ANALYTICAL SCIENCE & TECHNOLOGY
Vol.15, No.6, 540-549, 2002
Printed in the Republic of Korea

Crystallographic Analysis of Ar Encapsulate within Cs_3-A Zeolite

Woo Taik Lim,* Bok Jo Kim, Jong Sam Park, Chang Hwan Chang,*** Sung Wook Jung,*** and Nam Ho Heo★**

**Pohang Accelerator Laboratory, Pohang University of Science and Technology, P. O. Box 125, Pohang 790-600, Korea*
***Department of Environmental Engineering, Kyungwoon University, Kumi 730-850, Korea*
****Research Institute of Industrial Science and Technology, P. O. Box 125, Pohang 790-600, Korea*
Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701, Korea
(Received Sept. 6, 2002)

Abstract : The arrangement of encapsulated Ar atoms in the molecular-dimensioned cavities of fully dehydrated zeolite A of unit-cell composition $Cs_3Na_8HSi_{12}Al_{12}O_{48}$ (Cs_3-A) has been studied crystallographically to probe the confinement effect of guest species in microporous environment. Atoms of Ar were encapsulated in the cavities of Cs_3-A by treatment with 410 atm of Ar at 400 ℃ for two days, followed by cooling at room temperature. The crystal structure of Cs_3Na_8H-A(4Ar) (P_e = 410 atm, a = 12.245(2) Å, R_1 = 0.0543, and R_2 = 0.0552) has been determined by single crystal X-ray diffraction technique in the cubic space group $Pm\bar{3}m$ at 21 (1) ℃ and 1 atm. Encapsulated Ar atoms are distributed in three crystallographic distinct positions: 1.5 Ar atoms per unit cell opposite 6-rings, 1.5 opposite four-rings in the large cavity, and finally 1.0 in the sodalite-unit. The possible structures of argon clusters, such as Ar_2, Ar_3, and Ar_4, are proposed.

Key words : zeolite A, encapsulation, argon cluster, confinement effect

1. Introduction

Zeolite A is an aluminosilicate material with a stable crystalline framework consisting of two interconnecting nano-sized cavities, namely, α- and β-cages. The α-cages each with a diameter of 11.4 Å are connected three-dimensionally through 4.2 Å circular apertures and β-cages each with 6.6 Å diameter, and 2.2 Å apertures are connected through double-4-ring.[1]

Large quantities of gas molecules can be stored in zeolite cavities and released from the cavities if their kinetic diameters are somewhat larger than the effective diameters of the zeolite windows in a controlled fashion. It can be accomplished by heating the zeolite and gas at high pressure, followed by quenching to ambient temperature while the high pressure is maintained.[2-17] Controlled releasing can be achieved by relaxing the window blockage by reheating the zeolite and/or by exposing the zeolite to small polar molecules.[12,17-20]

Zeolite A as the storage medium of small nonpolar molecules, such as H_2, O_2, N_2, CH_4, Ar, Kr, and Xe, was widely studied experimentally[6-17,21-24] and sometimes with computer simulations[25-28] to illuminate the encapsulation characteristics and the behavior of

★ Corresponding author
Phone : +82+(0)53-950-5589 Fax : +82+(0)53-950-6594
E-mail : nhheo@knu.ac.kr

encapsulated molecules.

Since the several experiments on the encapsulation of gas molecules in zeolite A at the relatively high pressure by Heo *et al.*, the studies of rare-gas encapsulates have been focused on the single crystal X-ray crystallographic method.[11,13-17] They reported the positions of Ar, Kr, and Xe atoms encapsulated at the pressure of 660 and 1000 atm for Cs_3Na_8H-A(xAr), x = 5 and 6,[13] 635 and 1025 atm for Cs_3Na_8H-A(yKr), y = 5 and 6,[11,16] and 255, 450, and 1020 atm for Cs_3Na_8H-A(zXe), z = 2.5, 4.5, and 5.25,[14] in the cavities of fully dehydrated Cs_3Na_8H-A by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ at 21(1) ℃ and 1 atm. Their crystallographic studies resulted in the possible clustering of rare-gas atoms in the large cavities of zeolite A such as Ar_x, x = 4 and 5,[13] Kr_y, y = 4 and 5,[11,16] Xe_z, z = 2, 3, 4, 5, and 6.[14] In those structures of Cs_3-A(5Ar),[13] Cs_3-A(5Kr),[11] and Cs_3-A(4.5Xe),[14] four Ar, Kr, and Xe atoms in the large cavity formed a rhombus (planar) with an inter-rare gas atom distances of 4.75(8), 4.67(3), and 4.51(3) Å and an angle of 88(1), 95.6(5), and 95.1(5)°, respectively. In this rhombic ring of four Ar, Kr, and Xe atoms, the charge dipoles induced on the Ar, Kr, and Xe atoms by their interactions with the zeolite alternate around the ring, showing the effect of the electrostatic fields in the zeolite cavity.[11,13,14] In the case of the structures of Cs_3-A(6Ar),[13] Cs_3-A(6Kr),[16] and Cs_3-A(5.25Xe),[14] the five Ar, Kr, and Xe atoms in the large cavity have a trigonal-bipyramid arrangement with three such atoms at equatorial positions and two at axial positions with an inter-Ar, -Kr, and -Xe atoms distance of 4.63(9), 4.78(6), and 4.45(2) Å, respectively. These arrangement of encapsulated Ar, Kr, and Xe atoms in the large cavity are stabilized by alternating dipoles induced on those atoms by four-ring oxygens and six-ring Na^+ ions, respectively.

In the structure of Na-A(7Xe),[15] six Xe atoms in the large cavity of the native zeolite (Na_{12}-A) formed a distorted octahedral arrangement with four Xe atoms at equatorial positions (each two at Xe(2) and Xe(3)) and the other two at axial positions. These arrangements of the encapsulated Xe atoms in the large cavity are stabilized by alternating dipoles induced by eight- and six-ring Na^+ ions as well as four-ring oxygens, respectively.

In this work, Ar atoms, which are small gaseous atoms with high X-ray scattering power, have been encapsulated in the cavities of zeolite A at elevated temperature and much lower pressures (410 atm of Ar gas) than previous works[13] (660 and 1000 atm of Ar gas). Crystal structure of such zeolite-encapsulate should be thoroughly studied for the understanding encapsulation characteristics of Ar gas molecules, confinement effect, interactions between Ar gas molecules and/or framework atoms of zeolite, and the possible clustering among the confined Ar atoms by comparing those Cs_3-A(xAr), x = 5 and 6,[13] in the molecular dimensioned cavities of zeolite A. The formation of interesting Ar clusters due to the induced dipolar attractions (London forces) in the large cavity as well as Ar atom trapped in the sodalite-unit even at lower pressure than our previous works would be seen.

2. Experimental Section

2.1. Reagents and Experimental proceeding

Colorless single crystals of zeolite 4A, $Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$ (Na_{12}-A·$27H_2O$ or Na-A·$27H_2O$),[29] were synthesized by Kokotailo and Charnell.[30] A single crystal of hydrated Na-A, a cube 80 ㎛ on an edge, was lodged in a fine Pyrex capillary with thin and uniform walled thickness to minimize the effect of X-ray absorption and scattering during the subsequent diffraction experiment. Crystals of hydrated Cs_3-A (approximate composition Cs_3Na_8H-A) were prepared by the dynamic (flow) ion-exchange of Na-A with an aqueous solution (pH = 5.7), 0.04 M in Cs^+ and 0.06 M in Na^+ made by using $CsNO_3$ and $NaNO_3$ (both Aldrich 99.99%).[10,11,13-17] This solution composition was carefully chosen so that all eight- and six-ring sites of the zeolite would be fully occupied by Cs^+ and Na^+ ions with occupancies of 3.0 and 8.0 per unit cell, respectively.

A single crystal of hydrated Cs_3-A was lodged in a fine Pyrex capillary with both ends open. This capillary was transferred to a high-pressure line connected to the

vacuum line. After cautious increases in temperature of 25 ℃/hr under vacuum, followed by complete dehydration at 400 ℃ and 1 × 10^{-4} torr for two days, forced sorption of Ar into crystal was carried out at 400 ℃ for two days with 410 atm of Ar (Special Gas Co., 99.99%). Encapsulation was accomplished by cooling at pressure to room temperature with an electric fan. Following released of Ar gas from the chamber, both ends of the capillary were presealed with vacuum grease under nitrogen before being completely sealed with a small torch. No changes were noted in the appearance of the crystals upon examination under the microscope.

A CAD4/Turbo diffractometer equipped with a rotating anode generator and a graphite monochromator was used for preliminary experiments and for the subsequent collection of diffraction intensities, all at 21(1) ℃ using molybdenum radiation. The cubic space group $Pm\bar{3}m$ (no systematic absences) was used in this work for reasons discussed previously.[10-16] For this crystal, the cell constants, a = 12.245(2) Å at 21(1) ℃, were determined by a least-squares treatment of 15 intense reflections for which 20 < 2Θ < 30°. Each reflection was scanned at a constant scan speed of 0.5 °/min in 2Θ with a scan width of (0.59 + 0.82*tanΘ). Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of all lattice points for which 2Θ< 70° were recorded. Absorption correction (μR *ca.* 0.26)[31] was judged to be negligible for this crystal since semi-empirical Ψ-scans showed only negligible fluctuations for several reflections. Only those reflections in each final data set for which the net count exceeded three times its standard deviation were used in structure solution and refinement. This amounted to 280 reflections. Other crystallographic details are the same as previously reported.[11,13-17] A summary of the experimental conditions and crystallographic data is presented in *Table* 1.

Table 1. Summary of Experimental and Crystallographic Data

Ion exchange solutions	0.1 N 40 mol% ($NaNO_3$ + $CsNO_3$)
Dehydration Temperature	400 ℃
Dehydration Period	2 days
Encapsulation Temperature	400 ℃
Encapsulation Period	2 days
No. of Reflection obsd., m	280
No. of Variables, s	33
Unit Cell parameter, Å	12.245(2)
Space group	$Pm\bar{3}m$/221
Final Error Index	
R_1[a]	0.0543
R_2[b]	0.0552
Goodness-of-fit[c]	1.62

[a] $R_1 = \sum | F_o - | F_c | | / \sum F_o$, [b] $R_2 = (\sum_w (F_o - F_c)^2 / \sum_w F_o)^{1/2}$, [c] $Goodness\text{-}of\text{-}fit = | \sum_w (F_o - | F_c |)^2 / (m - s) |^{1/2}$

2.2. Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of all framework atoms [(Si,Al), O(1), O(2), and O(3)], Cs^+ at Cs, and Na^+ at Na in Cs_3Na_8H-A.[10] Refinement with anisotropic thermal parameters for all atoms in this model converged to $R_1 = \Sigma | F_o - | F_c | | / \Sigma F_o$ = 0.126 and $R_2 = (\Sigma w (F_o - | F_c |)^2 / \Sigma w F_o^2)^{1/2}$ = 0.161 with occupancies of 3.1(2) and 7.5(2) for Cs and Na, respectively. A refinement with Ar(1) at a peak (0.0622, 0.0774, 0.0774) in an ensuing difference Fourier function converged to R_1 = 0.067 and R_2 = 0.079 with resulting occupancy of 1.2(1) for Ar(1). Another difference Fourier function based on this model revealed a peak (0.3550, 0.3550, 0.3550) opposite a six-ring in the large cavity. The following refinement with this peak as Ar(3) converged to R_1 = 0.061 and R_2 = 0.067, resulting in occupancies of 1.3(1) and 1.1(1) for Ar(1) and Ar(3), respectively. A subsequent refinement including a peak found in the large cavity at (0.3254, 0.3254, 0.5) as Ar(2), further reduced the error indices to R_1 = 0.053 and R_2 = 0.052, with the refined occupancies of 3.01(1), 8.2(1),

Table 2. Positional, Thermal, and Occupancy Parameters[a]

	Wyckoff position	x	y	z	U_{11} or U_{iso}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy[c]	
											fixed	varied
(Si, Al)	24 (*k*)	0	1830(2)	3706(2)	22(1)	20(1)	20(1)	0	0	6(3)	24[d]	
O (1)	12 (*h*)	0	2205(7)	5000[e]	58(7)	50(7)	50(7)	0	0	0	12	
O (2)	12 (*i*)	0	2942(5)	2942(5)	58(7)	23(3)	23(3)	0	0	47(9)	12	
O (3)	24 (*m*)	1123(3)	1123(3)	3384(5)	37(3)	37(3)	37(3)	15(7)	6(6)	6(6)	24	
Cs	3 (*c*)	0	5000[e]	5000[e]	137(3)	81(3)	81(3)	0	0	0	3	3.01(1)
Na	8 (*g*)	2049(4)	2049(4)	2049(4)	79(3)	79(3)	79(3)	101(6)	101(6)	101(6)	8	8.2(1)
Ar (1)	24 (*m*)	424(28)	821(21)	821(21)	2(1)						1	1.6(1)
Ar (2)	12 (*j*)	3055(51)	3055(51)	5000[e]	29(4)						1.5	1.8(1)
Ar (3)	8 (*g*)	332(47)	3322(47)	3322(47)	19(3)						1.5	1.7(1)

[a]Position parameters $\times 10^4$ and thermal parameters $\times 10^3$ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant given for the corresponding parameter. The anisotropic temperature factor is $\exp[-2\pi^2 a^{-2}(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$. [b]Isotropic thermal parameters in units of $Å^2$. [c]Occupancy factors are given as the number of atoms or ions per unit cell. [d]Occupancy for (Si)=12, occupancy for (Al) = 12. [e]Exactly 0.5 by symmetry.

Table 3. Selected Interatomic Distances(Å) and Angels(deg)[a]

	Distances		Angles
(Si,Al)-O(1)	1.649(4)	O(1)-(Si,Al)-O(2)	108.4(4)
(Si,Al)-O(2)	1.652(7)	O(1)-(Si,Al)-O(3)	111.8(3)
(Si,Al)-O(3)	1.673(4)	O(2)-(Si,Al)-O(3)	107.0(2)
		O(3)-(Si,Al)-O(3)	110.7(3)
Na-O(1)	2.289(7)		
Na-O(2)	2.947(6)	(Si,Al)-O(1)-(Si,Al)	147.7(7)
Cs-O(1)	3.42(1)	(Si,Al)-O(2)-(Si,Al)	159.1(4)
Cs-O(2)	3.565(5)	(Si,Al)-O(3)-(Si,Al)	142.7(4)
Ar(3)-Na	2.70(4)	O(3)-Na-O(3)	117.5(3)
Ar(1)-Na	2.91(3)		
Ar(2)-Na	4.01(2)	Ar(1)-Na-O(3)	86.2(4)
Ar(2)-Cs	4.43(6)	Ar(3)-Na-O(3)	99(1)
Ar(3)-Cs	5.00(5)	Ar(1)-Na-Ar(3)	172(1)
Ar(1)-O(3)	3.27(1)	Ar(2)-Ar(3)-Ar(2)	87(1)
Ar(1)-O(2)	3.71(2)	Ar(3)-Ar(2)-Ar(3)	93(1)[b]
Ar(2)-O(1)	3.88(7)		
Ar(2)-O(3)	3.89(4)		
Ar(3)-O(3)	3.81(5)		
Ar(3)-O(2)	4.12(6)		
Ar(2)-Ar(3)	4.90(8)		

[a]The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. [b]Required to be the supplement of the Ar(2)-Ar(3)-Ar(2) angle.

1.3(1), 1.8(1), and 1.7(1) for Cs, Na, Ar(1), Ar(2), and Ar(3), respectively. The final cycles of refinement with all occupancies fixed at 3.0, 8.0, 1.0, 1.5, and 1.5, respectively, for Cs, Na, and Ar(*i*), *i* = 1 ~ 3, converged with no further changes in the error indices. Extensive but unsuccessful efforts were made to locate the 12th cation necessary for electroneutrality at the usual position opposite a four-ring in the large cavity.[10,11,13-17] A final difference Fourier function was featureless. Considering the moderate amount of H^+ in the ion-exchange solution (pH = 5.7), and the small deviation from unity which may be expected for Si/Al (perhaps 1.04),[10-16] the unit cell formula of the zeolite itself is taken to be $Cs_3Na_8H_x$-A, x = *ca.* 1. If the H^+ ions were lost as water during crystal dehydration, the formula would be Cs_3Na_8-A with 0.5 framework oxygen absences per unit cell. For simplicity, the notation Cs_3-A(4Ar) will be used for this crystal. The final structural parameters are given in *Table* 2. Selected interatomic distances and angles are given in *Table* 3.

The value of the goodness-of-fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 1.62; the number of observations, *m*, is 280. The number of parameters, *s*, is 33. All shifts in the final cycles of refinement were less than 0.1% of their corresponding estimated standard deviations. The quantity minimized in least-squares is $\Sigma w(F_o - |F_c|)^2$, where the weights (*w*) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observed structure factor. Atomic structure factors for Cs^+, Ar, Na^+, O^-, and $(Si,Al)^{1.75+}$ were used. The function describing $(Si,Al)^{1.75+}$ is the mean of the Si^{4+}, Si^0, Al^{3+}, and Al^0 functions. All scattering factors were modified to account for anomalous dispersion.[32,33]

3. Results and Discussion

3.1. Zeolite A Framework and Cations

The structural parameters of the framework atoms and cations are almost identical in all of the following structures: empty Cs_3-A,[10] Cs_3-A (*x*Ar), *x* = 5 and 6,[17] Cs_3-A (*y*Kr), *y* = 5 and 6,[11,16] and Cs_3-A (*z*Xe), *z* = 2.5, 4.5, and 5.25.[14] The occupancies of the Cs^+ ions in the eight-rings of the Ar encapsulate are slightly greater (closer to integer) than they were in Cs_3-A[10] and Cs_3-A (5Kr),[11] due to the (purposefully) higher Cs^+/Na^+ ratio in the ion-exchange solution used for the preparation of Cs_3-A in this work.

In Ar-encapsulate structure, three Cs^+ ions per unit cell fully occupy the centers of the eight-rings at equipoints of local symmetry C_{4h} (D_{4h} in $Pm\bar{3}m$), positions commonly found in partially or fully Cs^+-exchanged zeolite A.[10,11,13-17,34-37] Each Cs^+ ion is 3.42(1) Å from four O(1) oxygens and 3.565(5) Å from four O(2) oxygens (see *Table* 3). Although these distances are substantially longer than the sum, 2.99 Å, of the conventional ionic radii of O^{2-} and Cs^+ ($r_{O^{2-}}$ = 1.32 Å and r_{Cs^+} = 1.67 Å), these positions are well established experimentally[10,11,13-17,34-37] and theoretically.[38,39]

As in the crsytal strcture of dehydrated Na_{12}-A,[40] eight Na^+ ions per unit cell are located near the center of the eight six-rings per unit cell. Each Na^+ ion is 2.289(7) Å from three O(3) oxygens. These Na^+ ions extend 0.36 Å into the large cavity from the (111) planes at O(3) (see *Table* 4). The O(3)-Na-O(3) angles are close to 120° (117.5 (3)°), showing that Na^+ is nearly trigonal, quite different from its near tetrahedral geometry in hydrated Cs_3Na_8H-A and Cs_3Na_9-A.[10] As in the previously reported crystal structures of the empty Cs_3-A,[10] Cs_3-A(*x*Ar), *x* = 5 and 6,[17] Cs_3-A(*y*Kr), *y* = 5 and 6,[11,16] and Cs_3-A(*z*Xe), *z* = 2.5, 4.5, and 5.25,[14] the 12th cation per unit cell, because it could not be located crystallographically, is assumed to be, at least predominantly, a H^+ ion. Alternatively, it may have been lost as water.[10,11,13-17]

Table 4. Deviations of Atoms (Å) from the (111) plane at O(3)[a]

Na	0.36
Ar(1)	-2.55[a]
Ar(3)	3.06

[a]A negative deviation indicates that the atom lies on the same side of the plane as the origin, *i.e.*, inside the sodalite unit.

3.2. Argon Atom in the Sodalite Unit

Like as the crystal strcutures of Cs_3-A(xAr), x = 5 and 6,[17] an isolated argon atom at Ar(1) is found inside each sodalite-unit (see *Fig.* 1). The occupancies from least-squares suggest that a second Ar(1) might be placed in some fraction of the sodalite units. However doing so would lead to impossibly short Ar(1)-Ar(1) distances of 3.02 Å for Cs_3-A(4Ar). A dynamic process for the passage of an Ar atom through a six-ring, whose aperture is formally too small (2.2 Å), must exist at 400 ℃ and (likely) at somewhat lower temperature.

Fig. 1. Stereoview of a sodalite unit in the unit cell, showing an encapsulated Ar atom near a Na^+ ion on a 6-ring. The zeolite A framework is drawn with solid line between oxygens and tetrahedrally coordinated (Si,Al) atoms. Ellipsoids of 20% probability are shown.

Ar(1) on an off-site of threefold axis (x, y, y) is 2.55 Å from the center of the sodalite unit where it can be polarized by the electrostatic field of the zeolite. This Ar atom is closer to Na^+ and further away from the center of the sodalite units, when it was compared with Kr atom. The closest approach distances of this Ar(1) to two six-ring Na^+ ions and to two O(3) oxygens are 2.91(3) and 3.27(1) Å for Cs_3-A(4Ar). Considering the radii of the cations (r_{Na^+} = 0.97 Å and r_{Cs^+} = 1.67 Å),[41,42] framework oxygens (1.32 Å),[41,42] and argon atoms (1.92 Å as $r_{min}/2$ and as found in the solid).[43] These approach distances are substantially longer than the sum of the atomic and ionic radii of Ar and Na^+ (1.92 + 0.97 = 2.89 Å) and the sum of those Ar and O^{2-} (1.92 + 1.32 = 3.24 Å), respectively, indicating that Ar(1) is weakly held. Ar(1) is displaced 2.55 Å from the center of the sodalite unit toward a Na^+ ion, where it can be polarized by the electrostatic field of the zeolite, avoiding the center of the sodalite unit which by symmetry has no electrostatic field. Therefore, it can be concluded that there must be an attractive force between the polarized Ar atom at Ar(1) and the electrostatic field of the zeolite with an energy minimum at this position.

3.3. Argon Atoms in the Large Cavity

The 3 Ar atoms in large cavity of Cs_3-A(4Ar) are found at two crystallographically distinct positions. That there are two kinds of positions indicates that the argon atoms are not arranging themselves by simple packing within the highly symmetric zeolites, to form, for example, a tetrahedron. It is attributed to dipolar interactions among the sorbed atoms. 1.5 Ar atoms at Ar(2) lie opposite a four-ring and another 1.5 Ar atoms at Ar(3) lie on a three-fold axis opposite a six-ring, which may mean that 50% of the unit cells have 2 Ar atoms and the remaining 50% have 4 Ar atoms in the large cavities of Cs_3-A zeolite. It is also possible that some fraction of the unit cells have 3 Ar atoms in large cavity like as 2 Ar at Ar(2) and 1 Ar at Ar(3) or 1 Ar at Ar(2) and 2 Ar at Ar(3).

The closest approaches of these argon atoms to nonframework cations are 2.70(4) Å for Ar(3)-Na^+ and 4.43(6) Å for Ar(2)-Cs^+, while those to framework oxygens (Ar(2)-O(1)) are 3.88(7) Å (see *Table* 3). Considering the radii of the cations (r_{Na^+} = 0.97 Å and r_{Cs^+} = 1.67 Å),[41,42] framework oxygens (1.32 Å),[41,42] and argon atoms (1.92 Å as $r_{min}/2$ and as fond in the solid),[43] some of the argon atoms are sufficiently close to their neighbors to be considered as having relatively strong interactions. In particular, when the distances are compared to the sum of the above radii for Na^+ and Ar, 0.97 + 1.92 = 2.89 Å, the approach distances of the three-fold axis argon atoms, Ar(3), to the six-ring Na^+ ions (2.70(4) Å) indicate very strong Na^+-Ar interactions. In contrast, inter-argon distances of 4.90(8) Å between Ar(2) and Ar(3) in the large cavities are nearly an angstrom larger than those in solid Ar.

Cs^+-Ar interactions are much less important than Na^+-Ar interactions, as would be expected because Cs^+ is much larger than Na^+, so the electric field gradient at its

"surface" is much less. The Cs^+-Ar distances, 4.43(6) Å (see *Table* 3), are *ca.* 0.84 Å longer than the sum of the Cs^+ and Ar radii. In contrast, the Na^+-Ar distances, 2.70(4) Å, are shorter than the corresponding sum.

The argon atoms at Ar(3) in the large cavity appear to interact much more strongly with six-ring Na^+ ions than do those at Ar (1). These Ar(3)-Na^+ interactions (2.70(4) Å) are all shorter than the corresponding Ar(1)-Na^+ distances (2.91(3) Å). Similarly, the large-cavity Ar, Kr, and Xe atoms in Cs_3-A(*x*Ar), x = 5 and 6,[17] Cs_3-A(*y*Kr), y = 5 and 6,[11,16] Cs_3-A(*z*Xe), z = 2.5 and 4.5, and in 75% of the large cavities of Cs_3-A(5.25Xe),[14] respectively, interact much more strongly with Na^+ ions than do the small-cavity Ar, Kr, or Xe's.

The both interatomic distances between Ar atoms and zeolite cations are shorter than those found with Kr atoms, as expected from the smaller size of Ar atoms. However, those between Ar atoms opposite four-rings and framework oxides are longer, allowing the formation of the square plane rather than rhombus in the large cavity. This is probably because of smaller polarizability and larger mobility of Ar atoms compared to those of Kr atoms in the same large cavity.

3.4. Clustering of Ar Atoms

The two argon atoms each at Ar(2) and Ar(3) on the inner surface of the large cavity in the half of unit cells may be placed within their partially occupied equipoints in various ways (see *Fig.* 2 and 4). The inter-argon distance, 4.90(8) Å, suggests the possibility of an Ar(2)-Ar(3) interaction with favorably oriented induced dipoles (see *Fig.* 2 and 3). A longer distance, 6.61(2) Å, is also possible (see *Fig.* 4).

The next possible arrangement in the remaining half of unit cells is a planar four-Ar ring, [-Ar(2)-Ar(3)-Ar(2)-Ar(3)-], with Ar(2)-Ar(3) = 4.90(8) Å, Ar(2)-Ar(3)-Ar(2) = 87(1)° and Ar(3)-Ar(2)-Ar(3) = 93(1)°, is selected as the most plausible due to its higher symmetry and favorably oriented induced dipoles (see *Fig.* 5 and 6).

Fig. 2. Stereoview of the large cavity with one possible arrangement of two Ar atoms at Ar(2) and Ar(3). See the caption to *Fig.* 1 for other details.

Fig. 3. Schematic diagrams of two Ar atoms in the large cavity. The immediate environment of each Ar atom and the dipole moment it induces on each Ar are shown. The interactions between the polarized Ar atoms are indicated by dashed lines.

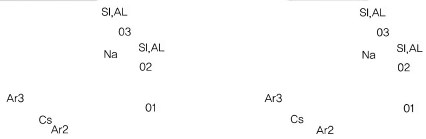

Fig. 4. Stereoview of the large cavity with another possible arrangement of two Ar atoms at Ar(2) and Ar(3). See the caption to *Fig.* 1 for other details.

Fig. 5. Stereoveiw of the large cavity with the only reasonable arrangement of four Ar atoms at Ar(2) and Ar(3). Inter-argon contacts are indicated by fine lines. See the caption to *Fig.* 1 for other details.

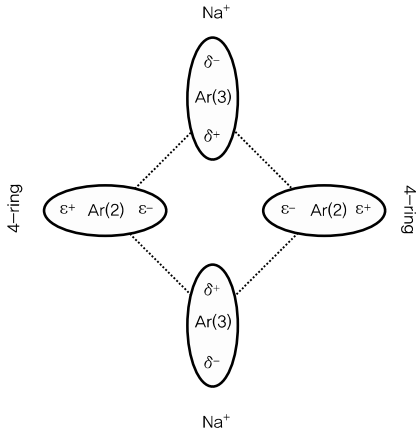

Fig. 6. Schematic diagram of the rhombus of four Ar atoms in the large cavity. See the caption to *Fig.* 3 for other details.

In this square plane, Ar atoms alternately approach Na^+ ions and four-oxygen rings and are polarized oppositely, allowing their inter-argon approaches to be attractive. This arrangement is similar to the previously found rhombus arrangement of four Ar, Kr, and Xe atoms in the large cavity of Cs_3-A(5Ar), Cs_3-A(5Kr), and the 75% unit cell of Cs_3-A(zXe), z = 4.5 and 5.25, respectively.

Another palusible arrangement of Ar atoms in the large cavities are 2 Ar atoms at Ar(2) and 1 Ar atoms at Ar(3) in the half of unit cells and 1 Ar atoms at Ar(2) and 2 Ar atoms at Ar(3) in the remaining half of unit cells (see *Fig.* 7 and 8).

The shortest distance, Ar(2)-Ar(3) = 2.10(1) Å, is impossibly short. Of the two longer Ar(2)-Ar(3) distances,

Fig. 7. Stereoview of the large cavity with one possible arrangement of three Ar atoms at Ar(2) and Ar(3). Inter-argon contacts are indicated by fine lines. See the caption to *Fig.* 1 for details.

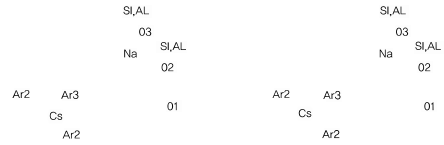

Fig. 8. Stereoview of the large cavity with another possible arrangement of three Ar atoms at Ar(2) and Ar(3). Inter-argon contacts are indicated by fine lines. See the caption to *Fig.* 1 for details.

4.90(8) and 6.61(3) Å, the first indicates a reasonable interaction. Possible Ar(2)-Ar(2) interactions are 3.36(1), 4.76(5), 5.83(2), and 6.74(3) Å. Among these, a planar three-Ar arrangements, [Ar(2)-Ar(3)-Ar(2)] with Ar(2)-Ar(3) = 4.90(8) Å and Ar(2)-Ar(3)-Ar(2) = 87(1)° and [Ar(3)-Ar(2)-Ar(3)] with Ar(2)-Ar(3) = 4.90(8) Å and Ar(3)-Ar(2)-Ar(3) = 93(1)° are selected as the most reasonable due to its higher symmetry and favorably oriented induced dipoles (see *Fig.* 9). In these three-Ar arrangements, argon atoms alternately approach Na^+ ions and four-oxygen rings; they are therefore polarized oppositely, allowing their inter-argon approaches to be attractive.

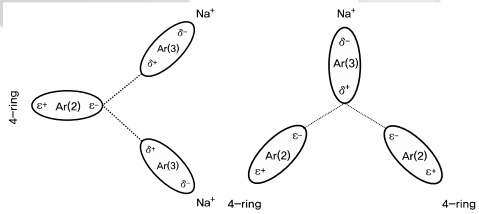

Fig. 9. Schematic diagrams of the bent linear of three Ar atoms in the large cavity. See the caption to *Fig.* 3 for other details.

Acknowledgement

W. T. Lim gratefully acknowledges the post-doctral fellowship of PAL (Pohang Accelerator Laboratory). We also gratefully acknowledge the support of the Central Laboratory of Kyungpook National University for the diffractometer and computing facilities.

Supplementary Material Available

Observed and calculated structure factors for Cs_3Na_8H-A(4Ar) are available upon request to the corresponding author.

References

1. Breck, D. W., Zeolite Molecular Sieve: Structure, Chemistry, and Uses, John Wiley & Sons, New York, 83-85 (1974)
2. Breck, D. W., Zeolite Molecular Sieve: Structure, Chemistry, and Uses, John Wiley & Sons, New York, 623-628 (1974)
3. Fraenkel, D., *CHEMTECH*, **1**, 60-65 (1981)
4. Barrer, R. M.; Vaughan, D. E. W., *J. Phys. Chem. Solids*, **32**, 731-743 (1971)
5. Fraenkel, D.; Shabtai, J., *J. Am. Chem. Soc.*, **90**, 7074-7076 (1977)
6. Kwon, J. H.; Cho, K. H.; Kim, H. W.; Suh, S. H.; Heo, N. H., *Bull. Korean Chem. Soc.*, **14**, 583-588 (1993)
7. Yoon, J. H.; Heo, N. H., *J. Phys. Chem.*, **96**, 4997-5000 (1992)
8. Heo, N. H.; Rho, B. R.; Kim, D. H.; Kim, J. T., *Hwahak Konghak*, **29**, 407-416 (1991)
9. Kim, D. H.; Kim, J. T.; Heo, N. H., *Hwahak Konghak*, **29**, 717-726 (1991)
10. Cho, K. H.; Kwon, J. H.; Kim, H. W.; Park, C. S.; Heo, N. H., *Bull. Korean Chem. Soc.*, **15**, 297-304 (1994)
11. Heo, N. H.; Cho, K. H.; Kim, J. T.; Seff, K., *J. Phys. Chem.*, **98**, 13328-13333 (1994)
12. Kwon, J. H., M. E. Thesis, Kyungpook National University 1993.
13. Heo, N. H.; Lim, W. T.; Seff, K., *J. Phys. Chem.*, **100**, 13725-13731 (1996)
14. Heo, N. H.; Lim, W. T.; Kim, B. J.; Lee, S. Y.; Kim, M. C.; Seff, K., *J. Phys. Chem. B*, **103**, 1881-1889 (1999)
15. Lim, W. T.; Park, M.; Heo, N. H., *Bull. Korean Chem. Soc.*, **21**, 75-80 (2000)
16. Lim, W. T.; Chang, C. H.; Jung, K. J.; Heo, N. H., *Bull. Korean. Chem. Soc.*, **22**, 1023-1029 (2001)
17. Lim, W. T., M. E. Thesis, Kyungpook National University 1995.
18. Barrer, R. M.; Vansant, E. F.; Peeters, G., *J. Chem. Soc., Faraday Trans. I*, **74**, 1871-1881 (1978)
19. Thijs, A.; Peeters, G.; Vansant, E. F.; Verhaert, I., *J. Chem. Soc., Faraday Trans, I*, **82**, 963-975 (1986)
20. Niwa, M.; Kato, S.; Hattori, T.; Marakami, Y., *J. Chem. Soc., Faraday Trans. I*, **80**, 3135-3145 (1984)
21. Samant, M. G.; de Menorval, L. C.; Dalla Betta, R. A.; Boudart, M., *J. Phys. Chem.*, **92**, 3937-3938 (1988)
22. Derouane, E. G.; Nagy, J. B., *Chem. Phys. Lett.*, **137**, 341-344 (1987)
23. Dooryhee, E.; Greaves, G. N.; Steel, A. T.; Townsend, R. P.; Carr, S. W.; Thomas, J. M.; Catlow, C. R. A., *Faraday Discuss. Chem. Soc.*, **89**, 119-136 (1990)
24. Jameson, C. J.; Jameson, A. K.; Gerald II, R.; de Dios, A. C. *J. Chem. Phys.*, **96**, 1676-1689 (1992)
25. Santikary, P.; Yashonath, S.; Ananthakrishna, G., *J. Phys. Chem.*, **96**, 10469-10477 (1992)
26. Cook, G. A., Argon, Helium, and the Rare Gases, Interscience, New York, 1, 228 (1961)
27. Jameson, C. J.; Jameson, A. K.; Baello, B. I.; Lim, H. M., *J. Chem. Phys.*, **100**(8), 5965-5976 (1994)
28. Jameson, C. J.; Jameson, A. K.; Baello, B. I.; Lim, H. M., *J. Chem. Phys.*, **100**(8), 5977-5987 (1994)
29. The nomenclature refers to the contents of the $Pm\bar{3}m$ unit cell: *e.g.*, Na_{12}-A represents $Na_{12}Si_{12}Al_{12}O_{48}$.
30. Charnell, J. F., *J. Crystal Growth*, **8**, 291-294 (1971)
31. International Tables for X-ray Crystallography, Kynoch Press: Birmingham, England; Vol IV, pp 61-66 (1974)
32. Cromer, D. T., *Acta Crystallogr.*, **18**, 17-23 (1965)
33. International Tables for X-ray Crystallography, Kynoch Press: Birmingham, England; Vol IV, pp

148-150 (1974)
34. Heo, N. H.; Seff, K., *J. Am. Chem. Soc.*, **109**, 7986-7992 (1987)
35. Vance, T. B., Jr.; Seff, K., *J. Phys. Chem.*, **79**, 2163-2167 (1975)
36. Firor, R. L.; Seff, K., *J. Am. Chem. Soc.*, **99**, 6249-6253 (1977)
37. Subramanian, V.; Seff, K., *J. Phys. Chem.*, **83**, 2166-2169 (1979)
38. Ogawa, K.; Nitta, M.; Aomura, K., *J. Phys. Chem.*, **82**, 1655-1660 (1978)
39. Takaishi, T.; Hosoi, H., *J. Phys. Chem.*, **86**, 2089-2094 (1982)
40. Yanagida, R. Y.; Amaro, A. A.; Seff, K., *J. Phys. Chem.*, **77**, 805 (1973)
41. Handbook of Chemistry and Physics, 64th ed. Chemical Rubber Co.: Cleveland, OH,; p F-187 (1983)
42. Shannon, R. D.; Prewitt, C. T., *Acta Crystallogr., Sect. B,* **25**, 925-946 (1969)
43. Breck, D. W., Zeolite Molecular Sieve: Structure, Chemistry, and Uses, John Wiley & Sons, New York, 634-641 (1974)