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The crystal structure of hydrated zeolites Tl-*A*, Ca-*A* and Ag-*A*

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Auszug

Die Kristallstrukturen des hydratisierten, mit Tl, Ca und Ag ausgetauschten synthetischen Zeoliths *A*, wurden in der Raumgruppe $Pm\bar{3}m$ verfeinert. Für die ersten beiden Formen standen Einkristalle zur Verfügung, während im Fall von Ag-*A* mit Pulverdaten gearbeitet wurde. In Bezug auf das Gerüst konnten innerhalb der Standardabweichungen keine wesentlichen Abweichungen zu den bekannten Werten von Na-*A* gefunden werden. Die wichtigsten Kationenpositionen liegen jeweils auf der dreizähligen Achse je zu beiden Seiten des Sechser-Rings, in einem derart kurzen gegenseitigen Abstand, daß eine gleichzeitige Besetzung ausgeschlossen werden muß. Im Falle von Ca-*A* erlaubten die gemessenen *b*-Reflexe die Diskussion einer partiellen Desymmetrisierung. Die Phasen der *b*-Reflexe wurden einerseits durch Abstandsverfeinerung (DLSR) eines Gerüstmodells mit festgelegter Si/Al-Verteilung und anderseits durch ein spezielles Ca-Modell bestimmt. Das Versagen der Verfeinerung in der Raumgruppe $F432$ wird auf die Vernachlässigung des Einflusses der Kationen auf das Gerüst zurückgeführt. Diesbezügliche Information kann von einer $F(a)$-Synthese nicht erwartet werden, da die Gerüstverschiebungen von der Größenordnung der Amplituden der Temperaturschwingungen sind. Im Falle von Tl-*A* lassen die Resultate der Verfeinerung gewisse Hinweise auf eine spezielle Anordnung der Wassermoleküle zu: In den großen Hohlräumen lassen sich pentagon-dodekaederförmige Tl-H_2O Komplexe erkennen, während in den kleineren Sodalithkäfigen eine entsprechende bipyramidenförmige Anordnung auftritt.

Abstract

The crystal structures of hydrated and Tl, Ca and Ag exchanged synthetic zeolites of type *A* have been refined in space group $Pm\bar{3}m$. Single-crystal data have been used except for Ag-*A* which was examined with powder data. There are no significant differences with respect to the well established framework of Na-*A*. The cations are mainly distributed among two positions on the three-

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fold axis to either side of the six-membered rings. The short distance between the two positions excludes the possibility of a simultaneous occupation. The step of a partial desymmetrization of Ca-A using b reflections has been discussed. The phases of the b reflections were determined with the aid of distance least-squares computations (DLSR) for the framework contribution and the assumption of a model for the Ca distribution. Satisfactory refinement could not be achieved, apparently because the influence of the Ca ions on the framework can not be neglected. $F(a)$-Fourier maps do not reveal any details, because framework displacements are in the order of the mean-square amplitudes of the thermal vibrations. For Tl-A the results of the refinement lead to some conclusions about the water molecules: In the large cage the water and the cations appear to form a pentagon-dodecahedral complex, while in the small cage a bipyramidal arrangement is apparent.

Introduction

A considerable amount of structural information on the synthetic zeolite of type A has become available since synthesis was first reported by BRECK *et al.* in 1956. According to REED and BRECK (1956), the principal feature of the framework structure can be described by a large α cage in the centre of the cubic cell surrounded by eight cubooctahedral β cages in the corresponding corners (Fig. 1). The Si/Al ordering of the aluminosilicate framework of Na-A, first recognized by BARRER and MEIER (1958), has been established by GRAMLICH and MEIER (1971). This ordering leads to a doubling of the cubic cell constants and lowers the maximum possible symmetry of $Pm\bar{3}m$ (A symmetry) to $Fm\bar{3}c$ (H symmetry), in accordance with the observed b reflections. In the large α cage the zeolitic water appears to form a pentagon-dodecahedral cluster. Because of the very similar scattering curves, it was difficult to distinguish crystallographically between oxygen atoms and sodium ions.

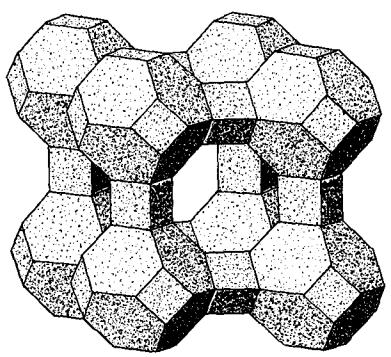

Fig. 1. Framework structure of zeolite type A (GRAMLICH and MEIER, 1971)

Further experimental work on hydrated Tl, Ca and Ag forms of the zeolite *A* is highly desirable in order to obtain further information about the influence of the cations on the framework and the water distribution.

Experimental

The single crystals of Na-*A* used in this work were kindly supplied by J. F. CHARNELL (cf. CHARNELL, 1971). The powder samples were prepared in the manner described by BORER (1969). We obtained the specific samples of Tl-*A*, Ca-*A* and Ag-*A* by ion exchange. Na-*A* has been treated several times with concentrated solutions of the respective salt in order to guarantee full sodium exchange. The products were washed with less and less concentrated solutions. The samples thus obtained have been equilibrated at 50% relative humidity as in BORER's case. This ion exchange may be characterized as follows:

Sample	Tl-*A*	Ca-*A*	Ag-*A*[1]
Solution	$TlNO_3$	$Ca(ClO_4)_2$	$AgNO_3$
Temperature	75°C	75°C	25°C
Degree of exchange	> 98%[2]	99%[3]	99%[3]
Duration of exchange	57 days	61 days	57 days

[1] kept under light cover.
[2] X-ray fluorescence.
[3] Atomic absorption.

The chemical properties are summarized in Table 1.

Table 1. *Chemical characterization* (based on *A* cell)
Formula (idealized): $M_{12}Al_{12}Si_{12}O_{48} \cdot qH_2O$
(after FISCHER and MEIER, 1965)

Sample	Tl-*A* (single crystal)	Ca-*A* (single crystal)	Ag-*A* (powder sample)
Size	55 μ	60 μ	1—3 μ
M	Tl	$Ca_{1/2}$	Ag
Water content[1] q	18	28	23
Density[2]	3.68 $\pm$ 0.1 g/cm³	2.00 $\pm$ 0.1 g/cm³	—
Cell parameter[3] a	12.35 $\pm$ 0.01 Å	12.24 $\pm$ 0.005 Å	12.30 $\pm$ 0.01 Å

[1] Determined thermogravimetrically.
[2] Determined by flotation on liquids.
[3] Determined by Jagodzinski camera (Fe$K\alpha$).

Intensity measurements

An automatic Picker four-circle diffractometer with graphite monochromatized Mo$K\alpha$ radiation was used for all single-crystal measurements. The lattice constants obtained by means of the standard least-squares orientation procedure of the diffractometer are in agreement with previously determined values based on powder data (see Table 1).

Some preliminary measurements of the *b* reflections of Tl-*A* showed that they were too weak to be used for quantitative analysis. 1900 *a* reflections were collected for 2θ up to 47°, corresponding to 329 symmetrically independent reflections in Laue symmetry $m3m$. Besides the usual Lorentz and polarization factors a correction for absorption was applied ($\mu R = 1.6$).

Preliminary examinations of the *b* reflections of Ca-*A* revealed reflections of the type *hhl* (*h* and $l = 2n + 1$). As a consequence, the space group $Fm\bar{3}c$ found for Na-*A* (Gramlich and Meier, 1971) had to be ruled out. The only extinctions found were those due to *F* centering. 1800 *a* reflections were collected for 2θ up to 50°, amounting to 383 symmetrically independent reflections. Within the same range 860 *b* reflections were collected corresponding to 180 symmetrically independent reflections. Lorentz and polarization corrections were applied in the usual way. The small value of the absorption coefficient ($\mu R < 0.06$) justified the omission of an absorption correction.

The powder measurements on Ag-*A* were carried out using a Picker powder diffractometer and Cu$K\alpha$ radiation with graphite monochromator. With the aid of the computer programme "Cufit" (Thöni, 1972) partially overlapping peaks were resolved. Thus 91 lines were measured up to $2\theta = 80°$. Only the usual Lorentz and polarization corrections were applied.

Stucture analysis of Tl-*A*

The refinement of the structure in space group $Pm\bar{3}m$ was performed with the X-ray 67 crystallographic computing system, starting with the framework coordinates of Na-*A* (Gramlich and Meier, 1971). A Patterson synthesis showed a first Tl position in the α cage. Difference Fourier maps revealed two additional Tl positions, whose coordinates, temperature and site-occupancy factors were alternately varied in subsequent least-squares cycles. A further difference Fourier map revealed two additional nonframework atoms which have been

refined using oxygen scattering factors. Least-squares computation was terminated when the weighted R value reached less than $R_w = 0.08$, based on reflections having intensities $> \sigma$. The final atom parameters are shown in Table 2. The interatomic distances which are of interest are listed in Table 3. Table 4 contains the observed and calculated structure factors.

Table 2. *Final atomic parameters of hydrated* Tl-*A zeolite based on space group* $Pm\bar{3}m$

(Standard deviations in parentheses)

Atomic coordinates

Atom	Position	Occupancy factor*	x	y	z
T**	$24k$	1	0	0.1840(7)	0.3714(7)
O(1)	$12h$	1	0	0.223(2)	$\frac{1}{2}$
O(2)	$12i$	1	0	0.2915(16)	0.2915(16)
O(3)	$24m$	1	0.1140(11)	0.1140(11)	0.3432(17)
Tl(1)	$8g$	0.72	0.2612(1)	0.2612(1)	0.2612(1)
Tl(2)	$8g$	0.20	0.1093(9)	0.1093(9)	0.1093(9)
Tl(3)	$24k$	0.10	0	0.4401(11)	0.4739(14)
I	$24l$	0.35	$\frac{1}{2}$	0.350(5)	0.211(4)
II	$12i$	0.32	0.096(4)	0.096(4)	0

* The occupancy factors for sites I and II are based on atomic oxygen (estimated standard deviations around 10%).

** T stands for (Si, Al).

Random mean-square displacements (Å^2)

Atom	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
T	0.021(5)	0.011(5)	0.015(5)	0	0	0.005(4)
O(1)	0.07(2)	0.04(2)	0.005(16)	0	0	0
O(2)	0.029(16)	0.017(12)	0.017(12)	0	0	0.015(14)
O(3)	0.036(10)	0.036(10)	0.069(16)	0.014(13)	0.019(10)	0.019(10)
Tl(1)	0.041(1)	0.041(1)	0.041(1)	0.004(1)	0.004(1)	0.004(1)
Tl(2)	0.096(7)	0.096(7)	0.096(7)	0.027(9)	0.027(9)	0.027(9)
Tl(3)	0.067(5)					
I	0.06(2)					
II	0.03(2)					

Table 3. *Interatomic distances and bond angles for* Tl-*A*

Aluminosilicate framework

	T—O(1)	1.65(1) Å		
	T—O(2)	1.64(1)		
	T—O(3)	1.68(1)		
O(1)—T—O(2)	109(1)°		T—O(1)—T	145(2)°
O(1)—T—O(3)	110(1)		T—O(2)—T	163(1)
O(2)—T—O(3)	106(1)		T—O(3)—T	144(1)
O(3)—T—O(3)	113(1)			

Cations and water molecules

	Tl(1)—Tl(2)	3.23(1) Å		
	Tl(2)—Tl(2′)	2.68(1), 4.67(1)		
Tl(1)—O(3)	2.75(1) Å		Tl(2)—II	1.36(1), 2.86(1) Å
Tl(1)—I	3.19(2)		Tl(2)—O(3)	2.87(2)
Tl(1)—O(2)	3.25(1)		Tl(2)—O(2)	3.44(1)
	Tl(3)—O(1)	2.68(3) Å		
	Tl(3)—I	2.84(6), 3.10(6)		
	Tl(3)—O(2)	2.89(2)		
	I—I′	2.40(8), 2.60(6), 3.68(8) Å		
	I—Tl(3)	2.84(6), 3.10(6)		
	I—O(1)	3.03(6)		
	I—Tl(1)	3.19(2)		
	II—Tl(2)	1.36(1), 2.86(1) Å		
	II—II′	1.67(4), 3.35(5)		
	II—O(3)	3.34(5)		
	II—O(2)	3.38(4)		

Structure analysis of Ca-*A*

Refinement of the *A* structure

This refinement in space group $Pm\bar{3}m$ was carried out using standard methods, starting with the framework coordinates of Na-*A* (GRAMLICH and MEIER, 1971). A first difference synthesis revealed two Ca positions on the threefold axis to either side of the six-membered ring at a very short mutual distance of 1.2 Å. Succeeding cycles of least-squares refinement and difference syntheses revealed six

Table 4. *Observed and calculated structure factors for* Tl-*A*
(Structure factors corresponding to intensities $< \sigma$ are marked by an asterisk)

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
1 0 0	83	160	12 5 0	23	-24	7 5 1	46	-42	8 6 2	104	105	10 4 4	101	-100
2	195	-197	6 6 0	237	235	8	52	43	9	53	-58	11	33	41
3	99	126	7	82	-85	9	60	-60	10	110	-113	12	42	50
4	360	353	8	112	-110	10	13*	-12	11	70	68	5 5 4	44	-38
5	91	-74	9	71	66	11	20	5	12	48	48	6	41	30
6	114	-92	10	114	107	12	22	-20	7 7 2	20	-10	7	85	-84
7	168	167	11	21	-20	6 6 1	58	-35	8	53	-56	8	20	-10
8	330	355	12	80	-82	7	19	-13	9	69	75	9	39	37
9	9	-9	7 7 0	33	39	8	43	48	10	33	30	10	24	17
10	23	27	8	51	46	9	24	-24	11	48	-49	11	48	-39
11	243	256	9	79	-77	10	19	-28	8 8 2	166	-174	12	49	-45
12	84	87	10	60	-58	11	15*	4	9	59	66	6 6 4	110	106
13	82	-77	11	42	45	12	22	-23	10	58	60	7	87	-96
1 1 0	47	-81	8 8 0	75	75	7 7 1	21	-14	11	67	-68	8	118	-115
2	29	-44	9	49	-51	8	23	24	9 9 2	0*	11	9	70	62
3	35	-53	10	53	-54	9	16*	-3	10	34	-32	10	51	50
4	231	-232	11	74	76	10	21	-18	3 3 3	0*	9	11	73	-77
5	107	-125	9 9 0	47	42	11	22	-26	4	24	24	7 7 4	66	79
6	12*	-31	10	37	41	8 8 1	0*	14	5	37	-29	8	80	81
7	83	-93	1 1 1	131	102	9	44	38	6	18	24	9	24	-11
8	24	9	2	6*	12	10	30	27	7	44	37	10	27	-29
9	12*	-24	3	190	190	11	18	11	8	92	-106	11	3*	13
10	5*	2	4	97	-88	9 9 1	38	12	9	54	-52	8 8 4	62	62
11	16	12	5	38	-19	10	8*	-8	10	15*	7	9	45	-40
12	46	-44	6	10*	-9	2 2 2	253	-254	11	18*	-4	10	61	-47
13	27	-13	7	45	-30	3	28	-15	12	25	30	9 9 4	33	38
2 2 0	422	406	8	95	93	4	394	409	13	35	-44	5 5 5	43	39
3	179	-169	9	17*	8	5	63	-64	4 4 3	91	107	6	52	49
4	326	-317	10	25	-10	6	262	-263	5	40	-46	7	39	-34
5	115	133	11	15*	-12	7	154	164	6	19	-26	8	101	87
6	237	252	12	23	-4	8	140	144	7	78	68	9	18*	-11
7	133	-140	13	24	19	9	31	-29	8	20	28	10	37	30
8	240	-234	2 2 1	0*	15	10	138	-132	9	12*	4	11	66	75
9	121	126	3	39	35	11	78	87	10	2*	7	6 6 5	22	14
10	101	121	4	15	5	12	103	107	11	4*	5	7	19	-7
11	80	-66	5	12	-21	13	75	-69	12	36	34	8	69	75
12	100	-93	6	38	-43	3 3 2	143	-138	5 5 3	18	20	9	28	-28
13	53	67	7	17	-3	4	77	-71	6	76	71	10	25	-14
3 3 0	87	-103	8	32	25	5	23	-15	7	31	-37	11	73	69
4	95	95	9	30	22	6	0*	9	8	25	-34	7 7 5	54	-59
5	52	-37	10	17	-28	7	19	-21	9	34	-31	8	13*	-23
6	31	-43	11	18	-7	8	115	-130	10	26	22	9	35	-15
7	19	16	12	18	18	9	30	30	11	16*	11	10	5*	-8
8	27	-49	13	26	6	10	20	13	12	20	10	8 8 5	45	-44
9	90	-97	3 3 1	77	86	11	48	-47	6 6 3	67	67	9	21	7
10	28	13	4	13	29	12	0*	-6	7	16	9	10	36	39
11	56	50	5	11*	20	13	15*	-15	8	54	-49	9 9 5	62	-61
12	17*	4	6	48	54	4 4 2	202	-191	9	28	14	6 6 6	123	-124
13	30	-40	7	60	64	5	86	82	10	23	30	7	29	33
4 4 0	444	445	8	36	39	6	181	192	11	3*	9	8	99	103
5	18	-6	9	13*	18	7	47	-43	12	20	6	9	56	-58
6	213	-208	10	62	56	8	145	-141	7 7 3	66	70	10	85	-83
7	78	82	11	0*	11	9	154	151	8	19	10	7 7 6	40	-27
8	111	121	12	27	31	10	101	100	9	20	12	8	41	-31
9	162	-169	13	25	9	11	96	-103	10	24	18	9	25	27
10	146	-136	4 4 1	17	-6	12	63	-55	11	18	8	10	5*	12
11	86	92	5	11*	-26	13	81	85	8 8 3	86	-87	8 8 6	98	-91
12	55	51	6	62	-58	5 5 2	16	18	9	47	-41	9	52	50
13	45	-49	7	20	-20	6	41	-43	10	14*	-7	7 7 7	18*	39
5 5 0	187	180	8	0*	10	7	25	11	9 9 3	10*	1	8	53	45
6	183	174	9	17	-25	8	62	50	10	16*	17	9	24	8
7	95	-76	10	20	-27	9	39	-32	4 4 4	223	200	8 8 7	11*	14
8	41	-45	11	50	-57	10	47	-44	5	178	-177			
9	43	-46	12	13*	-27	11	47	44	7	130	138			
10	57	50	13	33	25	6 6 2	201	-207	8	218	225			
11	48	37	6 5 1	8*	8	7	68	72	9	24	12			

non-framework positions I to VI. Oxygen scattering factors were assigned to these positions. Anisotropic temperature factors for the framework atoms and the cations were introduced in the last cycles. The occupancy factors of the two Ca positions converged to the theoretical value of 3/8 per position, indicating that all six Ca ions could be found in full agreement with the chemical analysis. Least-squares refinement proceeded to a final weighted R value of $R_W = 0.13$. The final parameters are listed in Table 5, followed by the interatomic distances in Table 6. The observed and calculated structure factors of the a reflections, together with the observed values of the b reflections are listed in Table 7.

Table 5. *Final atomic parameters of hydrated* Ca-*A zeolite based on space group* $Pm\bar{3}m$

(Standard deviations in parentheses)

Atomic coordinates

Atom	Position	Occupancy factor*	x	y	z
T	24*k*	1	0	0.1821(4)	0.3714(4)
O(1)	12*h*	1	0	0.2249(13)	½
O(2)	12*i*	1	0	0.2889(8)	0.2889(8)
O(3)	24*m*	1	0.1147(7)	0.1147(7)	0.3400(10)
Ca(1)	8*g*	0.375(25)	0.256(1)	0.256(1)	0.256(1)
Ca(2)	8*g*	0.375(25)	0.198(1)	0.198(1)	0.198(1)
I	1*a*	0.38	0	0	0
II	24*m*	0.44	0.211(2)	0.394(1)	0.394(1)
III	8*g*	0.30	0.430(3)	0.430(3)	0.430(3)
IV	3*c*	0.35	½	0	½
V	8*g*	0.53	0.311(2)	0.311(2)	0.311(2)
VI	8*g*	0.35	0.098(3)	0.098(3)	0.098(3)

* The occupancy factors for sites I—VI are based on atomic oxygen (estimated standard deviations around 10%).

Random mean-square displacements (Å²)

Atom	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
T	0.019(3)	0.017(2)	0.013(2)	0	0	0.003(2)
O(1)	0.021(8)	0.029(10)	0.018(9)	0	0	0
O(2)	0.041(10)	0.006(5)	0.006(5)	0	0	0.006(6)
O(3)	0.046(5)	0.046(5)	0.050(8)	0.031(7)	0.011(6)	0.011(6)
Ca(1)	0.044(5)	0.044(5)	0.044(5)	0.003(7)	0.003(7)	0.003(7)
Ca(2)	0.046(5)	0.046(5)	0.046(5)	0.024(8)	0.024(8)	0.024(8)
I	0.02(4)					
II	0.07(1)					
III	0.06(2)					
IV	0.07(4)					
V	0.05(1)					
VI	0.05(1)					

Table 6. *Interatomic distances and bond angles for* Ca-*A*

Aluminosilicate framework			
	T—O(1)	1.659(7) Å	
	T—O(2)	1.652(9)	
	T—O(3)	1.673(8)	
O(1)—T—O(2)	109.3(6)°	T—O(1)—T	143.2(10)°
O(1)—T—O(3)	111.9(5)	T—O(2)—T	165.4(5)
O(2)—T—O(3)	104.4(4)	T—O(3)—T	140.7(7)
O(3)—T—O(3)	114.1(4)		
Cations			
	Ca(1)—Ca(2)	1.21(1) Å	
Ca(1)—O(3)	2.65(1) Å	Ca(2)—O(3)	2.25(1) Å
Ca(1)—O(2)	3.18(1)	Ca(2)—O(2)	2.89(1)

Discussion of the desymmetrization

The results of the refinement of the *A* structure listed below must be assumed as a basis for further discussion:

1. No deviation from Laue symmetry $m3m$ is observed.
2. Only *F* centering is found.
3. All six Ca ions are localized in two positions on the threefold axis at a mutual distance of 1.22 Å, with site-occupancy factors of 3/8. A full desymmetrization in the cubic symmetry is therefore not possible.
4. Water positions I to VI and Ca—O distances point to a high degree of ordering, suggested by some extremely short distances.

Furthermore two classes of *b* reflections can be distinguished in a somewhat arbitrary way:

b_1 reflections, where h, k and l are all odd and unequal and
b_2 reflections, where h, k and l are all odd and at least two of them equal.

The b_1 reflections have structure amplitudes comparable with those found for Na-*A* (space group $Fm\bar{3}c$) by GRAMLICH and MEIER (1971). Therefore they may be due mainly to the Si/Al ordering similar to the one established by these workers. Distance-least-squares computations

(GRAMLICH and MEIER, 1971) lead to the results given in Table 8 and allowed phases for the b_1 reflections to be determined. On the other hand, the high degree of ordering of the Ca positions (see point 3 above) suggests that the b_2 reflections are mainly due to a special Ca distribution. The problem is therefore reduced to the task of finding a special Ca distribution, determining the phases of the b_2 reflections. No informa-

Table 7. *Observed and calculated structure factors for* Ca-*A based on* $a = 24.48$ Å
(structure factors corresponding to intensities $< \sigma$ are marked by an asterisk)

a reflections

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	837	1019	20	12	0	350	324	12	12	2	292	-252	18	14	4	241	289	16	10	8	62	90
4			564	-540	22			462	468	14			232	-231	20			81	43	18			29	- 55
6			833	828	24			169	-202	16			287	308	22			79	-109	20			156	-134
8			136	110	26			79	153	18			13*	- 32	24			51	- 2	22			131	-147
10			1106	1131	14	14	0	51	- 36	20			121	-109	16	16	4	596	-664	24			160	-196
12			1078	1082	16			54	-61	22			65	66	18			43	93	26			144	-132
14			280	151	18			355	-386	24			201	-250	20			102	69	12	12	8	149	-133
16			944	938	20			251	-228	26			72	39	22			152	-172	14			398	-379
18			165	285	22			0*	32	14	14	2	78	67	24			102	134	16			84	- 51
20			851	972	24			244	-240	16			176	184	18	18	4	191	279	18			58	- 53
22			1013	1022	16	16	0	13*	75	18			11*	- 39	20			32*	18	20			118	- 95
24			99	61	18			135	-113	20			170	-145	22			98	- 99	22			175	-175
26			107	69	20			8*	16	22			118	- 75	20	20	4	143	-151	24			203	-243
28			81	196	22			212	191	24			99	-119	6	6	6	484	-531	14	14	8	255	308
2	2	0	548	-571	24			185	133	16	16	2	121	29	8			466	447	16			309	296
4			405	-457	18	18	0	74	- 79	18			208	188	10			101	-172	18			176	116
6			211	158	20			33	- 55	20			102	94	12			222	236	20			22*	14
8			863	-769	22			121	-158	22			38	78	14			195	162	22			193	-171
10			346	-337	20	20	0	272	338	24			251	282	16			1269	-1310	24			60	- 87
12			192	231	2	2	2	754	-1045	18	18	2	159	194	18			307	-324	16	16	8	108	95
14			580	-578	4			208	210	20			44	- 85	20			60	78	18			146	109
16			187	173	6			838	776	22			174	-169	22			92	- 30	20			113	146
18			259	-301	8			559	-390	20	20	2	136	- 93	24			168	160	22			20*	- 10
20			64	- 48	10			224	-208	4	4	4	540	-609	26			377	-365	18	18	8	187	141
22			212	239	12			16*	-161	6			660	-491	8	8	6	542	528	20			35*	35
24			242	-232	14			387	-362	8			602	659	10			205	-146	10	10	10	747	822
26			73	- 84	16			192	149	10			423	305	12			221	162	12			672	621
28			18*	20	18			156	- 30	12			332	-322	14			436	444	14			396	-383
4	4	0	199	-129	20			344	-333	14			78	16	16			80	- 62	16			211	267
6			722	-626	22			147	-145	16			308	-246	18			113	94	18			58	53
8			538	-551	24			202	-169	18			464	449	20			119	131	20			262	294
10			88	- 18	26			24*	64	20			166	-175	22			74	-42	22			472	481
12			70	44	28			122	114	22			219	-234	24			237	241	24			48	71
14			392	-426	4	4	2	630	621	24			273	260	26			83	51	12	12	10	493	428
16			366	-397	6			715	704	26			124	- 80	10	10	6	181	157	14			206	-245
18			188	-242	8			210	165	28			203	-176	12			310	276	16			250	262
20			117	-116	10			289	253	6	6	4	1131	-1027	14			41	- 43	18			90	- 78
22			19*	- 18	12			80	53	8			117	113	16			214	-250	20			0*	27
24			143	-124	14			190	179	10			64	- 17	18			274	-251	22			392	416
26			61	- 74	16			215	292	12			136	-106	20			57	- 96	24			0*	38
28			74	- 97	18			353	309	14			153	75	22			149	164	14	14	10	125	-103
6	6	0	382	-342	20			84	- 57	16			681	-681	24			130	169	16			46	17
8			153	111	22			95	- 85	18			175	130	26			81	-101	18			180	-199
10			398	-323	24			153	176	20			95	55	12	12	6	341	268	20			170	-193
12			80	146	26			154	188	22			113	-115	14			191	195	22			0*	- 14
14			207	245	28			101	66	24			149	124	16			208	-190	16	16	10	155	- 84
16			290	-322	6	6	2	178	120	26			232	-247	18			19*	- 39	18			89	- 65
18			405	-415	8			56	4	28			235	-211	20			86	70	20			157	115
20			223	210	10			236	- 98	8	8	4	70	32	22			144	136	22			166	128
22			226	218	12			39	43	10			173	-101	24			69	99	18	18	10	196	-211
24			14*	- 26	14			644	688	12			58	- 37	14	14	6	593	644	20			108	-136
26			79	-113	16			227	235	14			205	217	16			97	- 64	12	12	12	75	54
28			169	-150	18			218	197	16			114	129	18			237	254	14			221	-221
8	8	0	1120	1043	20			285	259	18			326	370	20			251	285	16			318	222
10			263	182	22			137	135	20			153	131	22			54	72	18			145	-108
12			223	-247	24			172	149	22			223	-276	24			75	59	20			175	-164
14			218	-208	26			84	47	24			27	62	16	16	6	798	-814	22			221	193
16			69	95	28			58	46	26			212	155	18			253	-244	14	14	12	130	- 94
18			626	-613	8	8	2	112	194	10	10	4	217	169	20			9*	- 8	16			76	69
20			99	- 89	10			366	-442	12			110	115	22			154	-163	18			41	- 47
22			34	21	12			482	-479	14			27	- 5	18	18	6	17*	8	20			129	-130
24			226	-190	14			13*	- 62	16			182	105	20			93	74	22			85	- 78
26			25*	47	16			366	297	18			35	80	22			102	-126	16	16	12	85	- 16
28			0*	102	18			47	- 4	20			124	-119	20	20	6	189	167	18			96	128
10	10	0	1523	1640	20			75	-115	22			31	56	8	8	8	540	566	20			190	148
12			685	613	22			250	-313	24			69	141	10			583	-660	18	18	12	45	17
14			425	-358	24			241	-245	26			48	- 8	12			259	-258	14	14	14	185	274
16			140	162	26			112	98	12	12	4	409	-403	14			217	180	16			144	102
18			411	-456	10	10	2	139	109	14			183	-166	16			755	713	18			221	232
20			412	377	12			107	50	16			101	168	18			480	511	20			35*	85
22			654	595	14			304	-277	18			61	46	20			76	14	16	16	14	134	-192
24			17*	- 68	16			260	230	20			198	-209	22			304	-264	18			114	85
26			128	119	18			213	-249	22			14*	- 12	24			33*	6	18	18	14	161	115
12	12	0	745	745	20			119	-100	24			32*	9	26			56*	88	16	16	16	686	-647
14			27	- 91	22			107	107	26			0*	18	10	10	8	415	-461	18			195	-148
16			187	232	24			151	-179	14	14	4	204	168	12			158	-149					
18			51	-125	26			59	- 17	16			75	-122	14			300	-491					

Table 7. *(Continued)*

b reflections F_o ($F_o = 0$)

h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o	h	k	l	F_o
3	1	1	18	9	5	1	31	11	11	1	153	9	5	3	23	13	11	3	64	15	7	5	69	9	7	7	85	13	9	9	39
5			13*	11			46	13			46	11			51	15			38	17			81	11			80	15			47
7			50	13			53	15			31	13			37	17			106	19			34	13			74	17			53
9			32	15			95	17			42	15			79	19			61	21			45	15			27*	11	11	9	58
11			31	17			75	19			26	17			91	13	13	3	47	9	9	5	65	17			29*	13			54
13			51	19			55	13	13	1	53	19			67	15			34	11			53	19			69	15			89
15			38	21			32	15			39	21			45	17			48	13			56	9	9	7	36	17			57
17			36	23			36	17			21*	7	7	3	34	19			45	15			91	11			46	13	13	9	62
19			64	7	7	1	97	19			87	9			116	15	15	3	25*	17			46	13			17*	15			69
21			43	9			110	15	15	1	25*	11			66	17			42	19			73	15			29	17			57
3	3	1	27	11			102	17			76	13			91	5	5	5	128	21			83	17			30	11	11	11	60
5			153	13			112	3	3	3	93	15			42	7			32	11	11	5	55	19			20*	13			49
7			74	15			30	5			48	17			21*	9			76	13			51	11	11	7	87	15			13*
9			72	17			44	7			66	19			75	11			37	15			60	13			44	13	13	11	32
11			34	19			66	9			51	21			54	13			23*	17			25	15			20*	15			35
13			79	21			78	11			52	9	9	3	65	15			97	19			50	17			45	13	13	13	51
15			103	9	9	1	27	13			71	11			76	17			104	13	13	5	75	19			76	15	15	15	84
17			93	11			28	15			100	13			105	19			72	15			100	13	13	7	42	17	17	17	25*
19			85	13			22	17			102	15			45	21			66	17			35	15			29	19	19	19	50
21			33	15			51	19			38	17			44	7	7	5	75	19			48	17			26*				
23			48	17			35	21			56	19			66	9			58	15	15	5	52	15	15	7	48				
5	5	1	25	19			31	5	5	3	26	21			26*	11			36	17			78	9	9	9	52				
7			71	21			56	7			66	11	11	3	36	13			88	7	7	7	128	11			45				

tion could be deduced from $F(b)$ Fourier maps. Crystal-chemical reasons demand a Ca distribution as evenly distributed as possible, omitting any "Ca-clusters". The influence of both the Ca distribution and also the zeolitic water on the framework has been neglected.

A first model with maximum desymmetrization (a tetragonal arrangement of the Ca ions in the α and β cage) was found in symmetry $F\bar{4}3m$ (see Fig. 2). The highest ranking subgroup of framework symmetry $Fm\bar{3}c$ and the proposed symmetry of the Ca-ion arrangement $F\bar{4}3m$ is $F23$. However, a refinement in space group $F23$ is not feasible since the data possess Laue symmetry $m3m$.

Limiting ourselves to cubic symmetry a second model in symmetry $F432$ was proposed, as indicated in Fig. 3. The corresponding parameters are listed in Table 8, column 3. Refinement using b reflections only produced a weighted R value of $R_w(b) = 0.25$, the scale factor remaining within 10% of its value determined by the A refinement. The framework tetrahedra were markedly distorted. Starting with these parameters, we tried a full refinement with a and b reflections. The symmetry of positions I to IV located previously was that of the A structure ($Pm\bar{3}m$). Correlation effects were overcome by a separate variation of correlated parameters. This refinement terminated after 6 cycles corresponding to $R_w(a+b) = 0.12$. The parameters together with the magnitude of the difference vectors relating the A and H structure are listed in columns 5 and 6 of Table 8, respectively. These vectors are of the same magnitude as the root-mean-square displacements corresponding to the thermal parameters in Table 5. This fact agrees with the shifts found in Na-A, which are influenced by the Si/Al distribution only.

Table 8. *Comparison of different sets of parameters for* Ca-*A* (based on $a = 24.48$ Å)

		A structure		Partially desymmetrized structure		
		Refinement using a reflections	Averaged parameters of refinement in space group $F432$	Model in $F432$*	Refinement in space group $F432$	Magnitudes of difference vectors
Si	x	0	0	0	0.0024(6)	0.07 Å
(T)	y	0.0910	0.0910	0.0923	0.0925(4)	
	z	0.1857	0.1858	0.1840	0.1851(6)	
Al	x			0	−0.0024(6)	0.07
	y			0.1871	0.1865(6)	
	z			0.0888	0.0895(5)	
O(1)	x	0	0	0	0.001(1)	0.10
	y	0.1124	0.1122	0.1122	0.112(1)	
	z	¼	¼	0.2458	0.246(1)	
O(2)	x	0	0	0	0.007(1)	0.18
	y	0.1444	0.1444	0.1449	0.143(1)	
	z	0.1444	0.1444	0.1460	0.145(1)	
O(31)	x	0.0574	0.0573	0.0533	0.056(1)	0.13
[O(3)]	y	0.0574	0.0573	0.0585	0.059(1)	
	z	0.1670	0.1701	0.1679	0.171(1)	
O(32)	x			0.0533	0.054(1)	0.10
	y			0.1679	0.168(1)	
	z			0.0585	0.059(1)	
Ca(11)	x	0.0994	0.1001	0.0994	0.106(2)	0.32
[Ca(1)]	y	0.0994	0.1001	0.0994	0.106(2)	
	z	0.0994	0.1001	0.0994	0.106(2)	
	occ.**	0.375		0.5	0.5	
Ca:12)	x			0.0994	0.093(3)	0.26
	y			0.0994	0.093(3)	
	z			0.4006	0.406(3)	
	occ.			0.25	0.25	
Ca(21)	x	0.1281	0.1296	0.1281	0.132(4)	0.19
[Ca(2)	y	0.1281	0.1296	0.1281	0.132(4)	
	z	0.1281	0.1296	0.1281	0.132(4)	
	occ.	0.375		0.25	0.25	
Ca(22)	x			0.1281	0.126(2)	0.06
	y			0.1281	0.126(2)	
	z			0.3719	0.373(2)	
	occ.			0.5	0.5	

* Framework model generated with the aid of distance-least-squares computations (DLSR), Ca distribution according to Fig. 3. ** Occupancy factor.

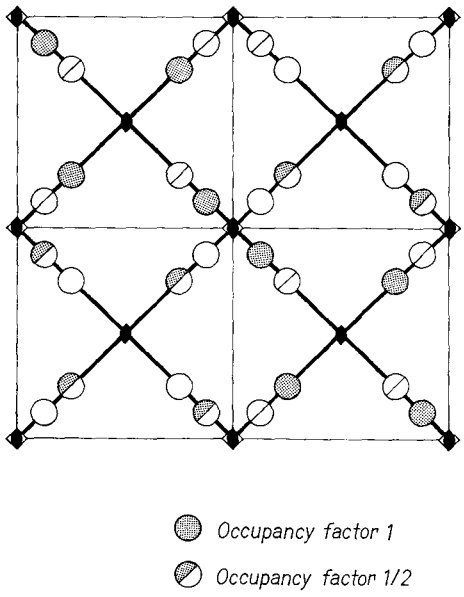

Fig. 2. Projection of a Ca model in space group $F\bar{4}3m$

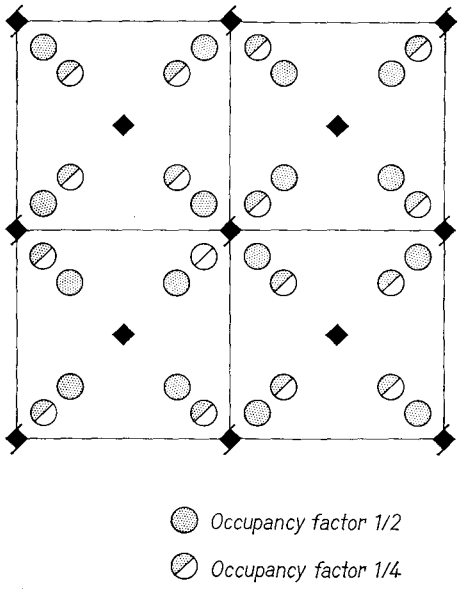

Fig. 3. Projection of a Ca model in space group $F432$

The main reason for this unsatisfactory refinement must be the omission of the influence of the Ca distribution on the framework displacements. We have no information about even the symmetry of these effects. If for example, the Ca distribution is really acentric, we would expect an analogous behaviour of the framework too. Furthermore the necessity of an actual desymmetrization at least to tetragonal symmetry makes the existence of domains or even a statistical behaviour of the framework displacements highly probable.

Table 9. *Final atomic parameters of hydrated* Ag-*A zeolite based on space group* $Pm\bar{3}m$

(Standard deviations in parentheses)

Atomic coordinates

Atom	Position	Occupancy factors*	x	y	z
T	$24k$	1	0	0.182(2)	0.366(1)
O(1)	$12h$	1	0	0.226(9)	$\frac{1}{2}$
O(2)	$12i$	1	0	0.293(5)	0.293(5)
O(3)	$24m$	1	0.109(3)	0.109(3)	0.338(5)
Ag(1)	$8g$	0.61(2)	0.229(1)	0.229(1)	0.229(1)
Ag(2)	$8g$	0.32(3)	0.151(3)	0.151(3)	0.151(3)
I	$24l$	0.5	$\frac{1}{2}$	0.39(1)	0.05(1)
II	$6e$	0.6	0	0.17(2)	0

* The occupancy factors for site I and II are based on atomic oxygen (estimated standard deviations around 25%).

Random mean-square displacements (Å^2)

Atom	$U_{11}(U)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
T	0.012(6)					
O(1)	0.06(2)					
O(2)	0.05(2)					
O(3)	0.04(2)					
Ag(1)	0.04(1)	0.04(1)	0.04(1)	0.03(1)	0.03(1)	0.03(1)
Ag(2)	0.06(2)	0.06(2)	0.06(2)	0.05(2)	0.05(2)	0.05(2)
I	0.07(9)					
II	0.03(2)					

Table 10. *Interatomic distances and bond angles for* Ag-*A*

Aluminosilicate framework			
	T—O(1)	1.72(4) Å	
	T—O(2)	1.63(6)	
	T—O(3)	1.65(4)	
O(1)—T—O(2)	105(4)°	T—O(1)—T	145(2)°
O(1)—T—O(3)	111(2)	T—O(2)—T	163(1)
O(2)—T—O(3)	109(1)	T—O(3)—T	144(1)
O(3)—T—O(3)	108(2)		
Cations			
	Ag(1)—Ag(2)	1.66(2) Å	
Ag(1)—O(3)	2.48(4) Å	Ag(2)—O(3)	2.41(6) Å
Ag(1)—O(2)	3.03(2)	Ag(2)—O(2)	3.09(3)

Table 11. *Observed and calculated intensities* ($\times 10^{-2}$) *for* Ag-*A* (corrected for Lorentz and polarization factors)

h k l	I_o	I_c	h k l	I_o	I_c	h k l	I_o	I_c	h k l	I_o	I_c	h k l	I_o	I_c	h k l	I_o	I_c
1 0 0	50	383	4 3 1	50	84	6 3 1	0	4	6 5 2			6 6 3			8 4 4	311	397
1 1 0	18	62	5 1 0			4 4 4	53	30	7 4 0	552	516	7 4 4	135	103	6 6 5	156	220
1 1 1	4	8	3 3 3	628	368	6 3 2	64	46	8 1 0			8 4 1			9 4 0		
2 0 0	65	116	5 1 1			7 0 0			5 5 4			9 0 0			8 5 3		
2 1 0	127	367	4 3 2	146	188	5 4 3	662	662	7 4 1	108	95	8 3 3	613	603	9 4 1	42	93
2 1 1	2	1	5 2 0			5 5 0			8 1 1			9 1 0			7 7 0		
2 2 0	182	176	5 2 1	19	29	7 1 0			7 3 3	0	28	7 5 3	0	37	7 5 5		
2 2 1	98	150	4 4 0	680	567	5 5 1	44	34	6 4 4	382	331	9 1 1	0	24	9 3 3	216	285
3 0 0			5 2 2	442	369	7 1 1			8 2 0			8 4 2			7 7 1		
3 1 0	24	41	4 4 1			6 4 0	398	373	7 4 2	574	570	7 6 0	304	384	8 6 0	44	16
3 1 1	120	195	4 3 3	96	76	6 4 1	417	420	8 2 1			9 2 0			10 0 0		
2 2 2	93	262	5 3 0			7 2 0			6 5 3	108	146	6 5 5			7 6 4		
3 2 0	0	23	5 3 1	130	62	5 5 2			8 2 2	405	378	7 6 1	123	184	9 4 2	105	142
3 2 1	352	315	4 4 2	335	337	6 3 3	133	158	6 6 0			9 2 1			8 6 1		
4 0 0	22	54	6 0 0			7 2 1			6 6 1	100	63	6 6 4	0	8	10 1 0		
3 2 2	744	712	6 1 0	66	141	6 4 2	94	127	8 3 0			7 6 2			7 7 2	158	151
4 1 0			5 3 2	0	22	5 4 4	124	123	7 4 3	773	794	8 4 3	363	349	10 1 1		
4 1 1	52	106	6 1 1			7 2 2			7 5 0			9 2 2			8 6 2	87	97
3 3 0			6 2 0	55	99	7 3 0	0	1	8 3 1			8 5 0			10 2 0		
3 3 1	14	37	4 4 3	354	312	5 5 3	104	86	5 5 5	255	254	7 5 4	539	523	8 5 4	80	42
4 2 0	623	664	6 2 1			7 3 1			7 5 1			8 5 1			10 2 1		
4 2 1	16	24	5 4 0			6 4 3	411	425	6 6 2	234	267	9 3 0			9 4 3	0	26
3 3 2	794	805	5 4 1	5	38	6 5 0			6 5 4	494	454	9 3 1	34	60	9 5 0		
4 2 2	558	550	5 3 3	0	0	6 5 1	0	3	8 3 2			8 5 2	0	0	7 7 3	33	34
4 3 0	156	236	6 2 2	375	350	7 3 2			7 5 2	36	63	7 6 3	0	39	9 5 1		
5 0 0			5 4 2	175	196	8 0 0	173	164	8 4 0	0	12	9 3 2					
			6 3 0														

Structure analysis of Ag-*A*

A Patterson synthesis revealed strong maxima in $(u,u,0)$Q and $(u,0,0)$Q with $u_1 = 0.5$ and $u_2 = 0.28$. This situation leads directly to the two Ag positions on the threefold axis in (x,x,x) with $x_1 = 0.25$ and $x_2 = 0.14$. Starting with framework coordinates of Na-*A* (GRAMLICH and MEIER, 1971) and the two Ag positions, the least-squares refinement was commenced with the aid of the ORFLS programme (BUSING *et al.*, 1967) which was adapted to powder data. This refine-

ment proceeded to an intensity R value[1] $R_I = 0.18$. The corresponding atomic parameters are listed in Table 9, followed by the interatomic distances in Table 10. The observed and the calculated intensities are listed in Table 11.

Discussion

The framework coordinates of Tl-A, Ca-A and Ag-A agree within a limit of 2σ with the values found for Na-A (GRAMLICH and MEIER, 1971). The two principal cation positions are on the threefold axis at

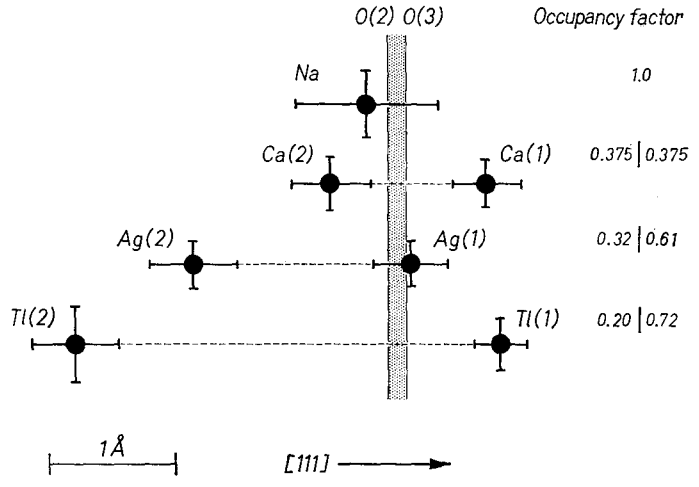

Fig. 4. Positions of the cations relative to the six-membere doxygen ring (together with mean amplitudes of vibrations and occupancy factors)

opposite sides of the six-membered ring. Their positions relative to the six-membered oxygen ring are illustrated in Fig. 4. The main distances to the framework oxygen atoms are listed in Table 12. The cations are coordinated with framework oxygen atoms O(3) as the distances agree well with expected values. As a consequence of that coordination, the short mutual distance forbid a simultaneous occupancy. The occupancy of these sites by water molecules can be ruled out because of the short distance to O(3) (less than 2.9 Å).

[1] $R_I = \Sigma |I_{obs} - I_{calc}| / \Sigma I_{obs}$, $I_{calc} = \sum_n m F^2_{calc}$
(m = multiplicity factor, n = number of overlapping reflections)

Table 12. *Cation-oxygen distances in zeolite of type A*

Form	Na-*A*[1]	Ca-*A*	Ag-*A*	Tl-*A*
M(1)—O(3)	2.36	2.66	2.48	2.75
M(2)—O(3)	—	2.26	2.42	2.88
Mean value	2.36	2.46	2.45	2.82
Expected value	2.35 [6][2]	2.45 [6][3]	2.50 [4][2]	2.80 [6][2]
M(1)—O(2)	2.97	3.19	3.03	3.25
M(2)—O(2)	—	2.89	3.10	3.44
Mean value	2.97	3.04	3.06	3.34
M(1)—M(2)	—	1.22	1.67	3.24

[1] According to GRAMLICH and MEIER (1971).
[2] Coordination number [in brackets] according to PAULING.
[3] Mean value in laumontite (SCHRAMM and FISCHER, 1971).

The results obtained for Tl-*A* are in full agreement with those found by RILEY and SEFF (1972). In addition our results lead to some conclusions concerning the zeolitic water. A model is proposed which explains the Tl-H_2O arrangements in the two cages and agrees well with the results of the structure refinement. Tl(1) in the α cage (symmetry $m3m$) is sixfold coordinated by three framework oxygen atoms O(3) and three H_2O molecules (site I) at distances of about 2.8—3.2 Å. The 12 H_2O (site I) and 8 Tl(1) appear to form a pentagon-dodecahedral complex (see Fig. 5), similar to that formed by 12 + 8 H_2O molecules in Na-*A* (GRAMLICH and MEIER, 1971). Two such pentagon-dodecahedra (symmetry $m3$) are superimposed corresponding to the order 2 of the factor group, in agreement with the site-occupancy factor found. In the small β cage (symmetry $m3m$) Tl(2) is also sixfold coordinated by three framework oxygen atoms O(3) and three H_2O molecules (site II) at distances of 2.9 Å. The three H_2O molecules (site II) and two Tl(2) appear to form a bipyramid as shown in Fig. 6. Eight such bipyramids (symmetry $\bar{6}$) are superimposed corresponding to the order 8 of the factor group, in agreement with the site-occupancy factors.

In Ca-*A* all six Ca ions could be localized on the threefold axis in full agreement with the chemical analysis, as well as 80% of the water. Position I is rather an artifact because of its relatively high point symmetry and also because of its unrealistically small separation of

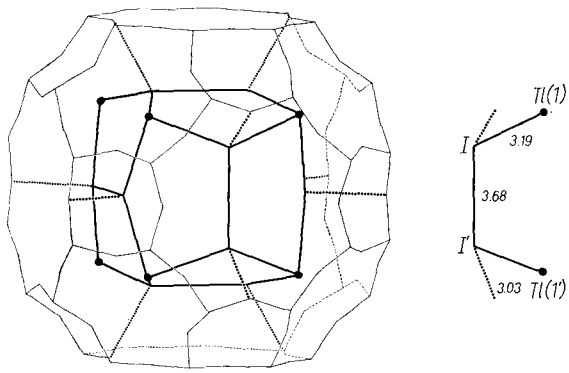

Fig. 5. Proposed Tl-H_2O complex in the α cage. The shortest approach distances (Å) of the complex and oxygen atoms of the framework are indicated by dotted lines

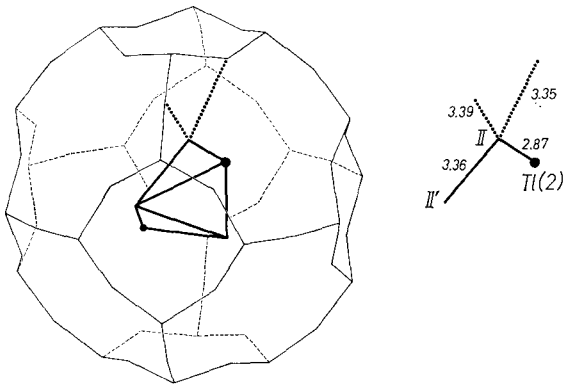

Fig. 6. Proposed Tl-H_2O complex in the β cage. The shortest approach distances (Å) of the complex and oxygen atoms of the framework are indicated by dotted lines

2 Å from position II. Any further interpretation of the water positions seems highly speculative since no actual desymmetrization was performed.

Positions I and II in Ag-*A* show extremely high standard deviations for site-occupancy factors as well as for coordinates. They have been revealed in a Fourier map and have formally been refined. Any crystal-chemical interpretation seems unjustified.

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References

R. M. BARRER and W. M. MEIER (1958), Structural and ion sieve properties of a synthetic crystalline exchanger. Transact. Far. Soc. **54**, 1074—1085.

H. BORER (1969), Doctoral Thesis, E.T.H. Zürich.

D. W. BRECK, W. G. EVERSOLE, R. M. MILTON, T. B. REED and T. L. THOMAS (1956), Crystalline zeolites I. The properties of a new synthetic zeolite, type *A*. J. Amer. Chem. Soc. **78**, 5963—5971.

W. R. BUSING, K. O. MARTIN and H. A. LEVY (1967), ORFLS—A Fortran crystallographic least squares program. Oak Ridge National Lab. Oak Ridge, Tennessee.

J. F. CHARNELL (1971), Gel growth of large crystals of sodium *A* and sodium *X* zeolites. J. Crystal Growth **8**, 291—294.

K. F. FISCHER und W. M. MEIER (1965), Kristallchemie der Zeolithe. Eine Zusammenfassung neuerer Ergebnisse. Fortschr. Miner. **42**, 50—86.

V. GRAMLICH and W. M. MEIER (1971), The crystal structure of hydrated NaA: A detailed refinement of a pseudosymmetric zeolite structure. Z. Kristallogr. **133**, 134—149.

T. B. REED and D. W. BRECK (1956), Crystalline zeolites II. Crystal structure of synthetic zeolite type *A*. J. Amer. Chem. Soc. **78**, 5972—5977.

E. RILEY and K. SEFF (1972), The crystal structures of hydrated and dehydrated thallium-exchanged zeolite *A*. J. Physic. Chem. **76**, 2593—2597.

V. SCHRAMM and K. F. FISCHER (1971), Refinement of the crystal structure of laumontite. Adv. Chem. Ser. **101**, 259—265.

W. THÖNI (1972), Cufit—a Fortran computer program for the parametrization of a measured profile by the method of least squares. Inst. Kristallogr. und Petrogr. E.T.H. Zürich.