Crystallographic Studies of Ag$^+$- and Ca^{2+}- Exchanged Zeolite A Reacting with Rubidium Vapor

루비듐 증기와 반응한 Ag$^+$ 이온과 Ca^{2+} 이온으로 치환된
제올라이트 A의 결정학적 연구

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ABSTRACT : Three crystal structures of dehydrated Ag$^+$- and Ca^{2+}-exchanged zeolite A (Ag$_4$Ca$_4$-A, Ag$_6$Ca$_3$-A and Ag$_8$Ca$_2$-A) treated at 250℃ with 0.1 Torr of Rb vapor have been determined by single-crystal x-ray diffraction techniques in the cubic space group *Pm3m* at 21(1) ℃ (a = 12.271(1) Å, 12.255(1) Å, and 12.339(1) Å, respectively). Their structures were refined to the final error indices, R(weighted) of 0.072 with 130 reflections, 0.050 with 110 reflections, and 0.083 with 86 reflections, respectively, for which I $>$3σ(I). In each structure, Rb species are found at three different crystallographic sites : 3 Rb$^+$ ions per unit cell are located at 8-ring centers, ca. 5.6 to 6.4 Rb$^+$ ions are found opposite 6-rings on threefold axes in the large cavity, and ca. 2.5 to 3.0 Rb$^+$ ions are found on threefold axes in the sodalite unit. Also, Ag species are found at two different crystallographic stites : ca. 0.7 to 2.1 Ag$^+$ lie opposite 4-rings and ca. 2.2 to 4.8 Ag atoms are located near the center of the large cavity. In these structures, the numbers of Ag atoms per unit cell are 2.2, 2.4, and 4.8, respectively, and these may form hexasilver clusters at the centers of the large cavities. The Rb$^+$ ions, by blocking 8-rings, may have prevented silver from migrating out of the structure. Each hexasilver cluster is stabilized by coordination to up to 13 Rb$^+$ ions. An excess absorption of about 0.8 Rb atom per unit cell indicates that the presence of a triangular symmetric (Rb$_3$)$^{2+}$ cation in sodalite cavity. At least one large-cavity six-ring Rb$^+$ ion must necessarily approach this cluster and may be viewed as a member of it to give (Rb$_4$)$^{3+}$, (Rb$_5$)$^{4+}$ or (Rb$_6$)$^{5+}$.

요약 : 세 개의 탈수한 Ag$^+$ 이온과 Ca^{2+} 이온으로 치환한 제올라이트 A (Ag$_4$Ca$_4$-A, Ag$_6$Ca$_3$-A, Ag$_8$Ca$_2$-A)를 0.1 Torr의 Rb 증기로 처리한 결정구조를 공간군 Pm3m을 써서 단결정 X-선 회절법으로 결정하였다. (단위세포상수 a는 각각 12.271(1) Å, 12.255(1) Å 및 12.339(1) Å 이다). 이들 구조의 최종 오차인수 R(무게)는 I $>$3σ(I)가 되는 130 회절반사로 0.072, 110 회절반사로 0.050 및 86 회절반사로 0.082이었다. 각각의 구조에서 Rb 종은 세 개의 다른 결정학적 위치에 위치하고 있다. 즉 단위세포당 3개의 Rb$^+$ 이온은 8-링 중심에 위치하고 약 2.5개 내지 3.0개의 Rb$^+$이온은 소다라이트 동공내 3회 회전축상에 위치한다. 또 Ag 종이 두 개의 다른 결정학적 위치에 위치하고 약 0.7~2.1개의 Ag$^+$이온은 4-링과 마주보는 위치에, 약 2.2~4.8개의 Ag 원자는 큰 동공 중심 가까이에 위치한다. 이들 구조에서 단위세포당 Ag 원자의 수는 각각 2.2, 2.4 및 4.8개이었고 이들은 큰 동공 중심에 헥사실버 클라스터를 만든다. Rb$^+$이온은 8-링을 막고 있어서 Ag가 골조 밖으로 이동하는 것을 막고 있고 각각의 헥사실버 클라스터는 13개의 Rb$^+$이온과 배위하여 안정화된다. 단위 세포당 약 0.8개의 Rb원자가 과잉으로 존재하여 삼각 대칭형의 (Rb$_3$)$^{2+}$ 클라스터가 소다라이트 동공내에 존재한다. 적어도 하나의 큰 동공의 6-링 Rb$^+$ 이온은 소다라이트 동공의 (Rb$_3$)$^{2+}$ 클라스터에 접근하므로 이들 클라스터는 (Rb)$_4$$^{3+}$, (Rb)$_5$$^{4+}$ 혹은 (Rb$_6$)$^{5+}$가 형성될 수도 있다.

INTRODUCTION

Ag$^+$ ions in zeolite A can be reduced by heating (Kim and Seff, 1977, 1978c), by reaction with reducing agents (Kim and Seff, 1984), or by sorption of metal vapors (McCusker, 1980). Tsutsumi and Takahashi found that Ag$^+$ ions in zeolite Y can be reduced to bulk clusters of Ag^0 by treatment with alcohol and alkyl benzenes (Tsutsumi and Takahashi, 1972). Ag$^+$ ions in Ag-A, Ag-Y, Ag-mordenite, and Ag-chabazite can also reduced by hydrogen (Beyer and Jacobs, 1982; Beyer et al., 1979; Kim and Seff, 1978b). Beyer et al.(1982) reported that the silver clusters (Ag$_3$)$^+$ and (Ag$_5$)$^+$ are formed at temperatures up to 150℃, but that silver crystallites external to the zeolite are created at higher temperatures (350 ℃) in Ag-Y and Ag-mordenite treated with H$_2$. Also, Ag$^+$ ions in zeolite A can be easily reduced by H$_2$, and reduced Ag atoms or clusters can be readily reoxidized to Ag$^+$ by O$_2$(Kim and Seff, 1978b). An (Ag$_6$)$^{3+}$ cluster was found crystallographically in the large cavity of partially Ag$^+$-exchanged zeolite A treated with H$_2$ (Kim and Seff, 1987).

The neutral cluster (Ag$_6$)^0, stabilized by coordination to 8 Ag$^+$ ions, has been found by x-ray diffraction methods (Kim and Seff, 1977, 1978c). This cluster may alternatively be viewed as (Ag$_{14}$)$^{8+}$. Grobet and Schoonheydt (1985) identified Ag$_6^{n+}$ (n<6) clusters in the sodalite cavities of dehydrated Ag-A zeolite by epr spectroscopy. This was reverified by the careful work of Morton and Preston (1986) on Ag-A using isotopically pure silver. Finally Schoonheydt and Leeman (1989) again identified an Ag$_6^{n+}$ cluster by epr spectroscopy in partially Ag$^+$-exchanged zeolite A treated with H$_2$.
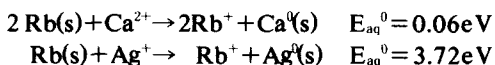
Recently fully Rb-exchanged zeolite A has been synthesized by the reduction of all Na$^+$ ions and Ca^{2+} ions in Na$_{12}$-A and Ca$_4$Na$_4$-A by rubidium vapor(Song and Kim, 1991). These redox reactions go to completion at 250℃ with ca. 0.1 Torr of Rb^0. In these structures, an extra Rb atom is associated with three (or more) Rb$^+$ ions to form a (Rb$_{n+1}$)$^{n+}$ cluster. The value of n may be 3, 4 or 5.

This work was initiated with the expectation

that the intrazeolitic redox potential for the reaction,

$$Ag_{12-2x}Ca_x - A + 12Rb^0 \rightarrow$$
$$Rb_{12} - A + (12-2x) Ag^0 + xCa^0$$
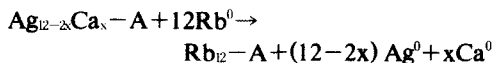
would be positive enough to ensure complete exchange. The E^0 values, not involving the zeolite, are easily calculated (Weast et al., 1989/1990a).

$$2 Rb(s) + Ca^{2+} \rightarrow 2Rb^+ + Ca^0(s) \quad E_{aq}^0 = 0.06 eV$$
$$Rb(s) + Ag^+ \rightarrow Rb^+ + Ag^0(s) \quad E_{aq}^0 = 3.72 eV$$

The resulting material would be of interest because the volume of exchangable cations would be large and some extra Rb^0 atoms may be present, forming Rb clusters as before. However, in this experiment, the reduced silver and calcium atoms may not be able to diffuse to the surface of zeolite because of the blockage of the 8-windows by the large Rb$^+$ ions. By such trapping, some new, perhaps larger, clusters might form and be identified. If hexasilver were to form, its occupancy might be full, which would allow its existence to be confirmed crystallographically. Furthermore, because of the atomic sizes and high scattering powers of Rb$^+$ and Ag$^+$, precise and reliable crystallographic determinations should be easy to achieve.

EXPERIMENTAL SECTION

Crystals of sodium zeolite 4A (stoichiometry : Na$_{12}$Si$_{12}$Al$_{12}$O$_{48}$ · 27H$_2$O) were prepared by Charnell's method(1971).

Three crystals of composition Ag$_4$Ca$_4$-A (crystal 1), Ag$_6$Ca$_3$-A (crystal 2), and Ag$_8$Ca$_2$-A (crystal 3) were prepared. To do this, exchange solutions of AgNO$_3$ and Ca(NO$_3$)$_2$ in the mole ratio of 1 : 200, 1 : 75, and 1 : 35, respectively, with a total concentration of 0.05M, were used. These ratios were obtained from a previous study of the crystal structures of dehydrated Ag$_2$Ca$_5$-A and Ag$_7$Ca$_{2.5}$-A (Song et al, 1989) which were prepared using exchange solutions in which AgNO$_3$/Ca(NO$_3$)$_2$ was 1 : 1000 and 1 : 50, respectively.

Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 0.5 cm / see for 4 days. The

crystals remained colorless.

Each crystal was lodged in a fine Pyrex capillary on a vacuum line. Afte complete dehydration at 350℃ and 5×10^{-6} Torr for 2days, rubidium vapor was introduced by distillation from a side-arm break-seal ampoule to the glass-tube extension of the crystal-containing capillary. The glass reaction vessels were than 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 distill onto the crystal.

Each crystal was allowed to react with 0.1 Torr or Rb(g) at 250℃ for 2hrs, after which it was sealed off from the reaction vessel by torch after cooling to room temperature. Microscopic examination showed that all these crystals had become black.

The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously (Riley et al., 1972; Seff, 1976). Preliminary crystallographic experiments and subsequent data collection were performed with a Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer, equipped with a graphite monochromator, a pulse-height analyzer, and PDP micro 11/73 computer, Molybdenum radiation ($K\alpha_1$, $\lambda = 0.70930$Å, $K\alpha_2$, $\lambda = 0.71359$Å) was used for all experiments. In each case, the cell constant, a = 12.271(1)Å, 12.255(1) Å, and 12.339(1) Å for crystals 1, 2, and 3, respectively, were determined by a least-squares treatment of 25 intense reflections for whic $20° < 2\theta < 30°$.

Reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq 1$:hlk, $h \leq 1 \leq k$) were examined by 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^{-1} in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 h to monitor crystal and x-ray source 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 (Frentz and Okaya, 1987). An absorption correction (μR ca. 0.38-0.40) was judged to be negligible for all crystals (John and Kathleen, 1974a). Of the 879, 874, and 891 pairs of reflections for crystal 1, 2, and 3, respectively, only the 130, 110, and 86 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

STRUCTURE DETERMINATION

Dehydrated Ag₄Ca₄-A treated with Rb(g)

Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] and Rb⁺ ions at Rb(1), Rb(2), and Rb(3) of dehydrated Na₁₂-A and Ca₄Na₄-A treated with Rb vapor. Anisotropic refinement of the framework atoms and Rb(i) species, i=1~3, converged to an unweighted R₁ index, $(\Sigma |F_o - |F_c||)/\Sigma F_o$, of 0.178 and a weighted R₂ index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.219. Subsequently, the occupancies at Rb(1), Rb(2), and Rb(3) refined to 3.1(1), 5.8(1), and 2.8 (1), respectively. A difference Fourier synthesis then revealed the position of Ag⁺ ions at Ag (1), (0.26, 0.26, 0.5), with peak height 1.7(4) eÅ⁻³, and Ag species at Ag(2), (0.34, 0.5, 0.5). with peak height 5.4(6) eÅ⁻³. Ag(1) refined with an unusually large isotropic thermal parameter, so it was fixed at the more reasonable value given in Table 1.

It is easy to distinguish Ag⁺ from Rb⁺ ions because their ionic radii are quite different, 1.26 Å and 1.47 Å, respectively. Furthermore, the approach distances between these ions and zeolite oxygens in dehydrated Rb₁₁Na₁-A (Firor and Seff, 1977), Rb₁₂.₅-A, and partially decomposed Ag₁₂-A (Kim and Seff, 1977, 1978c), are known and are indicative.

Allowing all occupancies of Rb(i), i =1~3 and Ag(j), j=1~2 to vary, except that of Rb(1) which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), and allowing all

Table 1-1. Positional, Thermal,[a] and Occupancy Parameters of Crystal 1 (Ag_4Ca_4-A treated with 0.1 Torr of Rb Vapor at 250°C for 24 hrs)

Atom	Wyc. Pos.	X	Y	Z	β_{11}[b] or B_{iso}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occu-pancy
(Si, Al)	24(k)	0	1846(5)	3743(5)	25(3)	44(4)	15(4)	0	0	-4(9)	24[d]
O(1)	12(h)	0	2360(20)	5000	140(20)	30(20)	50(20)	0	0	0	12
O(2)	12(i)	0	2920(10)	2920(10)	80(20)	50(10)	50(10)	0	0	70(30)	12
O(3)	24(m)	1138(7)	1138(7)	3510(10)	77(8)	77(8)	90(20)	10(30)	-10(20)	-10(20)	24
Rb(1)	3(c)	0	5000	5000	200(20)	184(9)	184(9)	0	0	0	3
Rb(2)	8(g)	2682(4)	2682(4)	2682(4)	114(3)	114(3)	114(3)	116(8)	116(8)	116(8)	5.58(6)
Rb(3)	8(g)	1060(10)	1060(10)	1060(10)	170(6)	170(6)	170(6)	240(10)	240(10)	240(10)	3.17(6)
Ag(1)	12(j)	2520(40)	2520(40)	5000	10 (Fixed)						0.79(6)
Ag(2)	6(f)	3420(20)	5000	5000	230(30)	300(20)	300(20)	0	0	0	2.19(5)

Table 1-2. Positional, Thermal,[a] and Occupancy Parameters of Crystal 2 (Ag_5Ca_3-A treated with 0.1 Torr of Rb Vapor at 250°C for 2 hrs)

Atom	Wyc. Pos.	X	Y	Z	β_{11}[b] or B_{iso}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occu-pancy
(Si, Al)	24(k)	0	1828(7)	3727(6)	27(4)	44(5)	21(5)	0	0	10(10)	24[d]
O(1)	12(h)	0	2310(20)	5000	190(30)	10(20)	30(20)	0	0	0	12
O(2)	12(i)	0	2930(10)	2930(10)	80(20)	60(10)	60(10)	0	0	-20(50)	12
O(3)	24(m)	1134(9)	1134(9)	3490(20)	100(10)	100(10)	110(20)	20(40)	80(30)	80(30)	24
Rb(1)	3(c)	0	5000	5000	220(10)	200(10)	200(10)	0	0	0	3
Rb(2)	8(g)	2701(4)	2701(4)	2701(4)	108(3)	108(3)	108(3)	70(10)	70(10)	70(10)	6.40(6)
Rb(3)	8(g)	1080(10)	1080(10)	1080(10)	80(10)	80(10)	80(10)	20(20)	20(20)	20(20)	2.45(5)
Ag(1)	12(j)	2680(60)	2680(60)	5000	10 (Fixed)						0.67(7)
Ag(2)	6(f)	3400(20)	5000	5000	170(30)	250(20)	250(20)	0	0	0	2.35(4)

Table 1-3. Positional, Thermal,[a] and Occupancy Parameters of Crystal 3 (Ag_6Ca_2-A treated with 0.1 Torr of Rb Vapor at 250°C for 2 hrs)

Atom	Wyc. Pos.	X	Y	Z	β_{11}[b] or B_{iso}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occu-pancy
(Si, Al)	24(k)	0	1840(10)	3760(10)	20(10)	60(10)	10(10)	0	0	0(30)	24[d]
O(1)	12(h)	0	2360(20)	5000	330(80)	90(10)	110(50)	0	0	0	12
O(2)	12(i)	0	3000(30)	3000(30)	10(40)	100(40)	100(40)	0	0	100(100)	12
O(3)	24(m)	1230(30)	1230(30)	3620(30)	290(40)	290(40)	20(30)	-200(200)	130(60)	130(60)	24
Rb(1)	3(c)	0	5000	5000	190(40)	200(20)	200(20)	0	0	0	3
Rb(2)	8(g)	2701(9)	2701(9)	2701(9)	101(7)	101(7)	101(7)	90(20)	90(20)	90(20)	5.88(13)
Rb(3)	8(g)	1130(10)	1130(10)	1130(10)	40(10)	40(10)	40(10)	-10(30)	-10(30)	-10(30)	2.78(11)
Ag(1)	12(j)	2680(40)	2680(40)	5000	12.6(2)						2.14(14)
Ag(2)	6(f)	3330(20)	5000	5000	220(4)	330(30)	330(30)	0	0	0	4.81(11)

[a]Positional and anisotropic thermal parameters are given x 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$=\exp[-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl]$. [c] Isotropic thermal parameters in units of $Å^2$. Occupancy factors are given as the number of atoms or ions per unit cell. [d]Occupancy for (Si) = 12; occupancy for (Al) = 12.

anisotropic thermal parameters to vary, except for that of Ag(1) which was refined isotropically, led to $R_1 = 0.073$ and $R_2 = 0.072$(Table 1).

The largest peak on the final difference Fourier function was at(0, 0, 0) with height 1.5(12) eÅ^{-3}. This peak was rejected because it was too close (2.27Å) to three Rb species at Rb(3).

Dehydrated Ag$_5$Ca$_3$—A treated with Rb(g)

Full-matrix least-squares refinement was initiated with the atomic parameters for all atoms and ions in crystal 1. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement, except for that of Ag(1), which was refined isotropically, converged to $R_1 = 0.067$, and $R_2 = 0.049$. Subsequently the occupancies at Rb (1), Rb(2), Rb(3), Ag(1), and Ag(2) refined to 3.05 (7), 6.38(6), 2.50(6), 0.66(7), and 2.40(5) ions or atoms per unit cell, respectively. The occupancy of Rb(1) was fixed at 3.0, its maximum occupancy by symmetry. The final R values converged at R_1 =0.070 and R_2=0.050. The final difference function was featureless except for some residual density (1.2(8) eÅ^{-3}) at (0.30, 0.5, 0.5), near Ag(2), deep in the large cavity.

Dehydrated Ag$_5$Ca$_2$-A treated with Rb(g)

Using the automic coordinates from the structure of crystal 1, simultaneous occupancy, positional, and thermal parameter refinement was done. Anisotropic refinement for all positions except for that of Ag(1), which was refined isotropically, converged to $R_1 = 0.095$ and $R_2 = 0.080$. The number of Rb$^+$ ions at Rb(1), Rb(2), and Rb(3) and Ag species at Ag(1) and Ag(2) refined to 3.1(1), 5.98(15), 2.65(11), 2.15(14), and 4.93(13), respectively. After the occupancy at Rb (1) was fixed at 3.0 as before, the final R values converged at $R_1 = 0.10$ and $R_2 = 0.083$.

These higher R values and the fewer diffraction data observed for this crystal indicate that treatment with Rb vapor did some structural damage. The final difference function was fea-

tureless except for some residual density (2.1(9) eÅ^{-3}) at (0.30, 0.5, 0.5), near Ag(2), deep in the large cavity.

For all structrues, 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$^+$, Ag$^+$, Ag^0, O$^-$ and (Si, Al)$^{1.75+}$ were used (John and Kathleen, 1974b). The function describing (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, 1974c). The final structure parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

DISCUSSION OF STRUCTURE

In all three structures, Rb$^+$ ions are found at three different crystallographic sites and Ag species are found at two such sites. The three structures are similar except for the occupancies at the Rb(2), Rb(3), Ag(1), and Ag(2) positions.

At Rb(1) in each structure, three Rb$^+$ ions fill equipoints of symmetry C$_{4h}$(D$_{4h}$ in Pm3m) at the centers of 8-ring (see Figures 1, 2, and 3). Each Rb (1) ion is ca. 3.27(2) Å from four O(1) oxygens and ca. 3.56 Å from four O(2)'s (see interatomic distances in Table 2). These distances are substantially longer than the sum of the ionic radii of O^{2-} and Rb$^+$, 2.79Å(Weast, 1989/1990b). Rb$^+$ ions were observed at this site in all previous studies of Rb$^+$ in zeolite A, with similar long contact distances (Firor and Seff, 1977; Pluth and Smith, 1983).

In the large cavity opposite 6-rings, ca. 5.58, 6.40, and 5.88 Rb$^+$ ions are found at Rb(2) in crystals 1, 2, and 3, respectively. In the sodalite unit opposite 6-rings, 3.17, 2.45, and 2.78 Rb$^+$ ions, respectively, are found at Rb(3). The sum of these threefold axis occupancies, at Rb(2) and Rb(3), are 8.75, 8.85, and 8.66 for crystals 1, 2, and 3, respectively. If the Rb species at Rb(2) and Rb(3) are all ions, this sum should not exceed eight; otherwise an unacceptably short distance (3.36-3.45

Table 2. Selected Interatomic Distances(Å) and Angles(deg) of Ag$_{12-2x}$Ca$_x$-A ($x = 4, 3$, and 2, respectively) Treated with Rb Vapor

	crystal 1	crystal 2	crystal 3
(Si, Al)-O(1)	1.67(1)	1.67(2)	1.66(2)
(Si, Al)-O(2)	1.66(2)	1.67(1)	1.71(4)
(Si, Al)-O(3)	1.670(6)	1.65(2)	1.70(3)
Rb(1)-O(1)	3.24(2)	3.30(2)	3.25(3)
Rb(1)-O(2)	3.62(2)	3.59(2)	3.50(3)
Rb(2)-O(2)	3.316(5)	3.334(1)	3.37(1)
Rb(2)-O(3)	2.864(9)	2.88(1)	2.81(3)
Rb(3)-O(2)	3.47(1)	3.46(1)	3.54(3)
Rb(3)-O(3)	3.01(2)	2.95(2)	3.08(4)
Ag(1)-O(1)	3.09(7)	3.32(8)	3.32(7)
Ag(1)-O(3)	3.02(3)	3.25(5)	3.04(6)
Ag(2)-O(1)	5.30(4)	5.31(4)	5.24(5)
Ag(2)-O(2)	5.54(5)	5.49(6)	5.39(7)
Rb(1)-Rb(2)	5.20(1)	5.18(1)	5.21(1)
Rb(1)-Ag(1)	4.34(3)	4.34(6)	4.37(4)
Rb(2)-Rb(2)	5.69(1)	5.63(1)	5.67(2)
Rb(2)-Rb(3)	3.447(7)	3.432(8)	3.35(1)
Rb(3)-Rb(3)	3.68(1)	3.74(2)	3.94(2)
Ag(2)-Rb(1)	4.21(2)	4.17(2)	4.11(3)
Rb(2)-Ag(2)	4.12(1)	4.08(1)	4.09(1)
Ag(1)-Ag(2)	3.24(6)	2.98(8)	2.98(8)
Ag(2)-Ag(2)	2.74(4)	2.77(5)	2.92(3)
O(1)-(Si, Al)-O(2)	105.5(7)	105.2(9)	101(1)
O(1)-(Si, Al)-O(3)	110.9(6)	110.1(8)	105(1)
O(2)-(Si, Al)-O(3)	107.8(4)	108.4(6)	108(2)
O(3)-(Si, Al)-O(3)	113.5(5)	114.3(7)	126(1)
(Si, Al)-O(1)-(Si, Al)	136(1)	139(1)	134(2)
(Si, Al)-O(2)-(Si, Al)	165.4(8)	161.8(8)	157(2)
(Si, Al)-O(3)-(Si, Al)	147.2(7)	146.5(9)	141(2)
O(3)-Rb(2)-O(3)	91.8(3)	90.3(4)	96.0(9)
O(3)-Rb(3)-O(3)	86.3(3)	87.7(3)	85.5(6)
Rb(2)-Rb(3)-Rb(3)	180	180	180
Ag(2)-Rb(1)-Ag(2)	180	180	180

Å) between Rb(2) and Rb(3) would exist. By difference, therefore, at least 0.7 to 0.8 of these very close Rb(2)-Rb(3) contact distances must exist per unit cell. Also, the presence of more than two Rb(3) species per sodalite unit (the mean for the three crystals is 2.8) requires 3.5 Å Rb(3)-Rb(3) contacts. Together, these observations indicate that the Rb species at Rb(3) must be partially reduced from Rb$^+$, to form, for example, (Rb$_3$)$^{2+}$ (Figure 4). The short 3.36 to 3.45 Å distance that at least nearly one Rb ion in this cluster must necessarily have with a large-cavity six-ring Rb$^+$ ion indicates that it should instead be viewed as (Rb$_{n+1}$)$^{n+}$, where $n = 3, 4$ or 5. It would consist of a central three-membered ring with one, two, or three of the approximately six Rb$^+$ ions in the large cavity included (Figure 4).

Each ion at Rb(2) is ca. 2.85(1) Å from the three O(3) oxygens of its 6-ring and ca. 1.58 Å from the (111) plane at O(3). Each partially reduced ion at Rb(3) is somewhat further inside the sodalite unit, ca. 2.97(3) Å from three O(3) oxygens and ca. 1.79 Å from their (111) plane Table 3).

In each structure, the Ag$^+$ ion at Ag(1) is statistically distributed over a 12-fold equipoint in the large cavity on a twofold axis opposite a 4-ring (Figures 2 and 3). This ion is rather far from framework oxygens (Ag(1)-O(1) = 3.20(7) Å and

Table 3. Deviations of Atoms (Å) from (111) Plane at O(3) of $Ag_{12-x}Ca_x$-A(x=4, 3, and 2, respectively) Treated with Rb Vapor

	crystal 1	crystal 2	crystal 3
Rb(2)	1.601(3)	1.657(3)	1.441(6)
Rb(3)	−1.846(7)	−1.775(7)	−1.911(10)
Ag(1)	3.014(28)	3.253(45)	3.042(28)
Ag(2)	5.411(14)	5.404(14)	5.163(16)

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

Ag(1)-O(3)=3.07(6) Å) probably because of an interaction with Ag(2) species. It is also possible that this distance is virtual, an artifact of the low occupancies. The other Ag position, Ag(2), is located near the center of the large cavity (Figure 1) and is occupied by Ag atoms (*vide infra*) produced by the reduction of Ag^+ by Rb^0.

Discussion of Metal Clusters

The sums of the Rb(i) and Ag(i) occupancies in crystals 1, 2, and 3 (see Table 1) are 14.7(2), 14.9(2), and 18.6(5), respectively. The unit cells clearly contain more metal species than the approximately twelve monovalent cations which 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, 1984). Therefore about three to seven metal atoms must exist per unit cell. These may be present as isolated atoms or neutral clusters, or they may associate with cations to form cationic clusters.

The distance between Ag(2) and its nearest framework oxygens, four at O(1), is very much longer (Ag(2)-O(1)=ca. 5.28 Å) than the sum of the approximate ionic radii, 2.58 Å (Weast, 1989/1990b). This indicates that the species at Ag(2) must be Ag^0 and not Ag^+. The shortest distance between Ag(2) and Ag(2), ca. 2.81 Å, which must exist whenever more than two silver species at Ag(2) are present per unit cell, is far too short to be an unmoderated Ag^+-Ag^+ distance. Crystal 3, at least, has more than two silver species at Ag(2). This Ag(2)-Ag(2) distance is close to the Ag-Ag distance, 2.89 Å (Weast, 1989/1990c), in silver metal. If the Ag(2) equipoint were filled in a frac-

tion of the large cavities, as is sensible to infer but not proven by these crystallographic results (*vide infra*), closest packed clusters of six silver atoms would exist in all three structures. The hexasilver molecule would be octahedral and would show the full symmetry of its site, O_h, at the center of the large cavity (Figures 1 and 5).

The occupancy at Ag(2) in crystal 3 is 4.81 (11) atoms per unit cell, higher by ca. 1 than had been achieved for the sodalite Ag_6 cluster in previous studies (Kim and Seff, 1977, 1978c). This indicates that pentasilver (approximately) may exist in all unit cells as an alternative to the hexasilver cluster. However, it is unlikely that the less symmetric pentasilver with eight Ag-Ag contacts (1.6 per atom) would be more stable than hexasilver with twelve such contacts (2.0 per atom), and that it would occupy a site of O_h symmetry (Kim and Seff, 1978a). The existence of hexasilver was initially proposed by such arguments (Kim and Seff, 1977, 1978c), and was subsequently verified by epr work (Grobet and Schooneydt, 1985; Morton and Preston, 1986; Schoonheydt and Leeman, 1989).

Without a mechanism for their stabilization, metal clusters like hexasilver would generally not be retained within the zeolite structure. Because a mechanism involving association with the ions at Rb(1) and Rb(2) is seen, it is reasonable to accept the fact that atoms of silver have formed and gave been retained within zeolite A. The structure and symmetry of this hexasilver cluster is exactly that found at the center of sodalite unit in partially decomposed fully dehydrated Ag^+-exchanged zeolite A (Kim and Seff, 1977, 1978c).

The distances from Ag(2) to Rb(1) and Rb(2) are ca. 4.16 Å and 4.10 Å, respectively. These are almost the same as the sum of the van der Waals radius of Ag^0 and the ionic radius of Rb^+, 4.14 Å (Dean, 1979; Huheey, 1983). Such a sum was found to describe Ag^+ to Ag^0 contacts quite accurately (Kim and Seff, 1977, 1978c). The relatively large thermal ellipsoids of the Ag atoms at Ag(2) indicate that the hexasilver cluster is loosely held (by association with Rb^+'s) at its position.

An excess absorption of one Cs atom per unit cell was noted in the corresponding Cs work and this was attributed to cationic crowding (Heo and
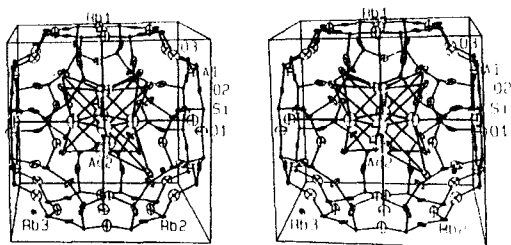
Fig. 1. A stereoview of the large cavity containing an Ag$_6$ molecule. The octahedral Ag$_6$ molecule, stabilized by coordination to 6 Rb$^+$ ions at Rb(1) and 7 Rb$^+$ ions at Rb(2) is shown. Ellipsoids of 20% probability are used.

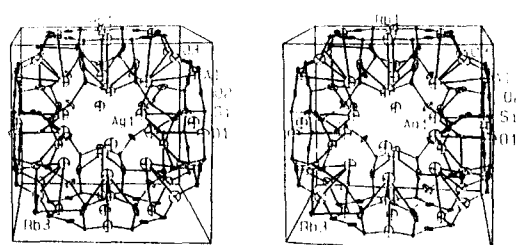**Fig. 2.** A stereoview of the large cavity of dehydrated Ag$_4$Ca$_2$-A treated with Rb vapor. 12 Ag species at Ag(1). 3 Rb$^+$ ions at Rb(1). and 3 Rb species at Rb (3) are shown. One-sixth of the unit cells may have this arrangement. Ellipsoids of 20% pobability are used.
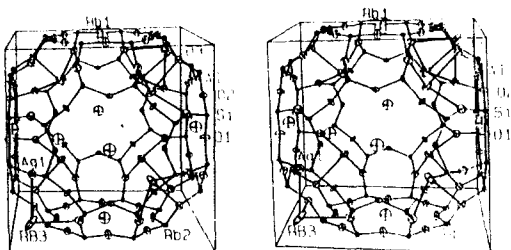
Fig. 3. A stereoview of the large cavity of dehydrated Ag$_6$Ca$_3$-A treated with Rb vapor. 3 Rb$^+$ ions at Rb(1), 6 Rb$^+$ ions at Rb(2), 2 Rb species at Rb(3), and one Ag species at Ag(1) are shown. Two-thirds of the unit cells may have this arrangement. Ellipsoids of 25 % probability are used.
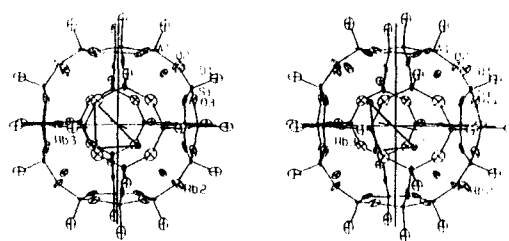

Fig. 4. A stereoview of a sodalite cavity. A (Rb$_3$)$^{2+}$ cluster is shown. Ellipsoids of 25% probability are used.
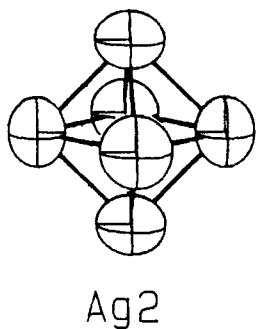

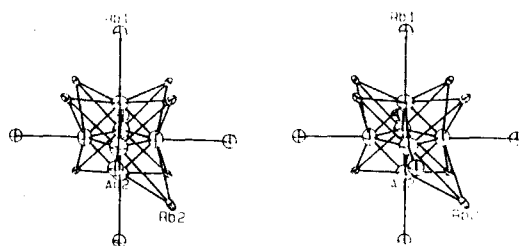**Fig. 5.** The octahedral Ag$_6$ molecule is shown using ellipsoids of 50% probability.

Fig. 6. The octahedral Ag$_6$ molecule, stabilized by coordination to 6 Rb$^+$ ions at Rb(1) and 7 Rb$^+$ ions at Rb(2), is shown. Eilipsoids of 25% probability are used.

Seff, 1987; Heo, 1987). This crowding is important in the Rb case also. However, the nature of the cationic cluster is quite different, clearly because the far smaller sizes of Rb^+ and Rb^0 allow one more Rb to fit into the sodalite cavity.

To maximize the number of favorable interactions and to avoid some questionable ones such as Ag(1)-Ag(2), each structure may be viewed as composed of two unit cell stoichiometries (Table 4). For example, about one-third of the unit cells of crystal 1 may contain three Rb^+ ions at Rb(1), seven Rb^+ ions at Rb(2), three Rb species at Rb(3) and six Ag atoms at Ag(2) (Figure 1). The Ag atoms at Ag(2) would form a hexasilver cluster which would be stabilized by association with seven ions at Rb(2) and three ions at Rb(1). Each of these latter Rb(1) ions is shared by two clusters, so the formula of an individual metal cluster may be viewed as $(Ag^0)_6(Rb^+)_{13}$ (Figures 1 and 5). The remaining two-thirds of the unit cells would have three Rb^+ ions at Rb(1), five Rb^+ ions at Rb(2), three Rb species at Rb(3) and one Ag^+ ion at Ag(1). Some degree of arbitrariness is used in selecting these idealized stoichiometries.

Table 4. Inferred Unit Cell Compositions for Crystals 1, 2, and 3.

Position of Cations ana Atoms		Crystal 1		Crystal 2		Crystal 3	
		1/3	2/3	1/3	2/3	5/6	1/6
8-ring	Rb(1)	3	3	3	3	3	3
6-ring	Rb(2)	7	5	7	6	7	0
	Rb(3)	3	3	3	2	3	3
opposite 4-rings	Ag(1)	0	1	0	1	0	12
center of large cavity	Ag(2)	6	0	6	0	6	0

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