2.355(6)	2.364(9)	2.68(1)	
M(III')–O(1)	2.44(5)	2.44(10)	2.58(5)	3.10(2), 3.15(3)	
M(III')–O(4)	2.41(5)	2.56(14)	2.77(5)	2.81(2), 2.87(2)	
M(III')–Al	2.97	3.07(10)	3.23(5)	3.22	
M(III')–Si	3.54	3.69(17)		3.28	
M(III'')–O(1)	2.45(4)	2.43(9)		2.95(4), 2.95(4)	
M(III'')–O(4)	2.58(5)	2.33(5)		2.38(4)	
M(III'')–Si	3.11	2.95(5)		3.31	
M(III'')–Al	3.72	3.43(8)		3.22	
M(III''')–O(1)	2.81(5), 2.85(5)				
M(III''')–O(4)	2.22(5)				
M(III''')–Al	3.04				
M(III''')–Si	3.05				

<sup>a</sup> Reference 4, D. H. Olson. Crystal was grown by J. F. Charnell in New Jersey. <sup>b</sup> This work. <sup>c</sup> Crystal was grown by V. P. Petranovskii in Russia. <sup>d</sup> Reference 5, A. K. Cheetham et al. Powder sample was prepared by the authors in California. <sup>e</sup> Reference 15, Kim et al. <sup>f</sup> Occupancy factors are given as the number of atoms or ions per unit cell. Occupancies without esd's were not varied in least-squares refinement. <sup>g</sup> Fixed at 32 in the final cycles of least-squares refinement.



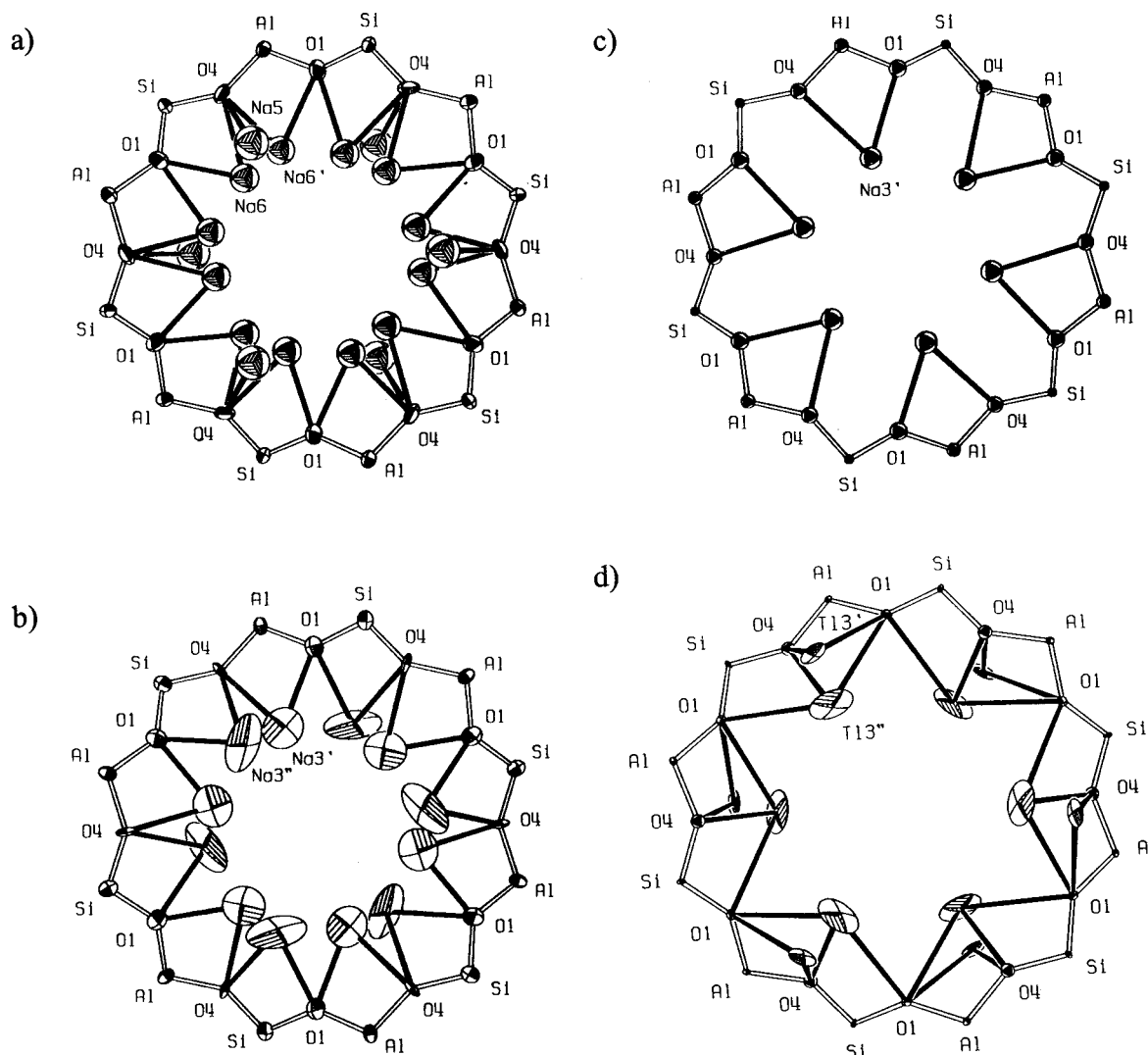
**Figure 4.** Stereoview of the supercage in dehydrated Na<sub>92</sub>–X. The Na<sup>+</sup> ions at sites III' and III'' have been placed at positions that minimize the total III', III'' repulsion energy. Ellipsoids of 20% probability are shown.

of the 12-ring or otherwise mobile on the inner surfaces of the zeolite. The ill-defined site III' positions found crystallographically may only represent areas of greater average electron density. Perhaps this motion would not occur (would be frozen out) at 5 K (Figure 5c). Figure 5d indicates that the barrier for the movement of Tl<sup>+</sup> ions about the ring should be higher than that for Na<sup>+</sup>.

The space group  $Fd\bar{3}$  requires long-range ordering at the Si and Al positions. The framework composition, Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub><sup>92-</sup> per unit cell, requires further that the Al position be occupied by 92 Al and 4 Si atoms. (Minor mixing of Al into the Si position may not be possible for Si/Al near 1.0).<sup>2,3</sup> A minority of the 12-rings must contain sequences (omitting oxygens) such as –Al–Si–Al–Si–Si–Si–Al–Si–Al–Si–Al–Si–, –Al–Si–Al–Si–Si–Si–Si–Si–Al–Si–Al–Si–, –Al–Si–Si–Si–Al–Si–Si–Si–Al–Si–Al–Si–, etc., which are consistent with Loewenstein's rule,<sup>1</sup> with Mellum's<sup>2</sup> and Peterson's<sup>3</sup> results, and with the space group  $Fd\bar{3}$  with disorder at the Al position. (For Na<sub>92</sub>–X, at least 12 of the 16 12-rings must be –Al–Si–Al–Si–Al–Si–Al–Si–Al–Si–Al–Si–.) Whenever a 12-ring is enriched in Si in one of these ways, new III' equipoints appear near others in position and perhaps in energy. These may be selected by Na<sup>+</sup> ions if they are lower in energy.

Cheetham's calculations indicate that they (O–Si–O sites) are not lower in energy<sup>5</sup> so that these new positions are not selected, but that the energy differences are small so that they may be occupied at ambient temperatures. This would generate additional III' positions that would be similar to those found and very difficult to resolve from them whether the ordering is regular, as proposed by Takaishi for instance,<sup>6–9</sup> or in accordance (full or partial) with Dempsey's rule (for –Al–O–Si–O–T–, Si is preferred at T),<sup>23</sup> or random. Olson appears to have successfully resolved some of these positions.<sup>4</sup>

In Na<sub>92</sub>–X·14Na,<sup>24</sup> a Na sorption complex of dehydrated Na<sub>92</sub>–X, the 12-ring Na<sup>+</sup> ions occupy only a single III' site near O(1)–Al–O(4) sequences of the zeolite framework. This is a simpler arrangement of site III' Na<sup>+</sup> ions than is found in empty Na<sub>92</sub>–X at ambient temperature (this work and ref 4) and is the arrangement found by Cheetham at 5 K.<sup>5</sup> Each sodium atom was captured by a pair of site III' Na<sup>+</sup> ions to give a linear (Na<sub>3</sub>)<sup>2+</sup> cluster. This occurred 14 times per unit cell; sorption ceased when all site III' Na<sup>+</sup> ions were complexed. By use of the III' and III'' positions found in this work, it appears that trans III'–III'' pairs of Na<sup>+</sup> ions would be too far apart (6.12–(9) Å) to capture a Na<sup>+</sup> ion, whereas the trans III'–III' distance (5.77(18) Å) is more suitable, more like the III'–III' distance



**Figure 5.** All site III' positions (near the edges of 12-rings) (a) in the single-crystal structure of  $\text{Na}_{88}\text{-X}$  (ref 4), (b) in the single-crystal structure of  $\text{Na}_{92}\text{-X}$  (this work), (c) in the structure of  $\text{Na-X}$  ( $\text{Si/Al} = 1.2$ ) determined by powder diffraction methods at 5 K (ref 5), and (d) in the single-crystal structure of  $\text{Tl}_{92}\text{-X}$  (ref 15). Except for (c), all structures were determined at ambient temperatures. In all structures the 12-rings are sparsely occupied; no more than two cations need to occupy any 12-ring. Ellipsoids of 20% probability are shown.

(5.86(8) Å) seen in the  $(\text{Na}_3)^{2+}$  cluster. Accordingly, all 28  $\text{Na}^+$  ions are at  $\text{Na}(\text{III}')$ , none at  $\text{Na}(\text{III}'')$ .

The distribution of 12-ring  $\text{Na}^+$  ions between two different III' sites in dehydrated  $\text{Na}_{92}\text{-X}$  may be partially explained by electrostatic repulsions between  $\text{Na}^+$  ions that share 12-rings. If 12-ring  $\text{Na}^+$  ions prefer to be near  $\text{O}(1)\text{-Al-O}(4)$  sequences (the III' position) as Cheetham et al. calculated,<sup>5</sup> but select  $\text{O}(1)\text{-Si-O}(4)$  sequences (the III'' position) whenever two coexist within the same 12-ring to minimize across-12-ring repulsive forces (see values in the previous paragraph), the occupancies at the III' and III'' positions would be 4 and 24, respectively, compared to the values found in this work, 10(4) and 18(4), respectively. (Of the 16 12-rings, four would have one and 12 would have two  $\text{Na}^+$  ions to give the total of 28  $\text{Na}^+$  ions at  $\text{Na}(\text{III}')$  and  $\text{Na}(\text{III}'')$ .) This suggests that across-12-ring repulsive forces are partly responsible for the population of the III'' position by  $\text{Na}^+$  ions.

No  $\text{Na}^+$  ions occupy site I in this structure. This is in agreement with Cheetham's result<sup>5</sup> and the  $\text{Na}_{92}\text{-X}\cdot 14\text{Na}$  structure<sup>24</sup> but differs from Olson's  $\text{Na}_{88}\text{-X}$  structure.<sup>4</sup>  $\text{Na}^+$  ions do not fit site I very well. Its distance to framework  $\text{O}(3)$ 's is 2.748(5) Å, much longer than the sum of the radii of  $\text{Na}^+$  and  $\text{O}^{2-}$  ( $0.97 + 1.32 = 2.29$  Å);<sup>25</sup> with only a 1+ charge, a  $\text{Na}^+$

ion cannot be expected to pull the six oxygens too much closer. The  $\text{Na}^+$  ions at sites I', II, and III' approach framework oxygens at expected distances (see Table 2). Perhaps Olson's crystal contained impurity cations. One  $\text{Ca}^{2+}$  ion, one  $\text{K}^+$  ion, and a fraction of a  $\text{Ba}^{2+}$  ion per unit cell are among the possibilities. Site I would be preferred by cations of that size and charge.<sup>18,25,26</sup>

**4.2. Comparison with  $\text{Tl}_{92}\text{-X}$ .** In the structure of dehydrated  $\text{Tl}_{92}\text{-X}$ ,<sup>15</sup>  $\text{Tl}^+$  ions occupy two different site III' positions in the supercell as found in this work. One of them, at  $\text{Tl}(\text{III}')$ , is close to site III, near two  $\text{O}(4)$  and two  $\text{O}(1)$  oxygens. The other, at  $\text{Tl}(\text{III}'')$ , is near one  $\text{O}(4)$  and two  $\text{O}(1)$  oxygens. Both  $\text{Tl}(\text{III}')$  and  $\text{Tl}(\text{III}'')$  are approximately equidistant from Al and Si atoms. Thus, the  $\text{Tl}(\text{III}')$  and  $\text{Tl}(\text{III}'')$  positions are qualitatively different from those occupied by  $\text{Na}^+$  ions presumably because  $\text{Tl}^+$  (radius = 1.47 Å)<sup>25</sup> is substantially larger than  $\text{Na}^+$  (radius = 0.97 Å).<sup>25</sup>  $\text{Tl}^+$  fits well into longer arcs of the zeolite framework such as the 12-ring bay at  $\text{O}(1)\text{-Al-O}(4)\text{-Si-O}(1)$  (see Figure 5) and into a cradle of four oxygen atoms near site III.

Difficulties were encountered in the least-squares refinements of the III' and III'' positions in  $\text{Tl}_{92}\text{-X}$ , much like those in this work, even though  $\text{Tl}^+$  is a heavy scatterer of X-rays and should be much easier to locate than  $\text{Na}^+$ . As with  $\text{Tl-X}$ , the III''

position in this work has a much larger and more anisotropic thermal parameter than III'. Attempts to refine III'' as two separate positions were unsuccessful in this work; with TI-X they yielded a third III' position, III''', with a far larger, far less reasonable thermal parameter. These results indicate crystallographically the absence of sharp minima at some III' sites for each ion and may indicate high ionic mobility at ambient temperatures as discussed for Na<sub>92</sub>-X in paragraph 5 of section 4.1.

## 5. Conclusion

The discrepancies between this work and the two previous structural determinations of dehydrated Na-X can be reconciled if the data collection temperatures, the qualities of the diffraction data, and the presence of impurity ions are considered, and if two (or more) III' sites are similar in energy. The placements of the Na<sup>+</sup> ions in zeolite X can be understood without involving ordering of Si atoms within the Al equipoint; there is no evidence for sharp inequivalencies among zeolite X samples, only continuous variations due to differences in composition.

## 6. Another Recent Redetermination

After this work was submitted for publication, we learned of yet a fourth crystallographic report of the crystal structure of dehydrated Na-X; Lecomte et al. had studied a low-silica (Si/Al = 1.06) single crystal at 25 °C.<sup>27</sup> Na<sup>+</sup> ions were found at four different crystallographic sites. Sites I' and II are occupied by 31.0(6) and 29.8(6) Na<sup>+</sup> ions, respectively, per unit cell; these values do not differ significantly from 32.0, full occupancy. The coordinates at these two sites agree well with the results of this work and those of the two previous investigations.<sup>4,5</sup> Two III' positions, Na(3) and Na(4), were found, occupied by 15.4(10) and 17.3(19) Na<sup>+</sup> ions, respectively. The shortest Na-(3) to framework oxygen distance is 2.75(2) Å, too long to be a closest Na-O approach. The Na<sup>+</sup> ions at Na(4) bind to one O(4) at 2.14(2) Å and to two O(1) oxygens at 2.75(4) and 2.82-(4) Å. Not found in this latest study<sup>27</sup> was the Na(III') position that had been found in this and the two previous determinations.<sup>4,5</sup> In fact, Na(3) and Na(4) are unlike any of the III' positions found in the three previous determinations. One or more common experimental errors, as discussed in section 1.3,

may have occurred. Many essential details of crystal preparation (postsynthesis) were not discussed.<sup>27</sup>

**Supporting Information Available:** Tables of observed and calculated structure factors squared with esd's. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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