[Contribution from the Research Laboratory of the Linde Air Products Company, A Division of Union Carbide and Carbon Corporation]

Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A

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The new synthetic zeolite, Type A, is cubic, $a_0 = 12.32$ Å., and X-ray data are consistent with space group O^1-Pm3m. The unit cell composition is $Me_{12/n}$ $[(AlO_2)_{12}(SiO_2)_{12}]\cdot NH_2O$ where Me is an exchangeable cation of charge n, and N varies from 20 to 30. The unit cell dimension varies slightly with the cation present. The aluminosilicate framework consists of 24(Si,Al)–O_4 tetrahedra which are joined to form 8-membered oxygen rings in the faces and distorted 6-membered rings on the 3-fold axes. A large cavity 11.4 Å. in diameter occupies the center of the cell and smaller 6.6 Å. cavities are located on the 3-fold axes. Probable positions of the cations in the lithium, sodium, thallium and calcium forms are indicated, and correlation of the structure with the adsorptive and ion-exchange properties of the Type A zeolite is discussed.

Introduction

A new synthetic crystalline zeolite, not known to exist in nature, has been reported recently and its properties described.[1] The novel adsorptive properties of certain zeolites after dehydration have been the subject of many investigations and are intimately related to their open crystal structure and pores of uniform dimensions.[2,3] In order to more completely understand the properties of the new zeolite, Type A, an X-ray structural analysis was undertaken and the results are reported here.

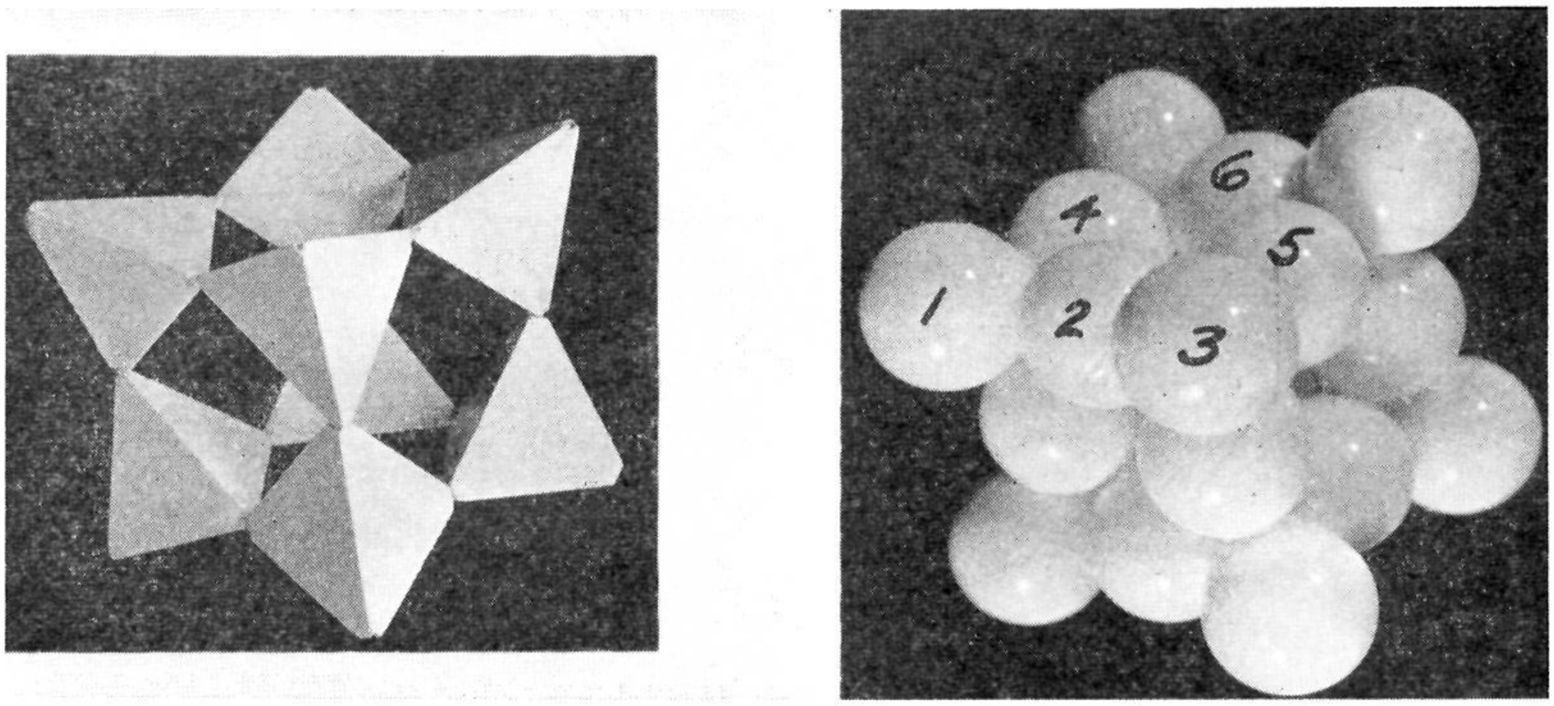

Fig. 1a, 1b.—Assembly of eight tetrahedra.

Only a few zeolite structures have been studied in detail. Analcite,[4,5] chabazite,[6,7] certain fibrous zeolites such as natrolite,[8] and the related felspathoids such as sodalite[9,10] have been the subject of structural investigations. Generally, these structures are based on the filling of space by Si-(Al)O_4 tetrahedra as discussed by Wells.[11]

Experimental

The composition of the Type A zeolite is expressed by the structural formula $Me_{12}/_n[(AlO_2)_{12}(SiO_2)_{12}]\cdot NH_2O$ where Me represents exchangeable cations of charge n. The aluminosilicate framework, $[(AlO_2)_{12}(SiO_2)_{12}]$, will be designated by [A].

The largest crystals of the Type A zeolite that have been prepared are about 25 μ in diameter, so that most of the structural work was done from X-ray powder diffraction data obtained on a geiger-counter spectrometer as previously described.[1] Peak intensities (with no correction for Lorenz and polarization effects) for the fully hydrated and dehydrated Li^+, Na^+, Ca^{++}, Ag^+ and Tl^+ exchanged A zeolite are presented in Table I. Resolution of some of the ambiguous reflections of the sodium form was possible from single crystal photographs of a hydrated 25-μ crystal taken on an oscillation camera with helium shielding. Exposures of about 48 hr. produced easily visible darkening for the stronger reflections. Visual estimates of intensities from these oscillation photographs appear in Table I.

Chemical composition, unit cell dimensions, densities and adsorption volumes for water and oxygen are shown in Table II.

Structure Determination

No systematic extinctions are observed and the data are consistent with the space group O_h^1-Pm3m. An attempt to obtain phase information by heavy ion substitution failed. Although the silicate framework is unaltered by cation exchange, apparently the cations do not occupy the same sites. From reflections obtained with the lithium form, it was felt that the alumino-silicate framework could be

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(1) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, This Journal, **78**, 5963 (1956).

(2) R. M. Barrer, *Ann. Rep. Progr. Chem., Chem. Soc. London*, **41**, 31 (1944); *Quart. Rev. (London)*, **3**, No. 4293 (1949).

(3) G. L. Kington and W. Laing, *Trans. Faraday Soc.*, **51**, 287 (1955).

(4) W. H. Taylor, *Z. Krist.*, **74**, 1 (1930).

(5) I. R. Beattie, *Acta Cryst.*, **7**, 357 (1954).

(6) J. Wyart, *Bull. Soc. Min. Fr.*, **56**, 81 (1933).

(7) I. R. Beattie, *Nature*, **172**, 999 (1953).

(8) L. Pauling, *Z. Krist.*, **74**, 213 (1930).

(9) L. Pauling, *ibid.*, **74**, 213 (1930).

(10) W. L. Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, p. 255.

(11) A. F. Wells, *Acta Cryst.*, **7**, 545 (1954).

TABLE I

POWDER DIFFRACTION DATA—A ZEOLITES

hkl	Hydrated sodium form oscillation pictures I, rel.	Intensity, arbitrary scale									
		$Li_8Na_4[A]$		$Na_{12}[A]$		$Ag_{12}[A]$		$Tl_{9.6}Na_{2.4}[A]$		$Ca_6[A]$	
		Hydrated	Dehydrated	Hydrated	Dehydrated	Hydrated	Dehydrated	Hydrated	Dehydrated	Hydrated	Dehydrated
100	VS	98	180	86	173	36	59	21	28	62	122
110	VS	63	130	59	100	10	20	4	9	22	13
111	VS	35	53	30	28	0	0	5	3	13	20
200	N.O.	4	6	...	....	10	7	19	22	4.5	2
210	S	23	67	21	55	14	43	2	2.5	6	12
211	N.O.	...	....	2	5	1	0	..	..	2.5	4
220	M	17	21	5	5	12	7	39	45	2	3
221	S	44	37	31	29	7	14	5	6	19	17
300	S										
310	N.O.	3	3	..	....	2	7	..	..	..	...
311	VS	41	47	46	39	9	13	11	15	17	14
222	W	...	....	...	....	5	2	12	14	2.5	1.5
320	S	24	13	14	4	0	10	14	9	7.5	2
321	S	31	21	40	17	10	13	1	1	21.5	21
400	N.O.	...	....	...	....	1	2	7	9	..	...
410	S	29	28	47	26	17	22	7.5	8	15.5	15
322	S										
411	M	4	5	8	5	4	3	2.5	4	5	3.5
330	W										
331	N.O.	...	....	...	....	1	3	..	..	1.5	1
420	S	3.5	3	10	5	11	2	20	27	4	2
421	W	12	14	4	4	0	2	..	..	1.5	2.5
332	S	24	20	19	18	11	23	4.5	3	12.5	12.5
422	M	5	4	4	2.5	6	2	18	25	2.5	0.5
430	N.O.	1.5	2.5	4	7	3	12	..	..	3	2
500	S										
431	N.O.	5.5	5	...	....	2	0	..	..	..	...
510	N.O.										
511	N.O.	4.5	5	3	3	2	7	..	..	1	3
333	N.O.										
520	N.O.	...	.....	1	2.6	1	3	3	3	1	...
432	N.O.										
521	W	...	5	2.6	2.5	0	0	..	..	..	...
440	M	...	....	6	3	5	0	8	8	4	3
441	N.O.	1	3.5	8.6	2.5	5	8	..	..	2	2.5
522	M										
530	W	2.5	3.5	2.6	3	2	7	..	..	3.5	1.5
433	W										
531	W	...	....	3.5	3	1	5	..	..	2	1.0
600	VS	13	15	8	5	2	3	5	6	2.5	4.0
442	N.O.										
620	N.O.	...	....					3.5	6		
622								5	7.5		
444								1.5	3		
640								2	4		

TABLE II

CHEMICAL COMPOSITION AND PHYSICAL DATA

Zeolite compn./unit cell	Density, g./cc.	a_0, Å.	Adsorption vol. Å.³/unit cell H_2O	O_2
$Li_8Na_4[A]\cdot 24H_2O$	1.91	12.04	735	0
$Na_{12}[A]\cdot 27H_2O$	1.99	12.32	833	610
$Ag_{12}[A]\cdot 24H_2O$	2.76[a]	12.38	733	0
$Tl_{9.6}Na_{2.4}[A]\cdot 20H_2O$	3.36[a]	12.33	584	0
$Ca_6[A]\cdot 30H_2O$	2.05	12.26	883	700

[a] X-Ray density, $[A] = [(AlO_2)_{12}(SiO_2)_{12}]$.

determined independently since the lithium ions would contribute little to the structure factors.

Aluminosilicate Framework.—Known zeolite structures are often described as frameworks of AlO_4 and SiO_4 tetrahedra linked at their corners (Fig. 1a). On this basis, the analysis of the A zeolite structure reduced to the problem of joining 24 tetrahedra to form a structure consistent with the possible space groups, and a 12.3 Å. unit cell which gives the accepted oxygen–oxygen distance, d_{O-O}, of 2.70 Å.

Since the calcium form will adsorb molecules with critical dimensions up to about 5 Å., any proposed structure should also provide an opening of about this size.

The zeolite chabazite, with enlarged 6-membered

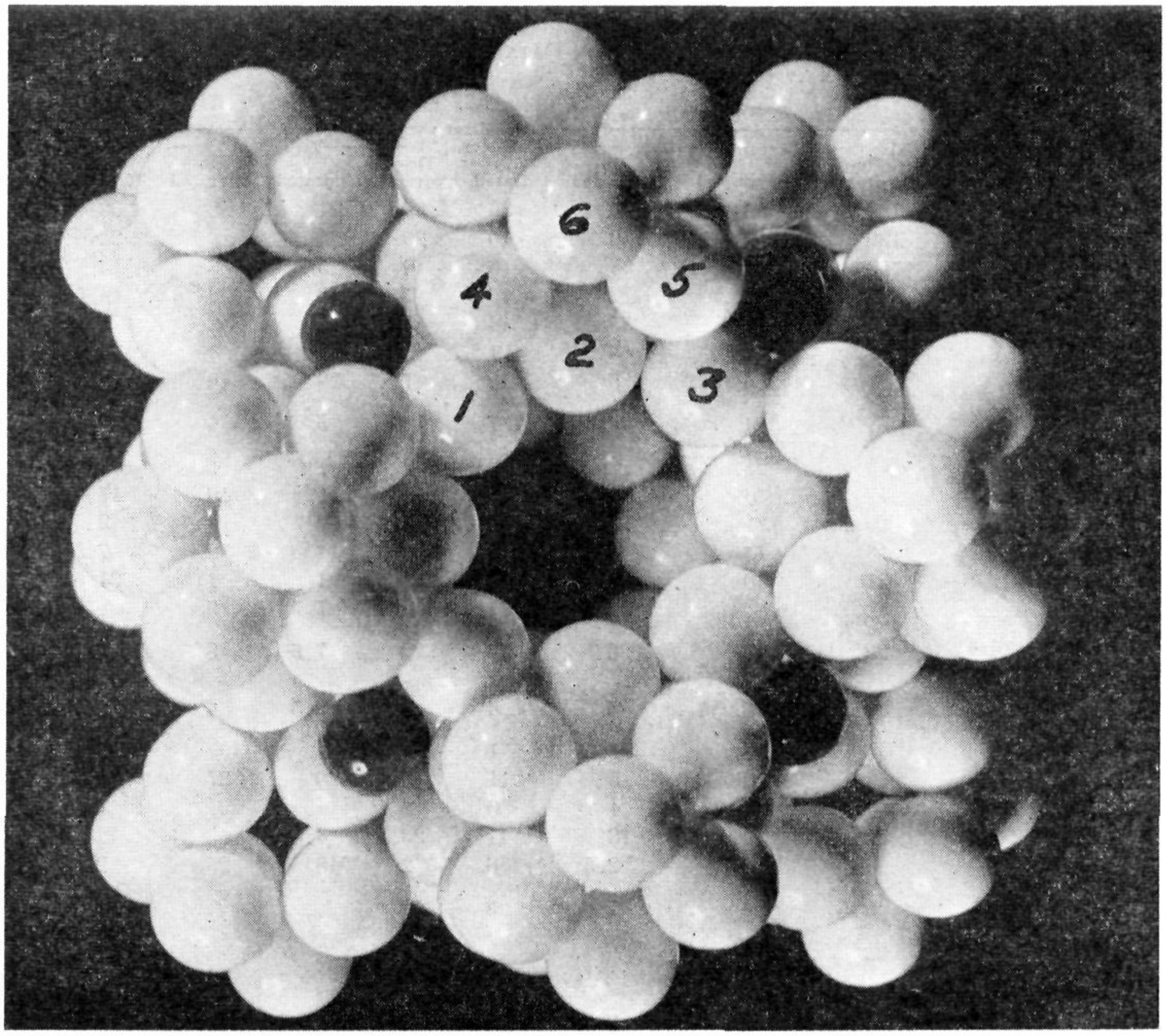

Fig. 1c.—Model of the A zeolite structure perpendicular to (100). Numbers indicate position of oxygen atoms in the structure corresponding to those in Fig. 1b.

oxygen rings of 3.1–3.3 Å. diameter will not admit hydrocarbon molecules that are readily adsorbed by calcium A, which suggests that at least an 8-membered oxygen ring is required.[1,3] Placing 8 tetrahedra in each face of a cube to form an 8-membered oxygen ring accounts for 24 tetrahedra in a unit cell of the right size, satisfies the space group, and gives a pore opening of sufficient diameter.

Figure 1c shows a model of the structure thus formed. Figures 1a and 1b show the assembly of 8 tetrahedra which is characteristic of the structure. These are located at the centers of the edges of the cell. Table III lists the positions of the atoms in the aluminosilicate framework which are fixed by the oxygen packing. The (O–O) distance is determined by this rigid structure and is given by the relation

$$d_{00} = \frac{3a_0}{2\sqrt{2}(1+\sqrt{2})} = 0.4392a_0 = 2.70\ \text{Å}.$$

TABLE III

ATOMIC POSITIONS IN THE ALUMINOSILICATE FRAMEWORK

No.	Atom	Position	
24	O_I	(0.110, .110, .345)	Adjacent to 6-fold ring
12	O_{II}	(0 , .220, .500)	Adjacent to 8-fold ring
12	O_{III}	(0.289, .289, 0)	Bridge oxygen
24	Si, Al	(0.370, .183, 0)	

And the average silicon or aluminum–oxygen distance, $d_{(\mathrm{Si,Al})-\mathrm{O}}$ is given by

$$d_{(\mathrm{Si,Al})-\mathrm{O}} = \frac{3\sqrt{3}\,a_0}{16(1+\sqrt{2})} = 0.1343a_0 = 1.66\ \text{Å}$$

Smith has correlated (Al,Si)–O distances in aluminosilicate structures with the Al/Si ratio. For Al/Si = 1, the average (Al,Si–O) distance was found to be 1.69 Å.[12]

To test the validity of this structure, structure factors were computed for the model described using the Hartree scattering factors for light atoms and ions. These were compared (Table IV) with unambiguous observed reflections of the lithium form. A reliability factor, $R = \Sigma/F_o - F_c/\Sigma F_o$ of 0.246 was obtained for 10 (*hk*0) reflections and 0.267 for 17 (*hkl*) reflections. All observed and calculated structure factors and structural interpretations are for the dehydrated zeolites. This agreement, with no adjustable atomic positions, and ignoring contributions of 4 residual sodium ions, suggested that this structure was basically correct. A Fourier projection using (*hk*0) data for the sodium form (Fig. 2a) shows the large, 8-membered oxygen ring and a 6-fold ring on the 3-fold axis. The corresponding positions of the atoms is shown in Fig. 2b while Fig. 3 illustrates a (110) sec-

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[12] J. V. Smith, *Acta Cryst.*, **4**, 4 (1954).

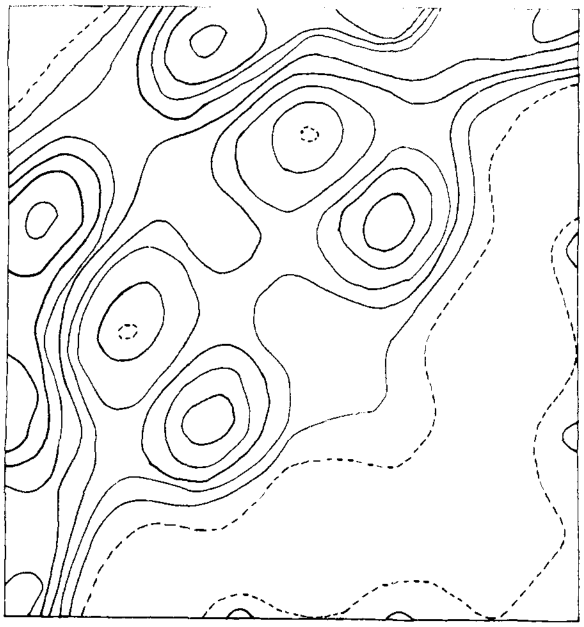

Fig. 2a.—Fourier projection on (100), $^1/_4$ of unit cell shown. Dotted line indicates electron density of one. Other contours are at intervals of two electrons per Å.^{2}

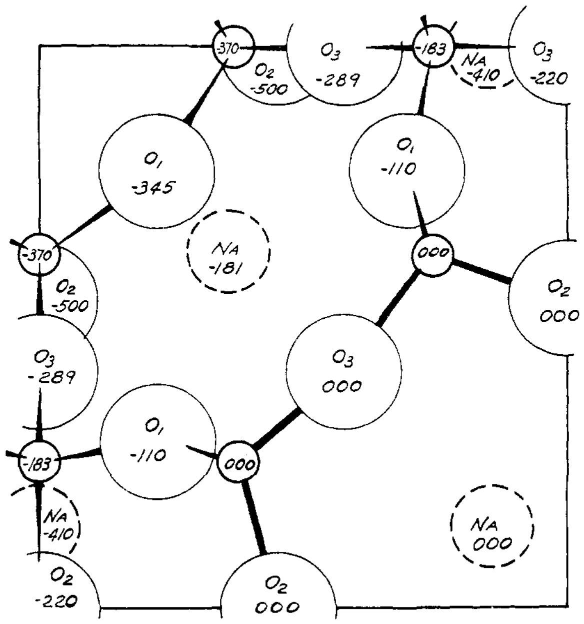

Fig. 2b.—Interpretation of Fourier projection shown in 2a

tion. The 4.2 Å., 8-membered ring gives access to a large, 11.4 Å. spherical cavity at the center of the cell of volume 775 Å.^{3}. The smaller 2.0 Å., irregular, 6-membered ring, through which the smaller 6.6 Å. cavity is entered (calculated volume 157 Å.^{3}), is similar to that found in the chabazite and sodalite structures.

Cation Positions.—Satisfaction of Pauling's electrostatic valence rule suggests that some of the ions should be adjacent to the 6-fold ring on the 3-fold axis while others should be in the 8-fold ring. Since more sites are available than there are cations to fill them, the cation distribution may be statistical. Minimization of the reliability factor was used as a criterion in placing the cations.

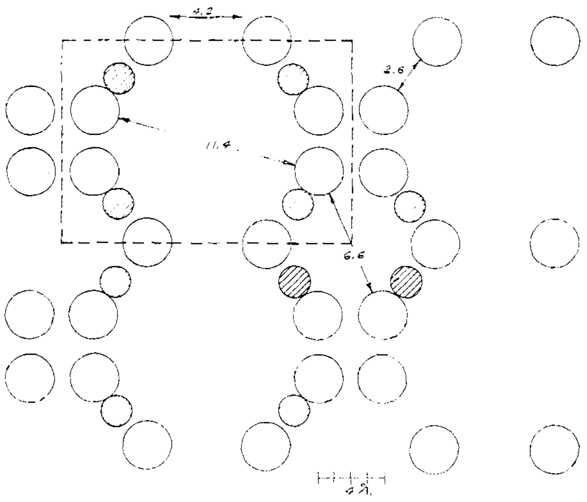

Fig. 3.—Diagram of the (110) section of the structure.

Sodium Zeolite A.—Fourier difference projections suggested the 8 positions, I, at the center of the 6-membered oxygen ring, (0.188, 0.188, 0.188) and the 12 positions, II, in the cube faces at (0.240, 0.240, 0). Reliability factors for 10 (*hK*0) reflections of 0.162, 0.134 and 0.144 were obtained by placing 4, 6 and 8 sodium ions at I, respectively. For other reasons (see Discussion) 8 sodium ions were placed at I (Table IV). The observed and calculated structure factors for this placement are shown in Table V. Because of the unusual coördination of the sodium ions, the atomic distances are distorted. These are shown, along with the ionic radii calculated on the basis of an oxygen radius of 1.35 Å., in Table VI.

Thallium Zeolite A.—A Patterson projection of (*hk*0) data for the dehydrated thallium form suggested placing 8 Tl ions on the 3-fold axis at $(^1/_4, ^1/_4, ^1/_4)$. Further refinement gave coördinates of (0.240, 0.240, 0.240), and a reliability of 0.20 for 11 observed reflections (Table V).

Lithium Zeolite A.—In the previous consideration of the structure of the aluminosilicate framework, the cations were neglected.

The results from the sodium zeolite A structure suggest that 4 sodium atoms be placed at II, and 8 lithium ions at I. This improves the reliability factor from 0.246 to 0.198 (Table IV). These positions are consistent with the adsorption data.

Aluminosilicate Superstructure.—Recent work by Loewenstein[13] shows that 2 aluminum ions cannot share the same oxygen ion and retain a coördination of 4. If this is true, then the Si/Al ratio must be equal to or greater than 1, and the Type A zeolites with a Si/Al ratio of 1 will have a regular alternation of tetrahedra. In this case possible space groups are O^1 or T_h^1 with $2a_0$ as the unit cell edge. Such considerations would make small changes in the atomic coördinates in Table IV, but the available data do not justify such refinement.

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(13) W. Loewenstein, *Am. Mineralogist*, **39**, 92 (1942).

TABLE IV

STRUCTURE FACTORS FOR LITHIUM A ZEOLITE

hkl	$F_{\text{calcd.}}$ for [A]	$F_{\text{obs.}}$ for Li_8Na_4[A]	$F_{\text{calcd.}}$ for Li_8Na_4[A]
100	156	148	146
200	24	55	50
300, (221)	118	*a*	128
400	−17	<40	−22
500, (430)	85	*a*	82
600, (442)	176	*a*	163
110	−115	126	−136
120	−62	102	−81
130	50	31	40
140, (322)	−41	*a*	−60
150, (431)	−26	*a*	−40
160	27	52	11
220	−116	103	87
230	−74	74	−52
240	−42	45	−52
250, (432)	30	<32	1
260	0	<28	−27
330, (411)	−84	*a*	−65
340, (500)	3	*a*	−9
350, (343)	−4	*a*	−37
360, (542)	18	*a*	−11
440	94	49	77
111	−149	121	
121	55	<14	
131	106	129	
141, (330)	−53	*a*	
151, (333)	−31	*a*	
161, (352)	11	*a*	
221, (300)	71	*a*	
231	38	69	
241	35	70	
251	38	52	
261, (450, 443)	12	*a*	
331	0	<25	
341, (150)	13	*a*	
351	8	<25	
361	22	<31	
441, (252)	11	*a*	
222	−5	<35	
232, (410)	−49	*a*	
242	26	58	
252, (441)	39	*a*	
262	49	<42	
332	−137	123	
342, (250)	−4	<23	
352, (161)	−48	*a*	
362, (700)	−85	*a*	
442, (600)	50	*a*	
333, (151)	−82	*a*	
343, (350)	31	*a*	
353	−35	<40	
444	46	76	

[a] Observed but ambiguous and not resolved.

TABLE V

STRUCTURE FACTORS FOR SODIUM AND THALLIUM A ZEOLITES

hkl	Tl_8Na_4[A] $F_{\text{calcd.}}$	Tl_8Na_4[A] $F_{\text{obs.}}$	Na_{12}[A] $F_{\text{calcd.}}$	Na_{12}[A] $F_{\text{obs.}}$
100	197	254	175	150
200	−585	458	−2	<22
300, (221)	8	*a*	65	78[b]
400	528	608	−21	<45
500, (430)	255	<258	144	161[b]
600, (442)	−299	*a*	216	168[b]
110	−112	143	−119	114
120	−100	86	−97	94
130	43	< 77	9	<17
140, (322)	4	*a*	−57	88[b]
150, (431)	−16	<135	−12	<32[b]
160	−3	<162	32	<51
220	465	660	−58	51
230	31	270	−12	43
240	−569	590	−51	61
250, (432)	−166	*a*	−39	29
260	465	421	−55	<38
330, (411)	−64	*a*	−12	40
340, (500)	−96	<130	−8	<32[b]
350, (343)	−34	<151	−87	62
360, (542)	103	<183	−49	<43
440	598	594	80	85
450, (443, 621)	182	*a*	16	*a*
460	−367	400		
R_{hk0} for unambiguous reflections only		0.198		0.144

[a] Observed but ambiguous and not resolved. [b] Reflections resolved by comparison with an oscillation picture. Inclusion of these gives $R = 0.211$.

TABLE VI

CATION POSITIONS AND DISTANCES

Cation	Position	Cation–oxygen distance, Å.	Cation radius, Å.
8 Na	(0.188, .188, .188)	2.35 ± 0.05	1.00 ± 0.05
4 Na	(0.410, .410, 0)	2.10 ± .10	0.75 ± .10
8 Tl	(0.240, .240, .240)	2.64 ± .06	1.29 ± .06

Discussion

This study of the Type A zeolite structure has maintained the interest of the authors because it has led to a logical correlation between structural features and adsorption phenomena previously presented.[1]

From the adsorption data for sodium zeolite A, an adsorption volume for water of 833 Å.^{3} per unit cell was calculated and a volume of only 610 Å.^{3} for oxygen. From the structure each unit cell has a 775 Å.^{3} cavity entered by 8-membered oxygen rings and a 157 Å.^{3} cavity entered by 6-membered oxygen rings. This certainly suggests that the water molecules can enter both the large and the small cavities whereas the oxygen molecules can only enter the former.

It was observed that on progressing gradually from the sodium to the calcium form, low-temperature nitrogen adsorption increased sharply when 4 sodium ions per unit cell had been exchanged. In the sodium zeolite A structure, 2 of the 8-membered rings in the faces each have 2 associated cations; the remaining 4 rings each have only one associated cation leaving an opening about 2.7 Å. in diameter, which is too small to admit nitrogen but large enough to admit oxygen. If 3 of the sodium ions per unit cell, located at II, are replaced by calcium ions, one of the cube faces will be entirely open allowing a nitrogen molecule entry but not through passage. Exchange of the next sodium ion (25–35% exchange) opens 2 faces per cell completing a continuous channel. This is evidence for the conclusion that Type II cations are preferably exchanged.

Finally, there seems to be a correlation of this structure with observed physical properties and reactions. The basic unit of 8 tetrahedra suggests rigidity and it was observed by means of X-ray diffraction photographs that a temperature of 800° is required for recrystallization. The X-ray diffraction pattern of the recrystallized material was the same as that of β-cristobalite which indicates that it may be a "stuffed" derivative of composition $(NaAlSiO_4)_4$ as discussed by Buerger.[14]

In highly alkaline solution, the sodium zeolite A converts irreversibly to a basic sodalite of composition $Na_6[(AlO_2)_6(SiO_2)_6]\cdot NaOH\cdot 8H_2O$, which has the same aluminosilicate framework as that surrounding the small cavity of the A zeolite structure.

Acknowledgment.—The authors are indebted to Mr. L. G. Dowell, Mr. G. H. Faber and Mrs. J. F. Griffin for their assistance in this work; and to Dr. P. A. Howell for his help in preparing the manuscript.

TONAWANDA, N. Y.

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[14] M. J. Buerger, *Am. Mineralogist*, **39**, 600 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Aluminum Diboride, AlB_2[1]

BY EDWARD J. FELTEN

RECEIVED JUNE 29, 1956

The purpose of the investigation was to find a relatively simple method for the preparation of aluminum diboride, AlB_2. The AlB_2 structure is the prototype of the structure of many of the transition metal diborides. The unit cell is hexagonal: $a_0 = 3.009 \pm 0.001$ Å., $c_0 = 3.262 \pm 0.001$ Å.

Introduction

The preparation of AlB_2 was first reported by Funk,[2] who heated an aluminum–boron mixture, rich in aluminum, at a temperature of about 1000°. Chemical analysis was cited as proof of the composition of the alloy. Steele and Mills[3] reported the preparation of an aluminum boride by the fusion of finely divided Al (3 parts) and finely powdered B_2O_3 (1 part) in an iron crucible. The composition of the boride formed was not specified. The first X-ray work on AlB_2 was done by Hofmann and Jäniche.[4] Using single crystals isolated by treatment of an aluminum–1% boron alloy with HCl, the structure of AlB_2 was established.

Recently the preparation of the aluminum borides has been critically reviewed by Lihl and Janitscheck.[5] The difficulties in the preparation of the aluminum borides by the various methods are discussed in detail. It is pointed out that the alloying of Al with elemental B yields AlB_{12} as well as AlB_2. The reaction of Al with sodium borate or B_2O_3 at temperatures above 1000° results in a product highly contaminated with Al_2O_3, while the reaction of the Al with gaseous boron compounds (ex. BCl_3) requires careful manipulation. The method preferred by the authors is a thermite reaction involving Al, B_2O_3, S and $KClO_3$, followed by treatment of the product with HNO_3 and HCl in order to isolate the AlB_{12} formed. The AlB_{12} is then made to react with Al at 1350–1450° to yield AlB_2.

In none of the above was AlB_2 prepared in good purity as a major reaction product. In the course of a study of various metal diborides, efforts were made to prepare AlB_2 by several methods; of these a simple procedure described below gave very satisfactory results.

Experimental

Powdered boron (99.5%; Cooper Metallurgical Associates, Cleveland, Ohio) and aluminum (Eimer and Amend A559) were mixed in the stoichiometric proportions. The mixture was placed in a graphite tube provided with a close-fitting graphite plunger. Veins had been milled lengthwise in the plunger to a depth of about 1/8″ in order to allow any trapped air or other gaseous products produced during the heating operation to escape. The assembly was then placed in a transparent fused silica tube. The silica tube was flushed several times with helium, then evacuated, placed in an electric furnace, allowing about a 12″ portion to protrude from the furnace and heated overnight at 800°. After cooling, the sample was removed and was found to be uniformly brown-grey in color. A representative sample was examined by X-ray diffraction methods using nickel-filtered Cu radiation. The principal component of the reaction was AlB_2, with Al, graphite and B_4C being present in small amounts. The amounts of graphite and B_4C may be kept at a minimum by careful removal of the reaction product from the graphite container as these compounds

TABLE I

DIFFRACTION DATA FOR AlB_2

hkl	*d* Spacings	Rel. intensity
001	3.264	4
100	2.608	39
101	2.307	100
002	1.631	13
110	1.505	28
102	1.383	7
111	1.367	3
200	1.303	4
201	1.210	12
112	1.106	11
202	1.018	2
210	0.9852	1
211	.9430	10
300	.8687	5
212	.8433	1
203	.8347	3
004	.8154	2

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] H. Funk, *Z. anorg. allgem. Chem.*, **142**, 269 (1925).

[3] B. D. Steele and J. E. Mills, *J. Chem. Soc.*, 74 (1930).

[4] W. Hofmann and W. Jäniche, *Naturwiss.*, **23**, 851 (1935).

[5] F. Lihl and P. Janitschek, *Z. Metallkunde*, **44**, 414 (1953).