

Location of Na⁺ Ions in Fully Dehydrated Na⁺-saturated Zeolite Y (FAU, Si/Al = 1.56)

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Zeolites are natural or synthetic crystalline, microporous, aluminosilicate materials with well-defined structures and unique characteristics. Faujasite-type zeolites have been widely used in range of applications as ion exchangers, catalysts, and adsorbents due to their industrial importance.^{1,2} Zeolite Y is more stable than zeolite X at high temperatures due to the higher Si/Al ratio.

The framework structure of zeolite Y is characterized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cubooctahedron), and the supercage (see Figure 1).³ Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs (32 S6Rs), 16 12-rings, and 32 single 6-rings (S6Rs). The exchangeable cations, which balance the negative charge of the zeolite Y framework, usually occupy some or all of the sites shown with Roman numerals in Figure 1. The maximum occupancies at the cation sites I, I', II, II', and III in zeolite Y

are 16, 32, 32, 32, and 48, respectively. Site III' in zeolite Y studied using space group $Fd\bar{3}m$ is a 192-fold position. Further description is available.⁵

The positions of the extraframework cations in zeolites directly affect the physical and chemical properties of zeolite. The cation sites depend on the distribution of surrounding Al atoms and the distortion of the zeolite framework.⁶ Position and fractional occupation of cationic sites change with the Si/Al ratio in zeolite.

This work was done to investigate the distribution of Na⁺ ions in fully dehydrated zeolite Y (Si/Al = 1.56) by single-crystal synchrotron X-ray diffraction technique.

Single-crystal synchrotron X-ray diffraction data were collected at 100(1) K using an Mar Research GmbH mar345 image plate detector at Beamline 1W2B in Beijing Synchrotron Radiation Laboratory. The crystal evaluation and data collection were done using $\lambda = 0.75000$ Å radiation with a detector-to-crystal distance of 50 mm. Preliminary cell constants and an orientation matrix were determined from 72 sets of frames collected at scan intervals of 5° with an exposure time of 1 second per frame. The basic scale file was prepared using the program HKL2000.⁷ The reflections were successfully indexed by the automated indexing routine of the DENZO program.⁷ The total reflections were harvested by collecting 72 sets of frames with 5° scans and an exposure time of 1 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects, and (negligible) corrections for crystal decay were also applied. The cubic space group $Fd\bar{3}m$ was determined by the program XPREP.⁸ The summary of the experimental and crystallographic data is presented in Table 1.

Full-matrix least-squares refinement (SHELXL97)⁹ was done on F_o^2 using all data. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in dehydrated $[K_{71}[Si_{117}Al_{71}O_{384}]]$ -FAU.¹⁰ Initial refinement was used anisotropic thermal parameters and converged to the high error indices (see Table 1). All shifts in the final cycles of refinement were less than 0.1% of their corresponding estimated standard deviations. The final error indices are given in Table 1. Structural parameters, are given in Table 2, and selected interatomic distances and angles are given in Table 3.

The total 75 Na⁺ ions have been found at five crystallographic sites within the unit cell in this structure: site I, I', II,

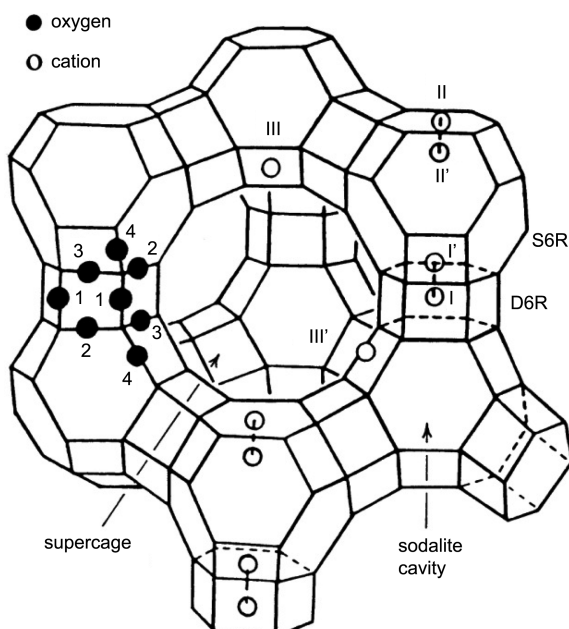


Figure 1. Stylized drawing of the framework structure of zeolite Y. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Loewenstein's rule (ref. 4) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

Table 1. Summary of experimental and crystallographic data

	[Na ₇₅][Si ₁₁₇ Al ₇₅ O ₃₈₄]-FAU
Crystal cross-section (mm)	0.32
Ion exchange T (K)	294
Ion exchange for Na ⁺ (mL, days)	15, 3
Dehydration T (K)	673
Crystal color	dark green
Data collection T (K)	100(1)
Space group, Z	<i>Fd</i> $\bar{3}m$, 1
X-ray source	1W2B, BSRF (Beijing Synchrotron Radiation Laboratory)
Wavelength (Å)	0.75000
Unit cell constant, a (Å)	25.018(1)
2θ range in data collection (deg)	59.11
No. of unique reflections, <i>m</i>	938
No. of reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	897
No. of variables, <i>s</i>	54
Data/parameter ratio, <i>m/s</i>	17.4
Weighting parameters, <i>a/b</i>	0.049/174.3
Initial error indices	
<i>R</i> ₁ / <i>wR</i> ₂ (<i>F</i> _o > 4σ(<i>F</i> _o)) ^a	0.2749/0.7797
Final error indices	
<i>R</i> ₁ / <i>wR</i> ₂ (<i>F</i> _o > 4σ(<i>F</i> _o)) ^a	0.0437/0.1207
<i>R</i> ₁ / <i>wR</i> ₂ (all intensities) ^b	0.0454/0.1254
Goodness-of-fit ^c	1.14

^a*R*₁ = Σ|*F*_o − |*F*_c||/Σ|*F*_o| and *wR*₂ = [Σ*w*(*F*_o² − *F*_c²)²/Σ*w*(*F*_o²)^{1/2}]; *R*₁ and *wR*₂ are calculated using only the reflections for which *F*_o > 4σ(*F*_o). ^b*R*₁ and *wR*₂ are calculated using all unique reflections measured. ^cGoodness-of-fit = [Σ*w*(*F*_o² − *F*_c²)²/(*m* − *s*)]^{1/2}, where *m* is the number of unique reflections and *s* is the number of variables, respectively.

and two different sites III'.

The 2 Na⁺ ions per unit cell at Na(I) lie at the center of D6Rs. Each Na⁺ ion at site I coordinates at 2.778(3) Å from 6 framework oxygen of the D6R, O(3), which is much longer than the sum of the conventional ionic radii of Na⁺

and O^{2−}, 0.97 + 1.32 = 2.29 Å.¹¹ This distance is likely to be virtual; only two of the 16 D6Rs contain Na⁺ ions; the actual distance is likely to be substantially shorter.

The 28 Na⁺ ions per unit cell occupy at sites I'. This is 32-fold position, but it is not fully filled. To avoid the very short distances between sites I and I' (2.21 Å) where intercationic electrostatic repulsion should be severe, the two I' sites of a D6R should not be occupied if its site I is filled. Accordingly, there are only (16-2) × 2 = 28 I' sites available for cations. These are fully occupied by 28 ions at Na(I'). Each

Table 3. Selected interatomic distances (Å) and angles (deg)^a

Distances			Angles
(Si,Al)-O(1)	1.6440(10)	O(1)-(Si,Al)-O(2)	112.7(1)
(Si,Al)-O(2)	1.6723(9)	O(1)-(Si,Al)-O(3)	110.4(1)
(Si,Al)-O(3)	1.6754(10)	O(1)-(Si,Al)-O(4)	111.0(1)
(Si,Al)-O(4)	1.6491(9)	O(2)-(Si,Al)-O(3)	105.2(1)
Mean (Si,Al)-O	1.6602	O(2)-(Si,Al)-O(4)	105.5(1)
		O(3)-(Si,Al)-O(4)	111.8(1)
Na(I)-O(3)	2.778(3)	(Si,Al)-O(1)-(Si,Al)	139.4(2)
Na(I')-O(3)	2.265(3)	(Si,Al)-O(2)-(Si,Al)	145.3(2)
Na(II)-O(2)	2.352(3)	(Si,Al)-O(3)-(Si,Al)	140.4(2)
Na(III'a)-O(1)	2.74(4)	(Si,Al)-O(4)-(Si,Al)	145.3(2)
Na(III'a)-O(4)	2.759(23)		
Na(III'b)-O(1)	2.830(17)	O(3)-Na(I)-O(3)	86.88(8), 93.12(8)
Na(III'b)-O(4)	2.14(4)	O(3)-Na(I')-O(3)	114.98(8)
		O(2)-Na(II)-O(2)	111.21(8)
		O(1)-Na(III'a)-O(1)	86.3(15)
		O(1)-Na(III'a)-O(4)	59.2(4)
		O(4)-Na(III'a)-O(4)	87.6(9)
		O(1)-Na(III'b)-O(1)	128.7(14)
		O(1)-Na(III'b)-O(4)	64.5(7)

^aThe numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Table 2. Positional, thermal, and occupancy parameters^a

atom	Wyckoff position	Cation site	x	y	z	^b <i>U</i> ₁₁ or <i>U</i> _{iso}	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	°Occupancy		
												initial	varied	fixed
Na ₇₅ [Si ₁₁₇ Al ₇₅ O ₃₈₄]-FAU														
Si,Al	192(<i>i</i>)		-543(1)	1251(1)	360(1)	122(4)	109(3)	95(3)	-20(2)	2(2)	-18(2)	192		
O(1)	96(<i>h</i>)		-1058(1)	0	1058(1)	192(8)	225(12)	192(8)	-35(7)	-13(9)	-35(7)	96		
O(2)	96(<i>g</i>)		-15(1)	-15(1)	1418(1)	191(7)	191(7)	219(12)	-63(7)	-63(7)	52(9)	96		
O(3)	96(<i>g</i>)		-330(1)	750(1)	750(1)	254(13)	188(8)	188(8)	20(9)	-8(7)	-8(7)	96		
O(4)	96(<i>g</i>)		710(1)	710(1)	3187(1)	214(8)	214(8)	212(12)	30(7)	30(7)	96(10)	96		
Na(I)	16(<i>c</i>)	I	0	0	0	821(209)	821(209)	821(209)	591(249)	591(249)	591(249)		1.9(3)	2
Na(I')	32(<i>e</i>)	I'	509(1)	509(1)	509(1)	315(8)	315(8)	315(8)	113(9)	113(9)	113(9)		28.3(4)	28
Na(II)	32(<i>e</i>)	II	2314(1)	2314(1)	2314(1)	199(5)	199(5)	199(5)	38(6)	38(6)	38(6)		31.4(4)	32
Na(III'a)	192(<i>i</i>)	III'	1031(16)	1469(16)	3921(12)	905(213)	905(213)	21(119)	-62(122)	62(122)	-435(250)		3.6(6)	5
Na(III'b)	192(<i>i</i>)	III'	648(16)	648(16)	4037(14)	1927(330)	1927(330)	313(169)	-249(168)	-249(168)	-401(418)		6.3(10)	8
												ΣNa ⁺ = 71.5(13)	75	

^aPositional parameters × 10⁴ and thermal parameters × 10⁴ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. ^bThe anisotropic temperature factor is exp[−2π²*a*²(*U*₁₁*h*² + *U*₂₂*k*² + *U*₃₃*l*² + 2*U*₂₃*kl* + 2*U*₁₃*hl* + 2*U*₁₂*hk*)]. ^cOccupancy factors are given as the number of atoms or ions per unit cell.

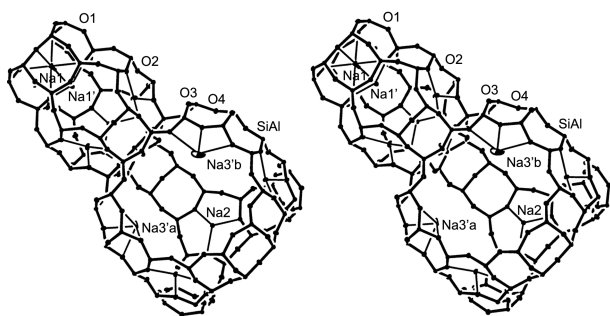


Figure 2. Stereoview of representative a double 6-ring (D6Rs), sodalite cavity, and a supercage in full dehydrated $[\text{Na}_{75}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]$ -FAU. The zeolite Y framework is drawn with heavy bonds. The coordination of Na^+ ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

Na^+ ion at $\text{Na}(\text{I}')$ lies inside of the sodalite cavity, 0.52 Å, from the plane of three O(3) framework oxygens of the D6Rs to which each is bonded. The $\text{Na}(\text{I}')\text{-O}(3)$ distance is 2.265(3) Å, which is almost the same with the sum of the ionic radii of Na^+ and O^{2-} , 2.29 Å.¹¹

The 32 Na^+ ions at $\text{Na}(\text{II})$ are found at site II in the supercage (see Figure 2). Each is recessed *ca.* 0.71 Å into the supercage from the three O(2) oxygens plane of its S6R and coordinates to these three O(2) framework oxygens at 2.352(3) Å, indicative of a good fit considering their conventional ionic radii.¹¹ The O(2)- $\text{Na}(\text{II})$ -O(2) angle is 111.21(8)°.

The remaining 5 and 8 Na^+ ions at $\text{Na}(\text{III}'\text{a})$ and $\text{Na}(\text{III}'\text{b})$, respectively, are found at another two sites III' (see Figure 2 and Table 2). These Na^+ ions are 4-coordinated by framework oxygen atoms, two O(1) and two O(4) atoms ($\text{Na}(\text{III}'\text{a})\text{-O}(1) = 2.74(4)$ Å, $\text{Na}(\text{III}'\text{a})\text{-O}(4) = 2.759(23)$ Å and $\text{Na}(\text{III}'\text{b})\text{-O}(1) = 2.830(17)$ Å, and $\text{Na}(\text{III}'\text{b})\text{-O}(4) = 2.14(4)$ Å). These distances are much longer than the sum of the Na^+ and O^{2-} radii.¹¹ However, these long distances were also seen in fully dehydrated $\text{Na}_{71}\text{-Y}$.¹² This is attributed to the reduced aluminum content of zeolite Y, as compared to zeolite X,¹³ which should lead to a smaller negative charge density for the zeolite framework, and therefore at each oxygen position.¹¹ This in turn should lead to longer Na-O distances.

The single-crystal structures of fully dehydrated $\text{Na}_{71}\text{-Y}$ ($\text{Si}/\text{Al} = 1.69$)¹² and $\text{Na}_{75}\text{-Y}$ ($\text{Si}/\text{Al} = 1.56$, this work) have shown that the sites I, I', and II are occupied with Na^+ ions and the remaining Na^+ ions are located at site III' in the supercage. When the structures of fully dehydrated $\text{Na}_{71}\text{-Y}$ ¹² and $\text{Na}_{75}\text{-Y}$ are compared, it can be seen that there are some difference in the fractional distribution of Na^+ ions. Na^+ ions are found at two nonequivalent sites I' and II, respectively, in the structure of $\text{Na}_{71}\text{-Y}$,¹² but there are no split at sites I' and II, respectively, in the structure of $\text{Na}_{75}\text{-Y}$. It seems due to the Si-Al ordering within the zeolite framework by the increased Si/Al ratio. With an increasing Si/Al ratio, many nonequivalencies arise in local geometry.¹³ This affects the Na^+ ions distribution, which become more complex.

In the structure of $\text{Na}_{71}\text{-Y}$,¹² the remaining Na^+ ions are located at two different sites III' in the supercage near triple

4-rings. These Na^+ ions bind strongly to only one oxygen atoms, O(1) or O(4). Unlike the structure of $\text{Na}_{71}\text{-Y}$, Na^+ ions are found at two sites III' in the supercage in the structure of $\text{Na}_{75}\text{-Y}$. One of them, at $\text{Na}(\text{III}'\text{a})$, is close to site III, near two O(4) and two O(1) oxygens. The other, at $\text{Na}(\text{III}'\text{b})$, is close to the side of the 12-ring, near one O(4) and two O(1) oxygens. This is attributed to the difference of the content of aluminum, resulting the density and distributions of negative charge through the framework between $\text{Na}_{71}\text{-Y}$ ($\text{Si}/\text{Al} = 1.69$)¹² and $\text{Na}_{75}\text{-Y}$ ($\text{Si}/\text{Al} = 1.56$).

Experimental Section

Large colorless single crystals of sodium zeolite Y, $[\text{Na}_{75}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]$ -FAU ($\text{Si}/\text{Al} = 1.56$), with diameters up to 0.32 mm were prepared by Lim *et al.*⁵ One of these was lodged in its own Pyrex capillary. Ion exchange was accomplished by flow method using 0.1 M aqueous NaCl solution (pH 8.80, Aldrich, 99.999%), was allowed to flow past the crystal for 3 days at 294 K. The resulting clear colorless crystal was dehydrated at 723 K and a dynamic vacuum of 1×10^{-6} Torr for 2 days. It was then sealed in its capillary by torch and removed from the vacuum line. After dehydration, microscopic examination showed that crystal had become dark green.

Supporting Information Available. Tables of calculated and observed structure factors (10 pages). The supporting materials are available *via* the Internet <http://www.kcsnet.or.kr/bkcs>.

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