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Accurate Redetermination of Crystal Structure of Dehydrated Zeolite A. Absence of Near Zero Coordination of Sodium. Refinement of Si,Al-Ordered Superstructure

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Abstract: Single-crystal X-ray diffraction data for Linde zeolite 4A dehydrated at 350 °C were refined with space group $Fm\bar{3}c$ (a = 24.555 Å). Sodium atoms occur near the center of most 6-rings (site 1; 62 atoms in a 64-fold position; x = 0.0996), off-center from most 8-rings (site 2; 23 atoms in a 24-fold position; y = 0.2165, z = 0.2111), and projecting into the large cavity opposite a 4-ring (site 3; 6 atoms in a 96-fold position, y = 0.1060). The combined population of 91.7 ± 1.0 Na atoms is less than the 96 atoms for an ideal $Na_{96}Al_{96}Si_{96}O_{384}$ formula, in conformity with electron microprobe analysis and X-ray data for dehydrated K-exchanged zeolite A. Alternate tetrahedra have mean T–O distances of 1.597 and 1.731 Å which correspond to occupancy mainly by Si and by Al, in conformity with earlier structure analyses. Although Na atoms have unusual coordinations, as found in many dehydrated but not hydrated zeolites, the Na–O distances do not satisfy the concept of near zero coordination: this supports the invalidation of zero coordination in dehydrated K-exchanged zeolite A. Na(1) has three nearest neighbors at 2.32 Å; Na(2) has one-sided coordination to O(2) at 2.38 Å and two O(1) at 2.56 and 2.67 Å; Na(3) has one-sided coordination to two O(3) at 2.59 and two O(1) at 2.61 Å. Because of low fractional occupancy of Na(3), the latter two distances are subject to an unknown error which should decrease the observed values. Whereas refinement in the pseudospace group gave an impossibly high population of 4.4 ± 0.1 for the effectively threefold Na(2) site, refinement in the true space group gave 23.2 ± 0.4 for the corresponding 24-fold site.

Introduction

Development of crystallographic techniques has allowed greater accuracy in determination of the crystal structure of Linde zeolite 4A since the original determination.[1] Particularly important was refinement of the hydrated variety in the true unit cell with a = 24.6 Å and space group $Fm\bar{3}c$ instead of the pseudocell with a = 12.3 and space group $Pm\bar{3}m$.[2] Because of controversy about the accuracy of recent structure determinations of modifications of the zeolite 4A, we have begun a systematic program of high-accuracy structure determinations. The first stage is thorough examination of modifications in which cations are supposed to have "zero-coordination". Detailed study of dehydrated K-exchanged zeolite A[3] showed that all K atoms lay at reasonable distances from framework oxygens and that the claim of zero-coordinated cations was based on least-squares refinement of a spurious electron-density peak resulting from low-accuracy diffraction data.[4] The new study confirmed that Al and Si atoms alternated throughout the framework to give the 24.6 Å true cell and presented analytical and crystallographic evidence that the Si/Al ratio was slightly greater than unity.

The corrected structure for dehydrated K-exchanged zeolite A has K atoms in similar positions to the Na atoms found in dehydrated zeolite 4A (i.e., the as-synthesized Na variety).[5] The latter structure was refined by Yanagida, Amaro, and Seff in the pseudocell, and the assumed 12 Na atoms were placed as follows: 8 near the center of 6-rings, 3 in the plane of 8-rings, and 1 in the large cavity opposite a 4-ring. All 12 Na atoms were found in unusual coordinations, as in many dehydrated zeolites, but the distances to nearest neighbors were reasonable (2.32 ± 0.01 to 2.59 ± 0.15 Å) when compared to other Na-bearing silicates. Surprisingly, a claim of "a near zero-coordinate sodium ion" was then made by Subramanian and Seff[6] for a dehydrated 4A crystal in which the twelfth Na atom was found to lie at 2.83 (7) Å from the nearest framework oxygen. Although the authors state that the diffraction data set was nearly twice as large as that collected for the earlier structure, there are some severe problems. The second crystal had been exposed at 150 °C to 7 × 10^{-3} torr of cesium vapor before dehydration at 350 °C in the hope that sodium would be exchanged. Although no chemical analysis was performed, it was concluded that exchange had not taken place. Technical problems in the crystallographic analysis result from the use of the pseudocell instead of the true cell and the assumption of integral population factors. Furthermore, the refinement was carried out by least-squares methods, and a final difference-Fourier map was not presented in the published paper. Subramanian and Seff claimed that "the Na^+ ion positions differ only in their precision from those reported earlier" by Yanagida, Amaro, and Seff, but the quoted precisions for the Na(3)–O distances are actually the same (0.07 Å) in both structures! Because of the implausibility of the claim of near-zero coordination in view of our refinement of dehydrated K-exchanged zeolite A, we undertook a new refinement of zeolite 4A in the true cell.

X-ray Diffraction Analysis

Crystals of zeolite 4A were prepared by a modification of Charnell's method[7] including a second crystallization using seed crystals from the first synthesis. A cube, 78 μm on edge, was lodged in a silica capillary, dehydrated under 10^{-5} torr at 350 °C for 2 days, sealed at temperature, and slowly cooled to room temperature. An octant of data out to $\sin \theta/\lambda$ = 0.59 for the true cell was collected with monochromatized Cu Kα radiation and a Picker FACS-1 diffractometer. Averaging of 3400 symmetry-related diffractions yielded 582 unique diffractions of which 443 were above background at the 2σ level, 339 belong to the pseudostructure, and 104 belong to the superstructure. This data set compares with the 290 and 90 diffractions listed for hydrated zeolite 4A.[2] Table I compares experimental conditions for the present study (Pluth and Smith, both pseudocell and full cell; briefly PSp,f) with those used by Yanagida, Amaro, and Seff (YASp) and Subramanian and Seff (SSp) for the pseudocell. Particularly important for obtaining a good detection level for weak diffractions was use of Cu Kα radiation instead of Mo Kα radiation and collection of a full octant of data.

The present cell dimension (25.555 ± 0.002 Å) was obtained by least-squares refinement of 2θ values for 15 Friedel pairs ($44 < 2\theta < 70$) and weighted wavelengths for Cu Kα. There is no obvious explanation of the discrepancies with the cell dimensions 24.526 (4) and 24.584 (4) Å measured by YAS and SS.

Estimated errors for PS intensities (σ_I) were calculated by $\sigma_I = P[S + t^2B + k^2(S + tB)^2]^{1/2}$ where P is scan rate, S is peak scan counts, B is total background counts, t is ratio of peak-to-background observation

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(6) V. Subramanian and K. Seff, *J. Phys. Chem.*, **81**, 2249 (1977).

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Table I. X-ray Diffraction Data and Structure Refinement

	PSp,f	YASp	SSp
cryst diameter	~78 μm	~67 μm	~85 μm
dehydration *T*, *P*, time	350 °C, 10^{-5}, 2 days	350 °C, 10^{-5}, 1 day	350 °C, 10^{-5} torr, 2 days
space group	$Fm\bar{3}c$	$Pm\bar{3}m$	$Pm\bar{3}m$
wavelength, Å	1.5418	0.71069	0.71069
monochromator	graphite	graphite	graphite
cell dimension, Å	24.555 (2)	12.263 (2)	12.292 (2)
diffractometer	Picker FACS-1	Syntex $P2_1$	Syntex $P2_1$
orientation	2° from *a*	?	?
scan technique	fixed $\theta-2\theta$	variable $\theta-2\theta$	fixed $\theta-2\theta$
speed	1°/min	(24–0.5°)/min	1°/min
range	1.0–1.6°	2.0–2.5°	2.0–2.5°
bkgd	fixed 20 s	variable, scan/bkgd = 1	variable, scan/bkgd = 1
total intensities	3400 (1852)[a]	881	~880
unique data set	582 (370)[a]	881	~880
significant data set	443 (339)[a] (2σ)	154 (3σ)	288 (3σ)
$(\sin\theta)/\lambda$ max	0.59	0.81	0.81
absorption coeff	49.4 cm^{-1}	4.3 cm^{-1}	4.3 cm^{-1}
absorption correction	yes	no	?
R	0.030 (0.041)[a]	0.069	0.061
weighted *R*	0.023 (0.043)[a]	0.086	0.049
S	2.1 (4.6)[a]	1.14	1.9

[a] Numbers in parentheses refer to pseudostructure.

times, and k is instability constant (0.02). Symmetry-equivalent diffractions were averaged by using

$$I = \sum_{i=1}^{n}(I_i\sigma_i^{-2})/\sum_{i=1}^{n}\sigma_i^{-2}$$

$$\sigma(\bar{I}) = [N/(N-1)\sum_{i=1}^{n}\sigma_i^{-2}]^{1/2}$$

where I_i and σ_i are the intensity and standard deviation of the *i*th of N equivalent diffractions. Lorentz and polarization effects were corrected by assuming a monochromator crystal half-perfect and half-mosaic. An analytical absorption correction used a Gaussian integration formula and gave maximum and minimum transmission factors of 0.685 and 0.734.

All PS diffractions obeyed $Fm\bar{3}c$ except for five weak diffractions: 111, intensity of 163 ± 22; 17,3,3, 21 ± 10; 23,7,7, 17 ± 8; 13,13,11, 16 ± 8; 15,15,15, 33 ± 14. Whereas Gramlich and Meier[2] found that all diffractions from zeolite 4A obeyed $Fm\bar{3}c$, Thöni[8] found violations for the *c* glide plane in hydrated Tl-A, Ca-A, and Ag-A, and Pluth and Smith found weak violations in dehydrated K-A[3]. Because the violations in the PS data for zeolite 4A are weak, they were ignored, but the possibility of lower symmetry than $Fm\bar{3}c$ must be considered.

Structure Refinement

Refinement of the PSf data in $Fm\bar{3}c$ by conventional least-squares techniques, using starting parameters for the framework for dK-A[3] and the cations from earlier structures,[5,6] converged rapidly even though population and displacement parameters were refined simultaneously and some correlation coefficients were as high as 0.8. All final parameters were crystal chemically reasonable (see later), and the total content of 91.7 ± 1.0 Na atoms is consistent with the crystallographic estimate of 89.8 ± 2.7 K atoms in dK-A[3] and the electron microprobe estimate of 94.4 Al atoms for hydrated Ca-exchanged zeolite A.[3]

By ignoring 104 superstructure diffractions, the PSp data were refined in the $Pm\bar{3}m$ pseudocell for comparison with the YASp and SSp refinements. Convergence was slow and the displacement parameters for Na(3) shifted slowly from nonpositive definite to physically meaningful values. The population of Na(3) refined to 4.38 (0.12) atoms, which implies more than one Na atom for each of the three eight-membered rings. This is crystal chemically implausible because two Na^+ in a 8-ring would lie within 2.5 Å. Subramanian and Seff found a similar problem and attributed it to correlation of population and thermal parameters. Because the PSf data, refined in the true cell, gave 2.9 ± 0.05 atoms of Na(2) in the corresponding pseudocell, it appears that refinement in the pseudocell caused a serious error in the population. This has serious implications for many of the structure determinations of Seff and coworkers in which populations were deduced from crystal structure refinement with the pseudocell and in which cation totals were not checked by an independent chemical analysis.

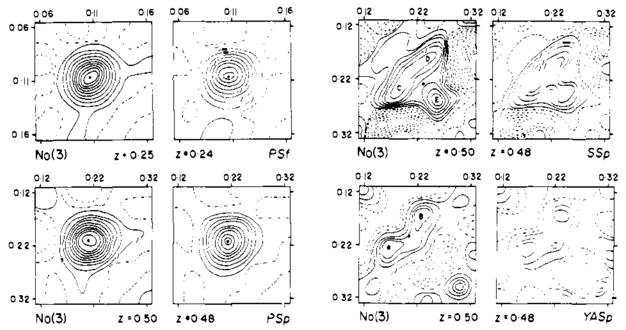

Figure 1. Difference-Fourier synthesis for the region around the Na(3) site. Framework atoms, Na(1) and Na(2), were included in the calculated structure amplitude. For each of the four sets of experimental data two sections are shown at $z = 0.50$ and $z = 0.48$ and 0.52 for the pseudocell and $z = 0.25$ and $z = 0.24$ for the corresponding true cell. Positive, negative, and zero contours are shown respectively by continuous, dashed, and dot-dashed lines. Contour levels are as follows: PSf, 0.09 e/Å^3; PSb, 0.08; YASp, 0.12; SSp 0.09. Dots show least-squares refinements of Na(3) site.

The reliability of the crystal-structure refinements was tested by difference-Fourier analyses. Figure 1 compares sections through the electron density of the Na(3) atom for the PSf, PSp, YASp, and SSp refinements. The calculated structure amplitudes were obtained for the framework and the Na(1) and Na(2) atoms, but ignoring the Na(3) atoms. This use of a difference-Fourier analysis eliminates problems from termination-of-series errors. Whereas the PSf and PSp difference maps show near circular contours around the Na(3) atom and low contours away from the peak, the YASp and SSp maps show noncircular contours around the positions proposed for the Na(3) atom from least-squares refinements (Table II). Furthermore both the positive and negative peaks away from the Na(3) atom are comparable in height to the positive peaks near the Na(3) atom. For the YASp data, the least-squares refinement was constrained by the assumed point symmetry of Wyckoff position 12(j) to give an average of the electron density between peaks A and B. For the SSp data, the least-squares refinement is presumably giving a constrained average of electron density extending across peaks C, D, and E. Peaks C and D correspond approximately to peaks A and B but do not match the circular peaks in both the PSp and PSf syntheses. We suggest that random experimental error in both the YASp and SSp data is responsible. Random experimental error might also be the cause of peak E, but it might be claimed that it results from a trace of Cs. Because the peak is not as broad as the peaks in the PSp and PSf syntheses, we prefer experimental error. We conclude that the Na(3) atom is well-defined by the PS data but not by the YAS and SS data. This conclusion from the difference-Fourier series is consistent with the relation between the sizes of the significant data sets and *R* factors in Table I.

Final parameters are compared in Table II and conventional refinement indices (defined in ref 3) given in Table I. The final cycle of least squares minimized $\sum w||F_o| - |F_c||^2$ with $w = \sigma_F^{-2}$. Atomic scattering factors and anomalous scattering corrections for Si^{2+}, Al^+, O^-, and Na^+ were taken from volume 4 of "International Tables for X-ray Crystallography". Factors for Si^{2+} and Al^+ were interpolated between factors for Si and Si^{3+} and for Al and Al^{3+}. Refinements in $Pm\bar{3}m$ used $(Si^{2+} + Al^+)/2$. The largest peak in the final difference-Fourier map (~0.3 e/Å^3 near the center of an 8-ring) is comparable to the random noise level of the whole map. Calculated and observed structure amplitudes are available as supplementary material. Computer programs are listed in ref 9. Selected bond distances and angles are compared in Table III. A stereoview of the large cage is given in Figure 2 and the bonding of the Na atoms in Figure 3.

Discussion

A simple but important conclusion is that the Na(3) atom in dehydrated Na zeolite is coordinated to framework oxygens and that the evidence[6] for near zero coordination is false. This supports

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(8) W. Thöni, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **142**, 142 (1975).

(9) In addition to local programs for data reduction, local variations of the following programs were used: FORDAP, Fourier program of A. Zalkin; NUCLS, a least-squares program resembling Busing and Levy's ORFLS; ORFFE, error function program of Busing and Levy; ORTEP, plotting program of C. Johnson.

Table II. Atomic Populations, Positions, and Displacements of Dehydrated Zeolite A

	PSp(Si,Al)	PSf		YASp(Si,Al)	SSp(Si,Al)
		Si	Al		
T					
position	24(k)	96(i)	96(i)	24(k)	24(k)
pop.	24	96	96	24	24
x	0	0	0	0	0
y	0.1836 (1)	0.09316 (5)	0.18715 (7)	0.185 (1)	0.1836 (2)
z	0.3722 (1)	0.18499 (6)	0.09042 (6)	0.372 (1)	0.3718 (2)
β_{11}	38 (1)	9.7 (3)	9.4 (3)	$B = 1.4$ (6)	32 (2)
β_{22}	35 (1)	7.9 (3)	6.5 (3)		27 (2)
β_{33}	26 (1)	5.9 (3)	8.7 (3)		17 (2)
β_{12}, β_{13}	0	0	0		0
β_{23}	5 (1)	1.2 (2)	2.0 (2)		6 (2)
Na(1)					
position	8(g)	64(g)		8(g)	8(g)
pop.	7.30 (7)	62.2 (2)		8	8
x, y, z	0.1991 (2)	0.09960 (4)		0.200 (1)	0.2014 (3)
$\beta_{11}, \beta_{22}, \beta_{33}$	55 (2)	15.7 (2)		70 (10)	59 (3)
$\beta_{12}, \beta_{13}, \beta_{23}$	21 (2)	5.4 (2)		10 (5)	16 (3)
Na(2)					
position	12(i)	96(i)		12(i)	12(i)
pop.	4.38 (12)	23.2 (4)		3	3
x	0	0		0	0
y	0.4290 (8)	0.2165 (6)		0.429 (3)	0.4302 (12)
z	0.4290 (8)	0.2111 (6)		0.429 (3)	0.4302 (12)
β_{11}	238 (21)	28 (2)		120 (60)	141 (27)
β_{22}	177 (12)	32 (4)		25 (15)	72 (12)
β_{33}	177 (12)	19 (3)		25 (15)	72 (12)
β_{12}, β_{13}	0	0		0	0
β_{23}	−64 (13)	−11 (12)		0	−19 (17)
Na(3)					
position	12(j)	96(h)		12(j)	12(j)
pop.	0.81 (10)	6.3 (4)		1	1
x	0.5	0.25		0.5	0.5
y, z	0.2087 (30)	0.1060 (7)		0.204 (7)	0.2307 (54)
β_{11}	10 (56)	24 (7)		$B = 2$ (2)	51 (58)
β_{22}, β_{33}	74 (35)	15 (4)			157 (63)
β_{12}, β_{23}	0	−2 (4)			0
β_{13}	−10 (38)	4 (14)			74 (82)

	PSp(Si,Al)	PSf	YASp(Si,Al)	SSp(Si,Al)
O(1)				
position	12(h)	96(i)	12(h)	12(h)
pop.	12	96	12	12
x	0	0	0	0
y	0.2275 (4)	0.11367 (10)	0.225 (1)	0.2277 (6)
z	0.5	0.24663 (17)	0.5	0.5
β_{11}	65 (5)	15.5 (5)	$B = 2.3$ (4)	52 (7)
β_{22}	76 (5)	18.4 (6)		48 (7)
β_{33}	28 (4)	5.5 (5)		31 (6)
β_{12}, β_{13}	0	0		0
β_{23}	0	0.0 (8)		0
O(2)				
position	12(i)	96(i)	12(i)	12(i)
pop.	12	96	12	12
x	0	0	0	0
y	0.2910 (3)	0.14459 (14)	0.290 (1)	0.2917 (4)
z	0.2910 (3)	0.14591 (14)	0.290 (1)	0.2917 (4)
β_{11}	90 (5)	23.9 (6)	$B = 2.6$ (4)	77 (8)
β_{22}	48 (3)	11.1 (1.0)		36 (4)
β_{33}	48 (3)	10.8 (1.0)		36 (4)
β_{12}, β_{13}	0			
β_{23}	22 (4)			21 (6)
O(3)				
position	24(m)	192(j)	24(m)	24(m)
pop.	24	192	24	24
x	0.1119 (2)	0.05379 (9)	0.114 (1)	0.1123 (3)
y	0.1119 (2)	0.05865 (9)	0.114 (1)	0.1123 (3)
z	0.3437 (3)	0.17152 (6)	0.345 (1)	0.3418 (4)
β_{11}	52 (2)	11.6 (6)	$B = 2.7$ (3)	48 (3)
β_{22}	52 (2)	11.9 (5)		48 (3)
β_{33}	56 (3)	13.6 (3)		42 (4)
β_{12}	11 (2)	3.6 (3)		10 (4)

Table II (*Continued*)

	PSp(Si,Al)	PSf	YASp(Si,Al)	SSp(Si,Al)
β_{13}	3 (2)	1.2 (4)		0 (3)
β_{23}	3 (2)	0.1 (4)		0 (3)

[a] Estimated standard deviations given in parentheses to same significance level as parameters. x, y, and z given as decimal fraction of cell edge. Isotropic B given in Å^2. Anisotropic displacement factor given as $10^4 \exp[-\Sigma_{j=1}^{3}\Sigma_{i=1}^{3}\beta_{ij}h_ih_j]$.

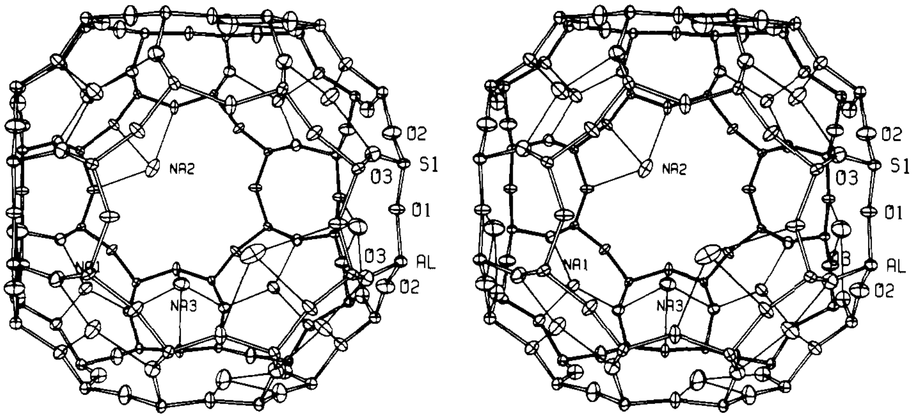

Figure 2. Stereoplot of PSf refinement of atomic positions in the large cage of dehydrated zeolite Na-A. Displacement ellipsoids at 30% probability level.

invalidation[3] of zero coordination in dehydrated K-exchanged zeolite A.

A second conclusion is that the coordinations of all Na atoms in dehydrated Na zeolite are unusual, as found previously for many zeolites, and are quite different from those found in hydrated zeolites and other inorganic materials in thermodynamic equilibrium at low temperature. Readers should be aware, of course, that in disordered structures the true distances between atoms with low fractional occupancy may be different from distances measured from electron density maps, which are averaged over all unit cells irrespective of occupancy. If distances in Table III are taken at face value, all sodium atoms of dehydrated zeolite A have either 3 or 4 oxygen neighbors at 2.3 to ~2.6 Å. We shall present plausible crystal-chemical arguments that the larger observed distances might be adjusted downwards to give true distances for unit cells actually occupied by sodium atoms.

The zeolite A framework contains three types of aluminosilicate rings, and each unit cell has 12 4-rings (4R), 8 6-rings (6R) and 3 8-rings (8R). For complete alternation of Al and Si, each 4R has two aluminums, two silicons, and two oxygens, and similarly for the 6R and 8R. The formal ionic radius of Na^+ when referenced to a radius of 1.40 Å for O^{2-} is 1.02 Å for six-coordination and a questionable 0.99 Å for four-coordination.[10] Because the ionic radius of Na is about equal to the free diameter of a 6-ring, Na(1) lies nearly at the center of the 6-ring. However Na is too small to "fill" the ring, and the ring puckers so that three O(3) atoms approach Na to give near triangular coordination with Na(1)–O(3) = 2.323 (2) Å while three O(2) atoms move away to 2.915 (1) Å. The position of O(2) will be affected directly by disorder of Na(2), as described next, but the positions of Na(1) and O(3) should be affected only indirectly. For an assumed radius of 1.40 Å for O^{2-}, the radius of Na(1) is deduced as 0.92 Å, which value fits reasonably as an extrapolation of the plot of Na–O distance vs. coordination number in Figure 2 of ref 10. Although minimum puckering would result if Na lay exactly in the middle of the 6R, Na(1) is actually displaced 0.21 Å into the large cage (see later).

Because Na(2) is much too small to "fill" an 8-ring, either the 8-ring could distort very severely so that (say) four oxygens become bonded to Na(2) and the other four oxygens move away or the ring could stay extended and Na(2) move to one side. The second choice is energetically favorable, and Na(2) moves 1.26 Å away from the center toward O(2) giving an apparent interatomic distance of 2.38 Å. The two adjacent O(1) atoms are close enough (2.56 and 2.67 Å) for bonding. Unfortunately these observed distances cannot be taken at face value because Na(2) actually has one-fourth occupancy of four sites on a space or time average, or both. When Na(2) occupies site a in Figure 3, the O(1) and O(2) atoms labeled e, f, and g may be closer to Na(2) than the centroid of their electron density, and when Na(2) occupies sites b, c, or d, the O(1) and O(2) positions may be farther away from Na(2) than the centroid. Indeed the displacement ellipsoids of O(1) and O(2) are elongated almost in the direction of Na(2), through this may result at least partly from vibration perpendicular to the Si–O–Al linkages. Consequently we suggest that the real Na(2)–O distance is less than the values indicated by the centroids of the electron density, perhaps even as low as the observed Na(1)–O distance.

The alternative choice for Na(2) opposite O(1) and with an O(2) on either side is apparently less favorable because of the geometrical linkages between the 8-, 6-, and 4-rings. Outward movement of O(2) in the 6R is necessary to accommodate Na(1), and it would be difficult for O(2) to simultaneously adjust to Na(2) if Na(2) lay opposite O(1) in the 8R. For the observed 8R, O(1)–O(1) is less (4.7 Å) than that (5.1 Å) for O(2)–O(2).

Each 6R and 8R has almost one Na on average, thereby accounting for almost 11 sodiums/pseudocell (actually 10.7 atoms, Table II). The remaining 0.8 sodium per pseudocell occupies a site opposite a 4R. This 12-fold site has only 7% occupancy by Na(3), and the actual sodium–oxygen distances may differ considerably from the distances between centroids of electron density. The free diameter of a 4R is much too small to accommodate Na, and Na(3) is forced to lie about 1.7 Å from the plane of two O(1) and two O(3), giving a one-sided square-pyramidal coordination. The Na(3)–O(1) and Na(3)–O(3) distances of 2.61 and 2.59 Å are about 0.2 Å greater than would be expected by simple comparison with the Na(1)–O(3) distances. However there are two possible explanations: (a) the centroid of electron density for O(3) is displaced from the actual position of O(3) when Na(3) is present, and (b) repulsion occurs between Na(3) and tetrahedrally coordinated atoms across shared edges. For dK-A, we pointed out that when oxygens are bonded to a cation, they should form weaker bonds to Si and Al than when they are not bonded. For a T–O–T angle of 150°, increase of the T–O distance in dK-A by 0.05 Å would force an oxygen outwards by ~0.16 Å if the tetrahedral (T) atoms remained in position. We now point to the possible effect of repulsion between Na and T ions across shared edges. In the 6R, Na(1) lies at ~3.25 Å from three aluminums and three silicons at the vertices of a hexagon, and the repulsive

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(10) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 24, 925 (1969).

Table III. Interatomic Distances (Å) and Angles (Deg) of Dehydrated Zeolite A

		PSf			
	PSp(Si,Al)	Si	Al	YASp(Si,Al)	SSp(Si,Al)
T-O(1)	1.659 (2)	1.595 (4)	1.723 (4)	1.65 (1)	1.666 (3)
T-O(2)	1.654 (2)	1.586 (4)	1.717 (4)	1.63 (1)	1.653 (3)
T-2O(3)	1.668 (1)	1.604 (3)	1.741 (3)	1.68 (1)	1.676 (2)
mean	1.662	1.597	1.731	1.66	1.668
Na(1)-3O(3)	2.334 (3)	2.3227 (15)		2.32 (1)	2.319 (5)
Na(1)-3O(2)	2.919 (3)	2.9146 (13)		2.90 (1)	2.931 (4)
Na(2)-O(2)	2.395 (13)	2.383 (7)		2.40 (6)	2.408 (22)
Na(2)-O(1)	2.623 (7)	2.557 (17)		2.64 (3)	2.632 (11)
Na(2)-O(1)	2.623 (7)	2.673 (18)		2.64 (3)	2.632 (11)
Na(3)-2O(3)	2.551 (34)	2.591 (15)		2.47 (7)	2.83 (7)
Na(3)-2O(1)	2.573 (33)	2.612 (15)		2.51 (7)	2.84 (7)
Na(1)-Na(3)	3.698 (4)	3.700 (2)		3.68 (7)	3.70 (7)
O(1)-T-O(2)	108.1 (3)	108.8 (2)	108.1 (2)	110.4 (8)	107.6 (4)
O(1)-T-O(3)	111.7 (2)	111.3 (1)	112.3 (1)	110.3 (8)	112.2 (3)
O(2)-T-O(3)	107.1 (2)	107.2 (1)	106.0 (1)	106.8 (9)	106.8 (3)
O(3)-T-O(3)	110.8 (2)	110.9 (2)	111.6 (2)	112.1 (9)	110.9 (5)
T-O(1)-T	142.1 (4)	142.2 (2)		145.1 (7)	142.0 (3)
T-O(2)-T	164.2 (4)	164.7 (2)		165.6 (15)	163.1 (3)
T-O(3)-T	145.6 (2)	144.8 (1)		145.5 (10)	144.3 (2)

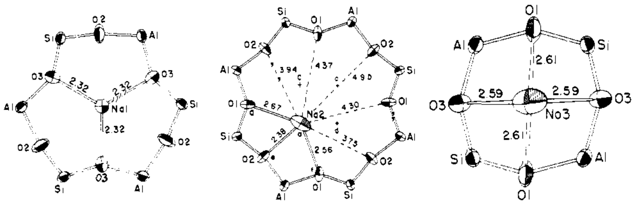

Figure 3. Plot of Na atoms and adjacent rings in dehydrated zeolite Na-A. Displacement ellipsoids at 50% probability level.

forces are symmetrical about Na(1). In the 8R, Na(2) undergoes asymmetric repulsion because the nearest Al and Si are at ~3.08 Å and the next nearest at ~3.8 Å, and the remaining five T atoms of the 8R at even greater distances. For the 4R, all four T atoms are on one side at only ~3.06 Å. A detailed investigation has just begun to calculate the electrostatic field potentials in cation-exchange variants of zeolite A (cf. study of zeolites X and Y[11]) and to investigate molecular-orbital effects (cf. ref. 12). In the meantime, there is no need to invoke the concept of zero coordination to explain the position of the Na(3) atom in dehydrated zeolite 4A: rather it is better to explore the perturbation on normal bonds as a result of unusually small coordination numbers.

The full refinement of the PSf data yields tetrahedral distances indicative of strong ordering of Si and Al into alternate tetrahedra, as also found for hydrated A[2] and dehydrated K-A.[3] The respective tetrahedral distances of 1.597, 1.608, and 1.602 Å for Si and 1.731, 1.728, and 1.736 Å for Al agree well, especially as different crystals were used, and T–O distances are affected somewhat by the type of bonding to nonframework cations[13] and molecules. For feldspar minerals[13] pure Si–O and Al–O distances are ~1.60–1.61 and ~1.74–1.75 Å. Electron microprobe analyses of A crystals[3] suggested that the Si/Al ratio is greater than unity, and the crystallographic data for dehydrated A and dK-A confirm this (see earlier). If the Si/Al ratio is near 1.03, the maximum degree of ordering would be attained with 100% Si in one tetrahedron and 97% Al and 3% Si in the alternating tetrahedron. Such a slight disorder would be consistent with the observed T–O distances.

Finally, we discuss the difference in cation positions for dA and dK-A and the possible effects from disorder of the tetrahedral cations. Simultaneous occupancy by cations of a 4R and the two adjacent 6R causes close approach of cations. Because the Na cation is smaller than the K cation, it need not project so far outwards from the framework oxygens: thus Na(1)–Na(3) is 3.7 Å in contrast to 3.3 Å for K(1)–K(6). Although X-ray analysis does not yield the positions of individual unit cells, it appeared plausible[3] that when site K(6) was occupied, site K(4,5) projecting into the sodalite unit was occupied rather that K(1). For dA, there is no evidence for splitting of site Na(1), but elongation of the displacement ellipsoid down the triad axis might be partly the result of a small displacement of Na(1) when site Na(3) is occupied. For larger cations than K, the splitting of the cation site in the 6R should be even greater, and indeed Firor and Seff have observed this in dehydrated varieties of Tl-exchanged[14] and Rb-exchanged[15] varieties of zeolite A; however, they interpreted their data in terms of zero-coordinated cations rather than cations bonded to oxygen atoms of 4R.

For completely regular alternation of Si and Al atoms, all framework oxygens have the same formal contribution from T ions on a simple electrostatic model, thereby providing no control over the choice of location of Na(2) and Na(3) ions. For an Si/Al ratio greater than unity, those framework oxygens bonded to two silicons must be fully satisfied on a simple electrostatic model and less favorable for bonding to Na than ones bonded to one silicon and one aluminum. Minimization of electrostatic energy would be obtained if Na(2) and Na(3) sites most distant from such satisfied oxygens were occupied. If the Na(1) sites are not fully occupied, as suggested by the value of 62.2 (3) atoms from the PSf refinement, each vacant site might result from more than three silicons in the surrounding 6R.

In conclusion, we emphasize the desirability of attaining the highest possible accuracy of collection of X-ray diffraction data for zeolites and of refining the data whenever possible in the true space group rather than a pseudospace group. Unfortunately the latter is not possible for most zeolites, but zeolite A is favorable when suitable data are collected. Finally we emphasize that although unusual coordinations are found for some cations in some dehydrated zeolites, these cations are coordinated to framework oxygens in structures refined by accurate crystallographic techniques.

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Supplementary Material Available: A listing (Table IV) of the observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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