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Crystallographic Study on Zeolite 4A Reacted with Rubidium Vapor

루비듐 증기와 반응한 제올라이트 4A에 대한 결정학적 연구

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ABSTRACT: Three fully dehydrated fully Rb^+-exchanged zeolite A single crystals have been prepared by the reduction of all Na^+ ions in dehydrated Na_{12}-A by rubidium vapor at various experimental conditions ($220 \leq T \leq 330$℃, $2 \leq t \leq 24$ hours, and $0.1 \leq P_{Rb} \leq 1.1$ Torr). Their structures were determined by single-crystal X-ray diffraction methods in the space group $Pm3m$ (a=12.245 (3) Å) at 22(1)℃. In these structures 12.6(2) to 13.5(2) Rb species are found per unit cell, more than the 12 Rb^+ ions needed to balance the anionic charge of the zeolite framework, indicating that the sorption of Rb^0 has occurred. In each structure, three Rb^+ ions per unit cell are located at the centers of 8-rings. Beyond that, the fractional occupancies observed are simply explained by two unit cell arrangments. In one, two Rb^+ ions are in the sodalite unit near opposite 6-rings, six are in the large cavity near 6-ring, and one is in the large cavity near a 4-ring. In the other, three Rb species in the sodalite cavity (forming a triangle 3.7 Å on an edge) each bond (3.4 Å) through a 6-ring to an Rb species in the large cavity to give an $(Rb_6)^{4+}$ cluster of symmetry $3m$ (C_{3v}). Five additional Rb^+ ions fill the remaining large-cavity 6-ring sites.

요약: 탈수된 제올라이트 Na_{12}-A에 여러 가지 실험조건 ($220 \leq T \leq 330$℃, $2 \leq t \leq 24$ hours 및 $0.1 \leq P_{Rb} \leq 1.1$ Torr) 하에서 Rb 증기로 처리하여 Na^+ 이온을 모두 환원시켜 Rb^+ 이온으로 치환한 제올라이트 A 단결정을 만들었다. 22(1)℃에서 입방 공간군 $Pm3m$ (a=12.245(3) Å)을 사용하여 단결정 X－선 회절법으로 그 구조를 결정하였다. 구조해석 결과 제올라이트 골조의 음이온 전하를 상쇄시키는 양이온 전하로써 필요한 단위포당 12개의 Rb^+ 이온보다 더 많은 12.6(2)에서 13.5(2)개의 Rb 종이 존재하여 Rb^0가 흡착되었음을 알 수 있었다. 각각의 구조에서 단위포당 3개의 Rb^+ 이온이 8-링 중심에 위치하고 있었다. Rb 종의 분수 점유수에서 두 가지 단위포의 배열이 존재함을 알 수 있었다. 그 한가지는 2개의 Rb^+ 이온이 소다라이트 동공내에 위치하고 있고, 6개의 Rb^+ 이온은 큰 동공내에, 1개의 Rb^+ 이온은 4-링 가까이의 큰 동공내에 위치하고 있다. 다른 단위포내에서는 세 개의 Rb 종이 소다라이트내에 한변의 길이가 3.7Å인 정삼각형을 이루면서 큰 동공내의 Rb 종과 6-링을 통해 각각 결합 (3.4Å)하여 대칭이 3m(C_{3v})인 $(Rb_6)^{4+}$ 클라스터를 만들고 있었다. 5개의 Rb^+ 이온은 나머지 6-링 위치를 점유하고 있다.

INTRODUCTION

Several researchers have attempted to exchange Na^+ of zeolite A with other cations. Breck (1974) reported that only 45% of the Na^+ ions in the structure of sodium zeolite A could be replaced by Cs^+ ions when ion-exchange was attempted with successive concentrated aqueous solutions at 25℃. A higher level of exchange, 60% was achieved using higher temperature exchange solutions (Breck, 1974). By straightforward exhaustive flow methods of exchange, Cs_7Na_5-A

(Vance and Seff, 1975), Cs_7K_5-A (Firor and Seff, 1977a) and Cs_9Tl_3-A (Subramanian and Seff,1979) were prepared. Most recently, fully Cs exchanged zeolite A has been synthesized by the reduction of all of the Na^+ ions in Na_{12}-A by cesium vapor (Heo and Seff, 1987; Heo et al., 1987). The redox reaction goes to completion at 350 ℃ with 0.1 Torr of Cs^0 to give Cs_{12}-A 1/2Cs. In this structure, each extra Cs atom associates with two or three Cs^+ ions to form linear $(Cs_3)^{2+}$ or $(Cs_4)^{3+}$ clusters (Heo and Seff, 1987). These clusters lie on threefold axes and extend through the centers of sodalite units.

Rb^+ ions, like Cs^+, are large and monopositive, and also exchanged only incompletely (about 90%) into zeolite A by flow methods (Firor and Seff, 1977b; Pluth and Smith, 1983). If completely Rb^+-exchanged zeolite A could be prepared, its total (exchangable) cationic volume would be large, and this might lead to an unusual arrangement of Rb^+ ions with interesting chemical properties. If extra Rb^0 atoms were sorbed, they would likely associate with Rb^+ ions to form cationic clusters, as Cs^0 atoms had with Cs^+.

This work was initiated with the hope that the intrazeolitic redox potential for the reaction

$$Na_{12}\text{-A} + 12Rb^0(g) \longrightarrow Rb_{12}\text{-A} + 12Na^0(s)$$

would be positive enough at the conditions employed to result in complete exchange. The standard aqueous (non-zeolitic) E^0 value of the above reaction is +0.19 v (Weast, 1989/1990a).

EXPERIMENTAL

Single crystals of the synthetic sodium zeolite 4A, stoichiometry of $Na_{12}Si_{12}Al_{12}O_{48}27H_2O$ (Na_{12}-A), were prepared by Charnell's method (Charnell, 1971). Each of three single crystals of Na_{12}-A (each about 0.08mm along an edge) was lodged in a fine Pyrex capillary on a vacuum line. After complete dehydration at 360℃ and 2×10^{-6} Torr for 2 days, rubidium vapor was introduced by distillation from a side-arm break-seal ampoule to the glass-tube extension of the crystal-containing capillary. This glass reaction vessel was then sealed off under vacuum and placed within two cylindrical coaxially attached horizontal ovens. The oven about the crystal was always maintained at a higher temperature than that about the rubidium metal so that rubidium would not be distilled onto the crystal (Song, 1991).

To prepare the first crystal, Rb(g) at 0.1 Torr (the vapor pressure of Rb(1) at 220℃) (Weast, 1989/1990b) was allowed to react with Na_{12}-A at 250℃ for 2 hours. The second crystal was treated similarly, but for 1 day. The third crystal was treated most strongly, with 1.1 Torr of Rb(g) (Rb(1) at 300℃) at 330℃ for 24 h. Each crystal was then sealed off from its reaction vessel by torch after cooling to room temperature. Microscopic examination of all three crystals showed that the originally colorless dehydrated Na_{12}-A had become completely black after exposure to rubidium vapor, probably because of the presence of finely divided sodium metal on their surfaces.

It is expected that the reaction of Rb^0 with Na^+ occurred only at the single-crystal surface of the zeolite. The kinetic diameter of Rb^0 atoms (ca. 5.2Å, estimated as previously described (Kim et al., 1990) is far too large to allow them to pass through 8-rings (d ca. 3.4 Å). This phenomenon was first observed when Cs^0 reacted quantitively with all Ca^{2+} ions in Ca_4Ag_4-A while simultaneously failing to react with the non-labile Ag^+ ions (Kim et al., 1990).

Diffraction intensities were subsequently collected at 22(1)℃. The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously (Seff, 1976; Seff and Mellum, 1984). An Enraf-Nonius 4-circle computer-controlled CAD-4 diffractometer, equipped with scintillation counter, pulse height analyzer, a PDP micro 11/73 computer, and a graphite monochromator, was used. Molybdenum radiation ($K\alpha_1$, λ=0.70930 Å; $K\alpha_2$, λ=0.71359Å) was used for all experiments. In each case, the unit cell parameter, 12.236(3), 12.246(3), and 12.254(3) Å for crystals 1 to 3, respectively, was determined by a least-squares treatment of 35 intense reflections ranging from 18° to 25° of 2θ

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \le k \le l$ and lhk, $l \le h \le k$) were examined using the ω-2θ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, from 0.25 to 0.32 deg/min in ω (Schagen, 1988). The intensities of three reflections in diverse regions of reciprocal

space were recorded every three hours to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70°$ were recorded. The raw data from each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; the reduced intensities were merged, and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT (Frantz and Okaya, 1987). Absorption corrections ($\mu R = 0.38$) were judged to be negligible for all crystals (John and Kathleen, 1974; Kim, 1991). Of the 869, 872, and 877 pairs of reflections for crystals 1 to 3, only the 156, 172, and 140 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

STRUCTURE DETERMINATION

Crystals 1 (treated with Rb(g) at 0.1 Torr, 250℃, 2 hours)

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] of dehydrated $Rb_{11}Na_1$-A (Firor and Seff, 1977b). Anisotropic refinement of the framework converged to an unweighted R_1 index, $(\Sigma||F_O| - |F_C||)/\Sigma F_O$, of 0.447 and a weighted R_2 index, $(\Sigma w(F_O - |F_C|)^2/\Sigma w F_O^2)^{1/2}$, of 0.537.

A subseguent Fourier difference synthesis revealed three large peaks at (0.0, 0.5, 0.5) of height 29.5(4) eÅ^{-3}, (0.2656, 0.2656, 0.2656) of height 47.2 (2) eÅ^{-3}, and (0.1034, 0.1034, 0.1034) of height 12.3 (2) eÅ^{-3}. Anisotropic refinement of the framework atoms and the Rb^+ ions at Rb(1), Rb(2), and Rb(3) (see Table I.1) converged to $R_1 = 0.063$ and $R_2 = 0.051$ with occupancies 3.10(5), 6.82(6), and 2.16(5), respectively. An ensuing difference Fourier synthesis revealed a peak of height 1.3(2) eÅ^{-3} at (0.26, 0.26, 0.5), Rb(4). This peak refined with an unusually large thermal parameter. Therefore, the isotropic thermal parameter of Rb(4) was fixed at the more reasonable value given in Table I. 1. Allowing all Rb(i), i=1-4 occupancies to vary except that at Rb(1), which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), and allowing all anisotropic thermal parameters to vary except for that of Rb(4), led to $R_1 = 0.052$ and $R_2 = 0.043$, with refined occupanciesas given in the last column of Table I. 1.

The largest peak on the final difference Fourier function was at (0.25, 0.25, 0.25) with heights of 1.3(4) eÅ^{-3}. This peak is residual electron density at Rb(2).

Crystals 2 (treated with 0.1 Torr Rb(g) 250℃, 24 hours)

Using the atomic coordinates from the structure of crystal 1, simultaneous occupancy, positional, and thermal parameter refinement was initiated. Anisotropic refinement of all positions converged quickly to $R_1 = 0.066$ and $R_2 = 0.049$. The number of Rb atoms and ions at Rb(1), Rb (2), Rb(3), and Rb(4) (see Table II. 2) refined to 3, 7.19(4), 2.51(5), and 0.48(6), respectively. A final difference Fourier synthesis was featureless except for one insignificant peak at the center of the large cavity (0.5, 0.5, 0.5 : density=2.0(7) eÅ^{-3}).

Crystals 3 (treated with 1.1 Torr Rb(g) 330℃, 24 hours)

Full-matrix least-squares refinement was initiated using the framework atomic parameters and rubidium positions from crystal 2. It converged to $R_1 = 0.062$ and $R_2 = 0.050$. The results of simultaneous refinement of occupancy, positional, and thermal parameters are presented in Table I. 3. The largest peak in the final difference Fourier synthesis was an insignificant one at the center (0.5, 0.5, 0.5) of large cavity.

All shifts in the final cycles of least-squares refinement for all three crystals were less than 0.1 % of their corresponding standard deviations.

For all structures, the full-matrix least-squares program used minimized $\Sigma w(F_O - |F_C|)^2$; the weight w of an observation was the reciprocal square of $\sigma(F)$, its standard deviation. Atomic scattering factors for Rb^+, O^-, and $(Si, Al)^{1.75+}$ is the mean of the Si^0, Si^{4+}, Al^0, and Al^{3+} functions. All scattering factors were modified to account for anomalous dispersion (Cromer, 1965; John and Kathleen, 1974). The final structural parameters and selected interatomic distances and angles are presented in Tables I and II, respectively.

Table I. [a]Positional, Thermal, and Occupancy Parameters

Atom	Wyckoff position	x	y	z	[b]β_{11} or B_{eq}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy
Crystal 1 (Dehydrated Na_{12}-A Treated with 0.1 Torr Rb Vapor at 250℃ for 2 h)											
(Si, Al)	24(k)	0	1834(3)	3716(3)	29(3)	29(3)	11(2)	0	0	8(6)	[d]24
O(1)	12(h)	0	2250(10)	5000	120(20)	60(10)	30(10)	0	0	0	12
O(2)	12(i)	0	2935(8)	2935(8)	60(10)	33(7)	33(7)	0	0	10(2)	12
O(3)	24(m)	1119(5)	1119(5)	3418(8)	56(5)	56(5)	80(10)	30(20)	40(1)	40(1)	24
Rb(1)	3(c)	0	5000	5000	97(7)	166(5)	166(5)	0	0	0	3
Rb(2)	8(g)	2671(2)	2671(2)	2671(2)	78(1)	78(1)	78(1)	58(4)	58(4)	58(4)	6.72(4)
Rb(3)	8(g)	1056(7)	1056(7)	1056(7)	93(6)	93(6)	93(6)	-30(10)	-30(10)	-30(10)	2.25(5)
Rb(4)	12(j)	2610(50)	2610(50)	5000	10(Fixed)						0.64(6)
Crystal 2 (Dehydrated Na_{12}-A Treated with 0.1 Torr Rb Vapor at 250℃ for 2 h)											
(Si, Al)	24(k)	0	1835(4)	3723(2)	21(3)	28(3)	17(3)	0	0	17(6)	[d]24
O(1)	12(h)	0	2280(10)	5000	70(10)	70(10)	3(9)	0	0	0	12
O(2)	12(i)	0	2931(8)	2931(8)	50(10)	47(7)	47(7)	0	0	10(20)	12
O(3)	24(m)	1119(5)	1109(5)	3436(8)	55(6)	55(6)	39(9)	10(20)	10(10)	10(10)	24
Rb(1)	3(c)	0	5000	5000	81(7)	142(5)	142(5)	0	0	0	3
Rb(2)	8(g)	2675(2)	2675(2)	2675(2)	70(1)	70(1)	70(1)	50(4)	50(4)	50(4)	7.19(4)
Rb(3)	8(g)	1087(6)	1087(6)	1087(6)	105(6)	105(6)	105(6)	-30(10)	-30(10)	-30(10)	2.51(5)
Rb(4)	12(j)	2610(50)	2610(50)	5000	8(2)						0.48(6)
Crystal 3 (Dehydrated Na_{12}-A Treated with 1.1 Torr Rb Vapor at 330℃ for 24 h)											
(Si, Al)	24(k)	0	1836(5)	3728(5)	24(4)	22(4)	17(4)	0	0	15(9)	[d]24
O(1)	12(h)	0	2290(20)	5000	90(20)	50(20)	20(10)	0	0	0	12
O(2)	12(i)	0	2930(10)	2930(10)	40(10)	50(10)	50(10)	0	0	-40(30)	12
O(3)	24(m)	1129(6)	1129(6)	3450(10)	59(7)	59(7)	70(10)	0(20)	40(1)	40(1)	24
Rb(1)	3(c)	0	5000	5000	84(9)	153(7)	153(7)	0	0	0	3
Rb(2)	8(g)	2659(2)	2659(2)	2659(2)	75(2)	75(2)	75(2)	57(5)	57(5)	57(5)	7.31(5)
Rb(3)	8(g)	1073(7)	1073(7)	1073(7)	112(7)	112(7)	112(7)	20(20)	20(20)	20(20)	2.68(6)
Rb(4)	12(j)	2710(80)	2710(80)	5000	10(Fixed)						0.40(8)

[a]Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. [b]The anisotropic temperature factor $=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. [c]Occupany factors are given as the number of atoms or ions per unit cell. Occupancies with e. s. d. 's were varied in least-squares. [d]Occupancy for(Si)=12 : occupancy for (Al)=12

DISCUSSION

All Na^+ ions in all crystals of the dehydrated Na_{12}-A studied were reduced by rubidium vapor. The reaction went to completion with 0.1 Torr of Rb(g) at 250℃ for 2 hours, and at stronger conditions. Rb^+ ions replaced all Na^+ ions in the crystal structures, and the product sodium metal was not found within the zeolite but was seen coating the external surfaces of the zeolite crystals. In all structures, Rb^+ ions are found at four different crystallographic sites (see Table I). The three structures differ in small ways, primarily in the occupancies at Rb(2), Rb(3), and Rb(4).

The product crystals contain more Rb species than are required to balance the anionic charge of the zeolite framework, which is variously estimated to be -11.75 (Blackwell et al., 1985) to -12 (Seff and Mellum, 1985) per 12.248 Å unit cell. Between 12.61(15) and 13.39(19) Rb atoms or ions are found (see Table I), of the order of one too many. This excess is attributed to rubidium atom sorption.

In each structure, three Rb^+ ions at Rb(2) fill the equipoints of symmetry C_{4h} (D_{4h} in *Pm3m*) at the center of the 8-rings (see Figs. 1 and 2), as

Table II. Selected Interatomic Distances(Å) and Angles(deg) for Na_{12}-A Treated with Rb Vapor

	Crystal 1	Crystal 2	Crystal 3
(Si, Al) - O(1)	1.652(7)	1.655(6)	1.655(8)
(Si, Al) - O(2)	1.651(9)	1.656(7)	1.660(10)
(Si, Al) - O(3)	1.666(6)	1.661(6)	1.669(8)
Rb(1) - O(1)	3.36(2)	3.34(1)	3.330(20)
Rb(1) - O(2)	3.573(7)	3.584(7)	3.592(9)
Rb(2) - O(2)	3.300(3)	3.306(2)	3.291(3)
Rb(2) - O(3)	2.837(5)	2.866(5)	2.822(7)
Rb(3) - O(2)	3.488(9)	3.459(7)	3.473(9)
Rb(3) - O(3)	2.891(9)	2.876(9)	2.910(20)
Rb(4) - O(1)	3.219(8)	3.22(6)	3.350(20)
Rb(4) - O(3)	3.22(3)	3.23(4)	3.330(60)
Rb(1) - Rb(2)	5.188(1)	5.191(1)	5.200(40)
Rb(1) - Rb(4)	4.33(4)	4.33(5)	4.350(70)
Rb(2) - Rb(2)	5.699	5.694	5.737(60)
Rb(2) - Rb(3)	3.427(5)	3.366(4)	3.366(5)
Rb(3) - Rb(3)	4.478(7)	4.613(7)	4.554(7)
	3.65(4)	3.766(5)	3.720(30)
O(1) - (Si, Al) - O(2)	107.46(6)	106.9(6)	106.6(7)
O(1) - (Si, Al) - O(3)	111.7(4)	112.0(5)	111.7(5)
O(2) - (Si, Al) - O(3)	107.6(3)	108.0(3)	107.3(4)
O(3) - (Si, Al) - O(3)	110.6(3)	109.8(3)	112.1(4)
(Si, Al) - O(1) - (Si, Al)	145(2)	142(1)	141.0(10)
(Si, Al) - O(2) - (Si, Al)	160.8(5)	161.7(5)	162.5(7)
(Si, Al) - O(3) - (Si, Al)	144.7(5)	146.2(5)	144.9(7)
O(3) - Rb(2) - O(3)	89.0(3)	89.4(3)	90.8(3)
O(3) - Rb(3) - O(3)	87.0(2)	88.9(2)	87.3(2)
Rb(2) - Rb(3) - Rb(3)	144.7(4)	144.7(5)	144.7(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

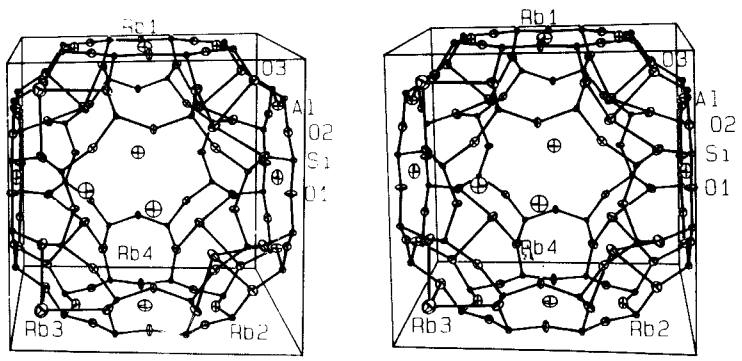

Fig. 1. A stereoview of a large cavity of dehydrated Rb^+-exchanged zeolite A exposed to excess Rb(g). About half of the large cavities have this structure with six Rb^+ ions at Rb(2), two at Rb(3), and one at Rb(4). Ellipsoids of 20 % probability are used.

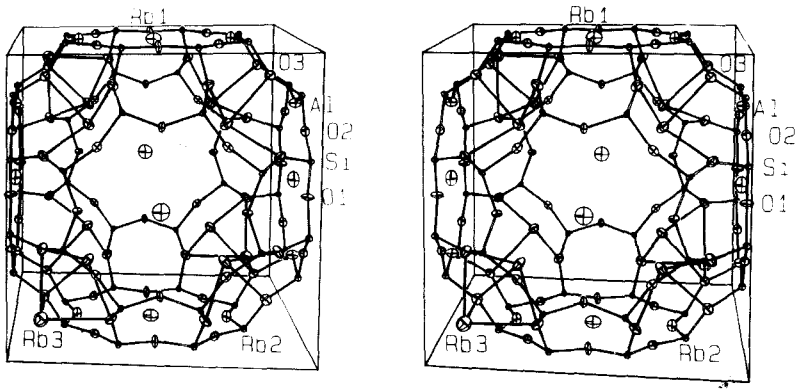

Fig. 2. A stereoview of a large cavity of dehydrated Rb^+-exchanged zeolite A exposed to excess Rb(g). About half of the large cavities have this structure with eight Rb^+ ions at Rb(2) and three at Rb(3). Ellipsoids of 20% probability are used.

they have in all previously reported structures of Rb^+-exchanged zeolite A (Firor and Seff, 1977; Pluth and Smith, 1983; Han et al., 1991; Song, 1991). Each Rb(1) cation is 3.34(2) Å from four O (1) oxygens and 3.58(1) Å from four O(2)'s (see interatomic distances in Table II; for simplicity, averaged values of geometry from Tables II and III are used.). These distances are substantially longer than the sum of the ionic radii of O^{2-} and Rb^+, 2.79 Å (Weast, 1989/1990c). In all previous studies of Rb^+ in zeolite A, similar long contact distances were observed for this site (Firor and Seff, 1977b; Pluth and Smith, 1983; Han et al., 1991; Song, 1991). The same is true for Cs^+ in zeolite A (Vance and Seff, 1975; Firor and Seff, 1977b; Heo and Seff, 1987). This is the favored site for these large cations in zeolite A.

In the large cavity, ca. 6 3/4 to 7 1/3 Rb^+ ions are found opposite 6-rings at Rb(2) (see Table I). In the sodalite unit, ca. 2 1/4 to 2 2/3 Rb's, respectively, are found opposite 6-rings at Rb(3). The sum of these occupancies therefore ranges from 9.0 to 10.0 for crystals 1 to 3, more than the usual limit of eight for 6-ring cations per unit cell (one per 6-ring). This suggests that some of these rubidium species are not simply Rb^+.

Rb(2) is 2.84(1) Å from the three O(3) oxygens of its 6-ring and 1.65 Å from the (111) plane at O (3). Rb(3) is correspondingly 2.89(1) Å from three O(3) oxygens and 1.73 Å from the (111) plane of three O(3)'s. Therefore, because there are more than eight 6-ring Rb species per unit cell, some very short Rb(2)-Rb(3) distances of 1.65+1.73=3.38 Å must exist.

The fractional occupancies observed at Rb (2), Rb(3), and Rb(4) are readily explained by proposing that two types of "unit cells" exist in these crystals (see Table IV). About 60% of these unit cells in crystal 1, and about 40% in crystals 2 and 3 have 6 ions at Rb(2), 2 at Rb(3), and 1 at Rb (4) (see Fig. 1). The ions in these Rb_{12}-A unit cells may be comfortably arranged to avoid unreasonably close cation-cation contacts; the "unit cells" of composition Cs_{12}-A in $Cs_{12.5}$-A (Heo and Seff, 1987) have this structure. The remaining unit cells, of Rb_{14}-A, have 9 ions at Rb(2) and 3 at Rb (3) (see Fig. 2). Arguments which follow justifying these cation arrangements are more often based upon the 12.245 Å unit cell with the sodalite unit at its center (see Fig. 3), where the shortest

Table III. Deviations of Atoms(Å) from the (111) Plane at O(3) for Na_{12}-A Treated with Rb Vapor

	Crystal 1	Crystal 2	Crystal 3
Rb(2)	1.666(1)	1.675(1)	1.607(2)
Rb(3)	-1.757(5)	-1.691(4)	-1.759(5)
Rb(4)	3.218(33)	3.228(36)	3.329(58)

A negative deviation indicates that the atom lies on the same side of the plane as the origin.

Table 4. Inferred Unit Cell Arrangements for the Three Crystals

Cation Name	Cation Position	Crystal number	1[a]		2 and 3[b]	
		Fraction with Arrangememt below:	60% Rb_{12}-A	40% Rb_{14}-A	40% Rb_{12}-A	60% Rb_{14}-A
Rb(1)	8-ring		3[c]	3	3	3
Rb(2)	6-ring (large-cavity side)		6	8	6	8
Rb(3)	6-ring (sodalite side)		2	3	2	3
Rb(4)	opposite 4-ring		1	0	1	0

[a] most mild (identical) conditions of synthesis were used.
[b] more strenuous (various) synthesis conditions were used.
[c] number of rubidiums per unit cell.

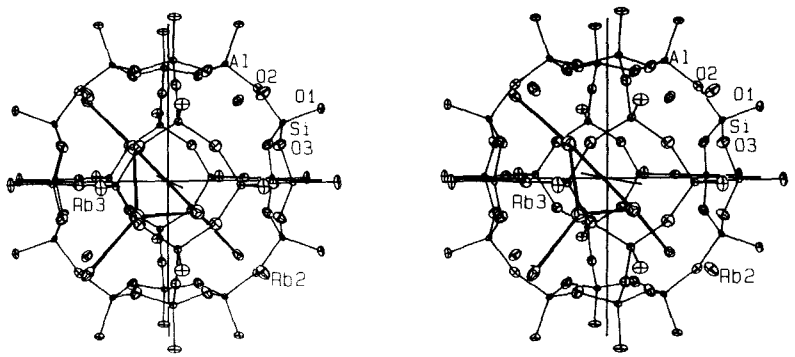

Fig. 3. A stereoview of about half of the sodalite cavities in dehydrated Rb^+-exchanged zeolite A exposed to excess Rb(g). Each Rb(3) of the central triangle of the cluster interacts further with an Rb(2) to form the complete$(Rb_6)^{4+}$ cluster. Ellipsoids of 20% probability are used.

Rb-Rb distances occur, rather than the unit cell shown in Figs. 1 and 2.

Sodalite units with three Rb(3)'s in them must have Rb(3)-Rb(3) distances of 2.63 or 3.71 Å, or both. (Those with only two Rb(3)'s may have 4.55 Å distances; see Table II). The shorter distance is impossibly short, even less than the sum of the cationic radii of two Rb^+ ions, 2.94 Å (Weast, 1989/1990c), and cannot be tolerated. To avoid it, the three Rb(3)'s must form an equilateral triangle with 3.71 Å distances (see Fig. 3). These distances are still quite short, as compared to the bond length in Rb metal, 4.95 Å (Weast, 1989/1990d) and this indicates that the electrons of the sorbed Rb atoms are at least partly delocalized over these three Rb(3) cations.

About half of the sodalite cavities have eight Rb(2) ions associated with their 6-rings on their large-cavity sides. These eight are better associated with sodalite units containing the Rb(3) triangle, to allow further electron delocalization, than with sodalite units which contain two Rb(3) cations, where the very short 3.38 Å approaches between Rb(2) and Rb(3) would be naked, that is, unameliorated by excess (bonding) electron density. It follows that this sodalite unit has, associated with its 6-rings, eleven (3+8) Rb species, nine of which may be counted as Rb^+ (to balance framework charge) and two as Rb^0. The two electrons from these two Rb^0's per sodalite unit must be delocalized over the shortest Rb-Rb contacts in the structure, those among the three Rb(3)'s in the sodalite cavity and the three Rb(2)'s (of the eight in the large cavities adjacent to the sodalite

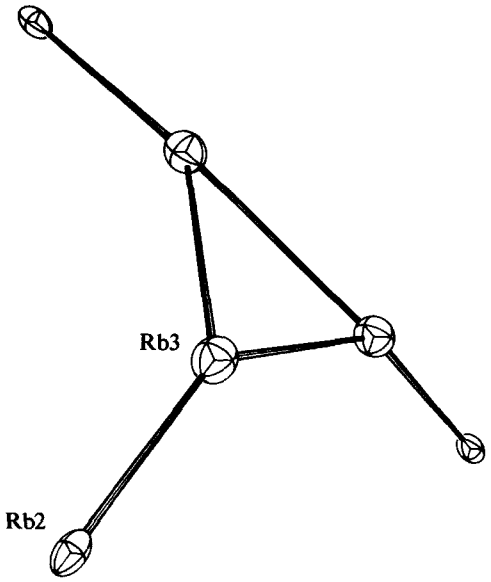

Fig. 4. The $(Rb_5)^{4+}$ cluster. It has *3m* (C_{3v}) symmetry. An Rb(2)-Rb(3) bond makes an angle of 160.53° (by symmetry) with the central Rb(3) plane. Ellipsoids of 20% probability are used.

unit) nearest to these Rb(3)'s, to give the $(Rb_6)^{4+}$ cluster shown in Figs. 3 and 4.

The ion at Rb(4) lies opposite a 4-ring. This Rb^+ ion is rather far from the framework oxygens (3.3 Å from O(1) and O(3)) perhaps because of repulsive interactions with Rb^+ ions on the sodalite-unit sides of adjacent 6-rings. This distance may be virtual, a bit too long; this particular 4-ring may be distorted from the mean 4-ring geometry due to the presence of its Rb^+ ion. It is clear by its low occupancy that Rb(4) is energetically the least favorable Rb^+ site.

Because some sodalite units must have at least three Rb species, the only alternative structure to consider is one with four Rb(3)'s arranged tetrahedrally and coordinated to Rb(2)'s so as to give a highly symmetric $(Rb_8)^{6+}$ cluster in some of its sodalite units. This may be viewed as the model proposed (see Table III) with an Rb(3) ion subtracted from the Rb_{12}-A unit cell (leaving one Rb(3) behind) and added to Rb_{14}-A (to increase three to four). This is unacceptable because the sodalite cavity without the cluster would then have its Rb^+ ions arranged unreasonably, one opposite a 4-ring while a Rb(3) site (preferred) remained available.

An excess absorption of about one-half Cs atom per unit cell was noted in the corresponding Cs work, and this was attributed to cationic crowding (Heo and Seff, 1987; Heo, 1987). This crowding is also important in fully dehydrated, fully Rb^+-exchanged zeolite A: hence the sorption of an excess Rb atom per unit cell. However, the nature of the cationic cluster is somewhat different, clearly because the smaller sizes of Rb^+ and Rb^0 have allowed one more Rb to fit into the sodalite cavity.

REFERENCES

Breck, D. W. (1974) Zeolite Molecular Sieves. New York, 537-541.

Blackwell, C. S., Pluth J. J., and Smith, J. V. (1985) The silicon/aluminum ratio of single crystals of zeolite A used single crystals analysis. J. Phys. Chem. 89, 4420-4422.

Charnell, J. F. (1971) Gel growth of large crystals of sodium A and sodium X zeolites. J. Cryst. Growth 8, 192-194.

Cromer, D. T. (1965) Anomalous dispersion corrections computed from self-consistent field relativitic Dirac-Slater wave function. Acta Crystallogr. 18, 17-23.

Firor, R. L. and Seff, K. (1977a) Zero-coordinate K^+. The crystal structure of dehydrated cesium and potassium exchanged zeolite A, Cs_7K_5-A. J. Am. Chem. Soc. 99, 6249-6253.

Firor, R. L. and Seff, K. (1977b) Zero-coordinate Rb^+. The crystal structures of dehydrated and hydrated eleven-twelfths rubidium-exchanged zeolite A. J. Am. Chem. Soc. 99, 1112-1117.

Frentz, B. A. and Okaya, Y. (1987) Principal computer programs used in this study were "Structure Determination Package Programs. These programs were supplied by Enraf-Nonius, Netherlands.

Han, Y. W., Song, S. H., and Kim, Y. (1991) Crystallographic studies of Ag^+ and Ca^{2+}-exchanged zeolite A reacting with rubidium vapor. J. Miner. Soc. Korea 4, 22-31.

Heo, N, H. (1987) A Crystallographic Study of the

Reactions of Dehydrated Zeolite A with Alkali Metals. Ph. D. Thesis, University of Hawaii.

Heo, N. H. and Seff, K. (1987) Reaction of dehydrated Na_{12}-A with cesium. Synthesis and crystal structure of fully dehydrated, fully Cs^+-exchanged zeolite A. J. Am. Chem. Soc. 109, 7986-7992.

Heo, N. H., Dejsupa, C, and Seff, K. (1987) Preparation and structure of fully Cs^+-exchanged zeolite A. J. Phys. Chem. 91, 3943-3944.

John, S. K. and Kathleen, L. (1974a) International Tables for X-ray Crystallography; Kynoch: Birmingham, England, Vol. II, 132.

John, S. K. and Kathleen, L. (1974b) International Tables for X-ray Crystallography; Kynoch: Birmingham, England, Vol. IV, 73-87.

John, S. K. and Kathleen, L. (1974c) International Tables for X-ray Crystallography; Kynoch: Birmingham, England, Vol. IV, 149-150.

Kim, Y. (1991) X-ray Crystallography (Dae Woo Natural Sciences Series No. 75). Minumsa, 169-172.

Kim, Y., Song, S. H., and Seff, K. (1990) Selective reduction at the single-crystal surface of all mobile cations in zeolite A. Structures of dehydrated Ag_2Ca_5-A and Ag_2Cs_{10}-A. J. Phys. Chem. 94, 5959-5963.

Pluth, J. J. and Smith, J. V. (2983) Crystal structure of dehydrated Rb-exchanged zeolite A. Absence of zero-coordinated rubidium preferential ion exchange of barium impurity. J. Am. Chem. Soc. 105, 2621-2624.

Schagen, J. D., Straven, L., van Meurs, F., and Williams, G. (1988) CAD4 Operators Manual. Enraf Nonius Delft, Chapter XI.

Seff, K. (1976) Structural Chemistry inside Zeolite A. Acc. Chem. Res. 9, 121-128.

Seff, K. and Mellum, M. D. (1984) The silicon/aluminum ordering and ratio in zeolite A. J. Phys. Chem. 88, 3560-3563.

Song, S. H. (1991) Chemistry and Crystallographic Studies of Calcium, Cesium, Potassium, Rubidium, and Silver in Zeolite A. Ph. D. Thesis, Pusan National University.

Subramanian, V. and Seff, K. (1979) Crystal structure of dehydrated cesium and thallium exchanged zeolite A, Cs_9Tl_3-A. J. Phys. Chem. 83, 2166-2169.

Vance, T. B., Jr. and Seff, K. (1975) The crystal structures of hydrated and dehydrated seven-twelfths cesium-exchanged zeolite A. J. Phys. Chem. 79, 2163-2167.

Weast, R. C. (1989/1990a) Handbook of Chemistry and Physics; 70th. ed.; Chemical Rubber Co.: Cleveland, D157-D158.

Weast, R. C. (1989/1990b) Handbook of Chemistry and Physics; 70th. ed.; Chemical Rubber Co.: Cleveland, D214-D216.

Weast, R. C. (1989/1990c) Handbook of Chemistry and Physics; 70th. ed.; Chemical Rubber Co.: Cleveland, F157.

Weast, R. C. (1989/1990d) Handbook of Chemistry and Physics; 70th. ed.; Chemical Rubber Co.: Cleveland, F189-190.