

The crystal structure of the synthetic zeolite L

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(Received April 10, 1968)

Auszug

Die Kristallstruktur des synthetischen Zeoliths Linde L, $K_6Na_3Al_9Si_{27}O_{72} \cdot 21H_2O$, wurde auf Grund von Pulverdaten bei Zimmertemperatur bestimmt. Der Zeolith ist hexagonal mit den Gitterkonstanten $a = 18.4 \text{ \AA}$ und $c = 7.5 \text{ \AA}$. Die Struktur wurde unter Annahme von Raumgruppe $P6/mmm$ verfeinert.

Das Aluminosilikatgerüst basiert auf den durch fünf Sechser- und sechs Viererringe begrenzten Käfigen, welche in Cancrinit, Erionit und Offretit vorkommen. Diese Käfige sind über parallele Sechserringe in der c -Richtung verbunden. Dadurch entstehen Säulen, in denen die Käfige mit hexagonalen Prismen alternieren. Die Säulen sind über Sauerstoffbrücken untereinander verbunden und umschließen weite Kanäle, welche parallel zur c -Achse verlaufen. Die Form der im Querschnitt runden Kanäle kann als eine Folge von weiten Stellen und Einschnürungen beschrieben werden. Die engen Stellen werden durch Zwölferringe mit 7,1 bis 7,8 \AA Durchmesser gebildet. Vier Kationenpositionen wurden gefunden; drei davon sind vollständig von Gerüstatomen umgeben. Die vierte Position befindet sich an der weitesten Stelle des Hauptkanals, nahe der Kanalwand. Die Wassermoleküle füllen die weiten Kanäle, sind teilweise geordnet und nur schwach an das Gerüst gebunden.

Eine Reihe bisher unbekannter Strukturen wurde entwickelt, welche eine gewisse Verwandtschaft mit Zeolith L zeigen. Alle diese Strukturen konnten in die Chabasit-Gruppe eingereiht werden, die zu diesem Zwecke in vier Untergruppen aufgeteilt wurde.

Abstract

The crystal structure of the synthetic zeolite, Linde L, $K_6Na_3Al_9Si_{27}O_{72} \cdot 21H_2O$, has been determined from powder data at room temperature. The zeolite is hexagonal with unit-cell dimensions $a = 18.4 \text{ \AA}$ and $c = 7.5 \text{ \AA}$. The structure has been refined assuming space group $P6/mmm$.

The aluminosilicate framework is based upon the polyhedral cages which are formed by five six-membered and six four-membered rings and are found in cancrinite, erionite and offretite. These cavities are linked through the planes of their upper and lower six-membered ring, thus forming columns in which hexagonal

prisms and polyhedra alternate, and which run parallel to the c axis. Each column is crosslinked to three others by single oxygen bridges which form part of planar twelve-membered rings circumscribing wide channels parallel to c . Each channel can be represented as a succession of sections, circumscribed top and bottom by twelve-membered rings shared with upper and lower adjacent sections. The rings have free diameters of 7.1 to 7.8 Å. Four cation positions were found, three of which are outside the main channels and closely surrounded by framework oxygen atoms. The fourth position is in the widest part of the main channel close to the channel wall. The water molecules filling the wide channels are only loosely bound to the framework and appear to have only partial regularity of arrangement.

Structures have also been developed for a considerable number of so far unknown zeolites with similarities to zeolite L. All these structures can be allocated to the chabazite family, which however on account of its size and structural variety can be divided into four subgroups.

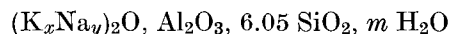
Introduction

The open character of the aluminosilicate frameworks of the zeolites provides many possibilities for different arrangements of linked (Si,Al)O₄ tetrahedra. Accordingly the zeolites form a numerous group, comprising nearly forty naturally occurring minerals, augmented by about half this number of novel synthetic species. Moreover, frameworks for many additional zeolites can be constructed which are representative of structures awaiting synthesis (SMITH and RINALDI, 1962; KOKOTAILO and LAWTON, 1964; MEIER and KOKOTAILO, 1965; KERR, 1963). All are of interest not only because of their great variety and structural elegance but also because zeolites have found important industrial applications.

Zeolite L (BRECK and ACARA, 1958) is a synthetic species for which a framework has been proposed (BRECK and FLANIGEN, 1967). It has interesting sorbent and molecular-sieve properties coupled with a considerable sorption capacity. However the structure proposed by BRECK and FLANIGEN does not appear to be compatible with some of the properties of zeolite L such as sorption capacity and density, and accordingly it was of interest to investigate the structure further. The results are presented in this paper, and in addition we have considered the frameworks for a range of novel but so far unknown zeolites related to zeolite L.

Experimental

Chemical analysis of a sample of (Na,K)-zeolite L supplied by Linde Air Products gave the following results:



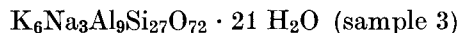
	<i>x</i>	<i>y</i>	<i>m</i>
1. original sample	0.91	0.08	4.0
2. K-enriched form	0.95	0.06	4.0
3. Na-enriched form	0.65	0.35	4.6

The exchanged forms were prepared at room temperature by three batchwise treatments with nearly saturated solutions of the appropriate chlorides. The water content *m* was determined after equilibration of the sample for one week at a water vapour pressure of 14 Torr. BRECK and FLANIGEN reported an analysis of the potassium form of zeolite L confirming the above results and also gave the measured density as 2.11 g/cm³.

The zeolite was found to be hexagonal with the cell parameters

$$a = 18.40 \pm 0.04 \text{ \AA}, \quad c = 7.52 \pm 0.03 \text{ \AA}.$$

The cell dimensions were determined by means of a Guinier photograph using lead nitrate as a standard. The above analytical results lead to an approximate unit-cell content of



The x-ray powder patterns of samples 2 and 3 were obtained with a General Electric XRD6 diffractometer using a flat sample, CuK α radiation and a proportional counter. Integrated intensities of powder lines with $2\theta \leq 80^\circ$ were measured using a planimeter. No absorption correction was applied.

Determination of the structure

Examination of the powder patterns showed no systematic absences, indicating a primitive lattice. A few very faint lines could not be indexed either on the given unit cell or on the basis of a multiple cell with $c = n \times 7.5 \text{ \AA}$ where *n* is 2,3,... Most of these lines could be attributed to erionite, offretite or K-zeolite F (BARRER and BAYNHAM, 1956). Accordingly such extra lines were discarded as originating from impurities. The water content indicated a free volume of 0.13 cm³/g for sample 2 and 0.15 cm³/g for sample 3. Sorption results for larger molecules, given by BRECK and FLANIGEN (1967), suggested that the framework should possess large openings such as could be provided by twelve-membered rings. The measured density requires about 36 tetrahedra per unit cell.

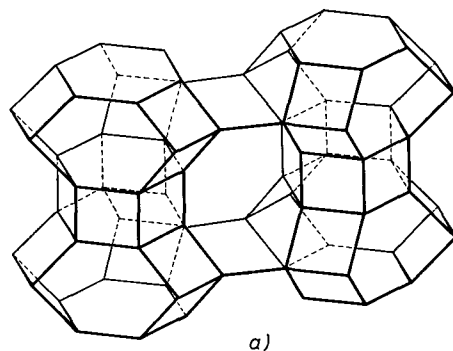


Fig. 1a. Framework structure of proposal 1. In this figure and all similar structural diagrams Al or Si is centred at each apex and the centres of the oxygen atoms lie about halfway between the apices, near but not on the lines connecting pairs of apices

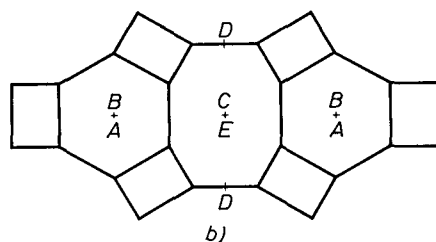


Fig. 1b. Projection of proposals 1 and 2 along the c axis. The labelled positions refer to cation sites in zeolite L. Site A (Na,K) at the centre of the hexagonal prism is taken at $z = 0$. Sites B [K(1)] and C [K(2)] are at $z = \frac{1}{2}$, the height of the centres of cancrinite cavities. Sites D [Na(2)] and E are at $z = 0$

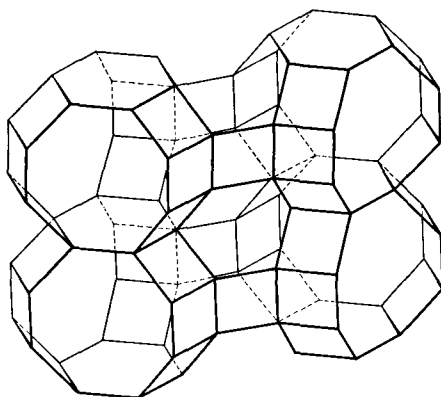


Fig. 2. Framework structure of proposal 2

Two framework structures, proposals 1 and 2 (Figs. 1 and 2), were found to have the required cell constants as well as the above properties. Assuming Si and Al to be statistically distributed, both frameworks have symmetry $P6/mmm$ which is compatible with the powder pattern. A third proposal due to BRECK and FLANIGEN (1967) was also taken into consideration despite its obvious discrepancies in cell parameters, density and sorption properties.

A computer programme DLS (MEIER and VILLIGER, 1969) was used to generate the initial framework coordinates based on a mean (Si,Al)—O distance of 1.65 Å, the value required by a Si:Al ratio of 3:1 (SMITH and BAILEY, 1963). A Wilson plot of the observed intensities suggested a very low overall temperature factor of $\sim 0.1 \text{ \AA}^2$. Taking into account that the value for the temperature factor found from low-angle reflections is often too small, or even negative, an initial overall temperature factor of 0.4 \AA^2 was used. The scattering factors applied were those listed in the International tables for x-ray crystallography, Volume III. Silicon, aluminium and oxygen were assumed to be half ionized and the appropriate averages were taken. The cations inserted during the later stages of refinement were taken to be fully ionized whereas water molecules were inserted with the same scattering power assumed for the framework oxygen atoms.

The initial reliability values based on framework atoms and data from sample 3 were as follows:

Proposal	1	2	3*
highest possible symmetry			
(statistical Si/Al distribution)	$P6/mmm$	$P6/mmm$	$P6_3/mmc$
$R(I)$	0.85	1.21	1.18
$R(F)$	0.36	0.44	0.56

$$R(I) = (\sum |I_{\text{obs}} - I_{\text{calc}}|) / \sum I_{\text{obs}}; \quad R(F) = (\sum ||F_{\text{obs}}| - |sF_{\text{calc}}||) / \sum F_{\text{obs}}$$

I_{obs} = uncorrected observed relative intensity.

$$I_{\text{calc}} = \sum_{i=1}^n M_i \cdot LP_i \cdot (sF_i)^2$$

n = number of non-equivalent reflections contributing to a powder line.

M_i = multiplicity factor for each reflection.

LP_i = Lorentz-polarisation correction factor for each reflection.

sF_i = scaled calculated structure amplitude;

* based on reflections with $l = 4n$; $c = 30.1 \text{ \AA}$

The scale factor is included here because of the requirements of the computer programmes available.

The application of the *LP* correction to the calculated value $(sF_i)^2$ leads to an artificially high initial $R(I)$ value. This procedure however makes it possible to treat coincidences of reflections properly even if the observed "powder line" consists of a number of unresolved reflections. More important, it enabled us to ascribe individual least-squares weights taken from estimated standard deviations of observed intensities without applying an artificial weighting scheme.

The function minimized in the least-squares refinement was

$$\sum \omega (I_{\text{obs}} - I_{\text{calc}})^2; \quad \omega = 1/\sigma^2 I_{\text{obs}}$$

where σ denotes the standard deviation and the summation was taken over all observed powder lines.

For purposes of Fourier synthesis, " F_{obs} " values were assigned proportional to the calculated structure amplitudes and the $R(F)$ value was calculated accordingly (BROUSSARD and SHOEMAKER, 1960).

Proposal 3 was ruled out inter alia on account of the high $R(F)$ value. Proposals 1 and 2 were investigated more closely. The facts that both structures have nearly the same $hk0$ projection and that most of the observed lines consist of $hk0$ and hkl reflections made it difficult to decide which proposal was to be preferred. Comparison of observed and calculated intensities of non-overlapping lines was in favour of proposal 1.

Refinement

Both proposals were refined according to the procedure described below. The initial Fourier maps based on framework coordinates and data collected from sample 3 appeared to be reasonable in both cases. During the refinement of proposal 2 the framework-oxygen atoms nearest to the centre of the main channel tended to move towards the mirror plane at $z = 0$, indicating that there was something amiss with this structure. The refinement of proposal 2 terminated at $R(F) = 0.25$ and the corresponding coordinates gave some very improbable (Si,Al)—O distances. For these reasons proposal 2 was not considered further.

The first three-dimensional Fourier map of proposal 1 was based on framework coordinates and application of an artificially high overall temperature factor of 4.0 \AA^2 , in order to reduce series-termination effects. For the same reason any additional peaks which appeared

Table 1. *Parameters of hydrated zeolite L at room temperature*
(estimated standard deviations are given in brackets)

Atom	Position based on $P6/mmm$	Fractional occupancy*	x	y	z	B^{**}
Si,Al(1)	12 q		0.0946 (0.0030)	0.3595 (0.0033)	1/2	1.2 Å ²
Si,Al(2)	24 r		0.1662 (0.0022)	0.4989 (0.0026)	0.2137 (0.0043)	0.6
O(1)	6 j		0	0.2674 (0.0065)	1/2	1.0
O(2)	6 m		0.1646 (0.0028)	0.3292	1/2	1.0
O(3)	12 o		0.2620 (0.0019)	0.5240	0.260 (0.010)	2.5
O(4)	24 r		0.1004 (0.0030)	0.4078 (0.0027)	0.330 (0.006)	1.0
O(5)	12 o		0.4261 (0.0028)	0.8522	0.275 (0.010)	1.3
O(6)	12 p		0.1360 (0.0043)	0.4691 (0.0043)	0	0.8
Na,K***	2 c	0.7	1/3	2/3	0	4.0
K(1)	2 d	1.0	1/3	2/3	1/2	1.0
K(2)	3 g	0.9	0	1/2	1/2	3.0
Na(2)	6 j	0.6	0	0.303 (0.007)	0	2.0
H ₂ O(1)	6 m	0.7	0.0700 (0.0042)	0.1400	1/2	4.0
H ₂ O(2)	6 k	0.25	0	0.09 (0.02)	1/2	7.0
H ₂ O(3)	1 b	0.5	0	0	1/2	15.0
H ₂ O(4)	12 n	0.25	0	0.135 (0.021)	0.243 (0.061)	4.0
H ₂ O(5)	12 o	0.25	0.092 (0.008)	0.184	0.203 (0.034)	5.0
H ₂ O(6)	2 e	0.7	0	0	0.189 (0.046)	10.0
H ₂ O(7)	6 l	0.7	0.116 (0.006)	0.232	0	6.0
H ₂ O(8)	6 j	0.5	0	0.195 (0.013)	0	5.0

* Estimated standard deviation of the order of 0.05.

** Estimated standard deviation of 0.5 Å² for framework atoms and cations, 1.0 to 2.0 Å² for water molecules.

*** Refined assuming the scattering factor of Na⁺.

were considered to be worthwhile refining only if they had roughly the same heights in the map based on observed reflections as in the map based on the differences ($F_{\text{obs}} - F_{\text{calc}}$).

The peaks thereby selected and later called (Na,K), K(1), K(2), Na(2), H₂O(7) and H₂O(8), as in Table 1, were inserted with scattering powers proportional to their heights in the difference synthesis.

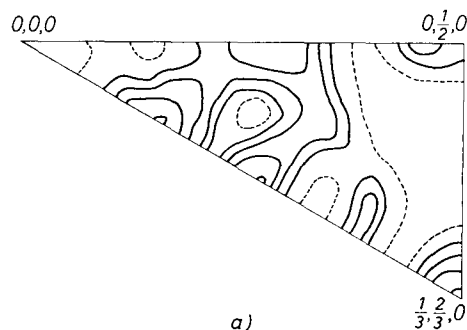


Fig. 3a. Difference fourier section ($F_{\text{obs}} - F_{\text{calc}}$) based on initial framework-atom positions and intensity data taken from sample 3 (Na-enriched form)

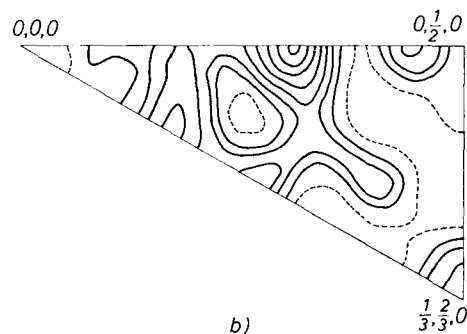


Fig. 3b. As Fig. 3a, but data taken from sample 2 (K-enriched form). Contours are at equal, arbitrary intervals starting with zero (broken lines). Note the difference in peak heights at $0 \frac{1}{3} 0$ (site D) due to ion exchange

The $R(I)$ value fell afterwards from 0.85 to 0.54 and the $R(F)$ value from 0.36 to 0.29. A difference Fourier map based on intensities collected from the K-exchanged sample 2 showed clearly that the position Na(2) was now occupied by potassium (Fig. 3). Apart from this, no significant difference was found between the two samples, and it was decided to continue with data from sample 3 only. Attempts to refine any newly-found positions together with coordinates from framework atoms by means of least-squares calculations resulted in

some improbable Si,Al—O distances. In particular, shifts of z coordinates were generally much too large, a behaviour which was probably due to the frequent overlapping of $hk0$ and hkl reflections.

A second Fourier map was calculated revealing a few more peaks located in the main channel. Due to their low electron density they were put in as oxygen atoms with a fractional occupancy of 0.5. The $R(I)$ and $R(F)$ values afterwards dropped to 0.46 and 0.26 respectively. The least-squares refinement was then commenced, varying at first only the x and y coordinates of non-framework atoms. A third Fourier map showed all the atoms stated in Table 1 and also indicated

Table 2. *Interatomic distances*
(estimated standard deviation in brackets)

Si,Al(1)—O(1)	1.72 (0.06) Å	O(1)—O(2)	2.65 (0.03) Å
Si,Al(1)—O(2)	1.64 (0.05)	O(1)—O(4)	2.64 (0.08)
Si,Al(1)—O(4)	1.53 (0.05)	O(2)—O(4)	2.61 (0.06)
Mean	1.64	O(4)—O(4)	2.55 (0.09)
		Mean	2.61
Si,Al(2)—O(3)	1.62 (0.04) Å	O(3)—O(4)	2.71 (0.06) Å
Si,Al(2)—O(4)	1.74 (0.06)	O(3)—O(5)	2.68 (0.06)
Si,Al(2)—O(5)	1.64 (0.03)	O(3)—O(6)	2.81 (0.09)
Si,Al(2)—O(6)	1.70 (0.03)	O(4)—O(5)	2.76 (0.05)
Mean	1.68	O(4)—O(6)	2.67 (0.05)
		O(5)—O(6)	2.76 (0.07)
		Mean	2.73
			Coordination
Na,K—O(3)	3.00 (0.07) Å		6-fold
Na(2)—O(6)	2.82 (0.10)		2-fold
Na(2)—O(4)	3.12 (0.06)		4-fold
Na(2)—H ₂ O(7)	3.01 (0.12)		2-fold
K(1)—O(3)	2.90 (0.08)		6-fold
K(1)—O(5)	3.40 (0.08)		6-fold
K(2)—O(4)	3.32 (0.10)		8-fold
K(2)—O(5)	2.90 (0.08)		4-fold
O(1)—H ₂ O(1)	3.2 (0.3)		
O(1)—H ₂ O(2)	3.2 (0.3)		
O(1)—H ₂ O(4)	3.1 (0.3)		
O(2)—H ₂ O(1)	3.0 (0.2)		
O(2)—H ₂ O(5)	3.2 (0.3)		

Table 3. Observed and calculated intensities and structure factors

h k l	I _o	I _c	F _c	h k l	I _o	I _c	F _c	h k l	I _o	I _c	F _c
1 0 0	1530	1638	- 52.79	2 1 3	3	4	(3.88	6 4 1			0.84
1 1 0	3	28	11.91	6 1 1			(9.40	3 0 4	9	4	(- 15.03
2 0 0	37	37	- 15.91	4 4 0	46	109	108.30	9 0 0			(- 2.20
0 0 1	335	420	- 98.49	7 0 0			(33.57	6 3 2	16	11	(9.67
1 0 1	8	20	- 9.81	5 3 0			(- 18.79	8 0 2			(- 33.47
2 1 0	705	296	42.45	5 1 2	36	40	(- 24.77	7 3 1			(22.43
1 1 1	179	198	35.87	3 0 3			(7.84	6 1 3			(22.20
2 0 1	< 1	4	5.80	6 2 0			(- 23.54	2 2 4	94	97	(- 19.96
3 0 0	11	15	- 15.47	4 4 1			(- 91.93	8 2 0			(- 35.58
2 1 1			(- 10.32	2 2 3			(- 53.15	9 0 1			(- 22.05
2 2 0	400	385	(- 87.84	7 0 1	221	209	(- 1.79	7 2 2			(- 55.29
3 1 0	113	65	27.44	5 3 1			(14.31	3 1 4			(21.73
3 0 1	183	224	- 51.78	6 0 2			(- 6.42	8 2 1			(- 50.20
4 0 0	51	35	- 31.67	3 1 3			(- 8.17	4 4 3	135	109	(37.05
2 2 1	500	444	- 81.01	4 3 2	6	4	(11.82	4 0 4			(15.84
3 1 1	47	2	4.41	6 2 1	26	26	(13.13	7 0 3			(68.87
0 0 2	15	2	- 12.88	4 0 3			(- 36.37	5 3 3			(- 19.76
3 2 0			(- 10.16	7 1 0	12	4	(7.53	6 5 0			(- 51.27
1 0 2	302	324	(73.66	5 2 2	12	6	(- 10.03	9 1 0	49	26	(0.04
4 0 1			(11.20	5 2 3	12	6	(- 15.02	8 1 2			(- 7.32
4 1 0	460	349	(44.94	5 4 0			(3.71	3 2 4			(- 11.62
1 1 2			(- 67.17	7 1 1	65	65	(- 22.10	7 4 0			(15.41
2 0 2	58	27	- 23.40	6 1 2			(29.22	5 5 2	9	9	(28.96
3 2 1	252	237	- 50.58	4 1 3			(31.24	6 2 3			(4.11
5 0 0			(- 139.72	6 3 0	28	16	(- 34.84	4 1 4			(- 1.19
4 1 1	617	602	(28.59	8 0 0	< 1	7	(32.27	6 4 2	1	2	(11.57
2 1 2			(- 35.64	5 4 1			(- 26.58	6 5 1			(- 1.01
3 3 0	367	336	(- 48.24	4 4 2	21	22	(7.12	9 1 1	12	17	(32.54
3 0 2			(85.05	5 0 3			(16.19	8 3 0			(67.06
4 2 0	73	106	- 52.60	7 2 0			(32.47	7 4 1			(7.54
5 0 1	499	493	(17.61	6 3 1			(8.09	7 3 2	86	70	(7.40
2 2 2			(116.27	7 0 2	20	34	(- 19.00	7 1 3			(- 17.07
5 1 0			(- 5.85	5 3 2			(- 18.30	5 0 4			(- 58.91
3 1 2	51	41	(- 24.20	7 3 3			(- 22.00	9 0 2	13	18	(47.65
3 3 1	31	38	33.46	8 0 1			(- 22.06	3 3 4			(- 8.81
4 2 1	59	46	- 26.76	4 2 3	7	10	(- 12.15	10 0 0	14	4	(27.96
4 0 2	17	1	3.56	6 2 2	13	15	(- 25.05	4 2 4			(- 5.83
5 1 1			(- 31.28	7 2 1			(13.79	9 2 0			(- 34.29
6 0 0	308	243	(113.18	5 1 3			(26.44	8 3 1			(- 29.05
4 3 0			(- 0.60	0 0 4	177	170	(270.38	8 2 2	145	156	(- 81.85
3 2 2	150	156	(- 52.63	8 1 0			(- 5.59	5 4 3			(- 36.40
5 2 0	38	51	(43.66	1 0 4			(- 24.10	5 1 4			(- 16.05
4 1 2			(10.08	5 5 0			(78.32	6 3 3			(24.92
6 0 1			(61.51	7 1 2			(- 12.77	9 3 2			(30.79
0 0 3	90	92	(- 40.61	1 1 4			(- 17.73	6 3 4	26	20	(- 13.33
4 3 1	86	93	(44.01	6 4 0	116	123	(- 9.82	8 0 4			(37.70
1 0 3			(- 18.09	6 0 3			(- 76.24	11 1 1			(- 10.47
6 1 0			(- 69.38	4 3 3			(- 22.86	9 4 1	26	7	(18.70
5 2 1			(- 24.15	2 0 4			(- 17.02	8 3 3			(- 10.04
5 0 2	152	136	(- 9.71	8 1 1			(- 13.41	5 0 5			(- 12.57
1 1 3			(- 19.31	2 1 4			(0.59	10 3 0			(44.37
2 0 3	16	2	5.38	7 3 0			(20.68	11 0 2	19	31	(62.62
3 3 2			(9.72	5 5 1	67	71	(29.53	7 2 4			(- 1.60
4 2 2	19	3	8.45	5 4 2			(4.71	3 3 5			(- 8.71
				5 2 3			(- 52.62	10 0 3			(39.51
								4 2 5	12	11	(- 16.59

some changes in scattering power. The next few least-squares cycles were made varying the coordinates of non-framework atoms in x , y and z . The positions of framework atoms were then adjusted in the same manner, starting by refining x and y coordinates and then extending the refinement to z coordinates. A difference map calculated to check the progress of the refinement showed no significant new peaks.

Afterwards the least-squares refinement was made in the following way. In the first cycle the scale factor and all the coordinates were varied; in the second, occupancy factors of non-framework atoms; and in the third, all isotropic temperature factors. This procedure was repeated until shifts were smaller than the corresponding standard deviations. Attempts to exclude some of the very incompletely occupied water positions led to framework-oxygen shifts towards the excluded positions. It was therefore assumed that those positions had to be included.

Until that stage, which was reached with an $R(I)$ value of 0.22 and $R(F)$ value of 0.18, all measurements were given unit weight in order to adjust mainly the strong powder lines. The weighting system was then changed to individual weights based on estimated standard deviations. The refinement procedure was continued in the same way as described above, and resulted in an $R(I)$ value of 0.14 and an $R(F)$ value of 0.13. A final weighted difference Fourier map showed no residual electron density of more than 1 to 2 $e/\text{\AA}^3$.

Fourier maps were generated with the aid of the University of Washington X-Ray 63 System. The least-squares refinement was made with the ORFLS computer programme (BUSING, MARTIN and LEVY, 1959) which was modified to permit the refinement of any powder pattern. All computations were made on the IBM 7090 computer at Imperial College.

The final coordinates with their estimated standard deviations are listed in Table 1. Bond lengths of interest are assembled in Table 2. The corresponding standard deviations were calculated using the programme ORFFE due to BUSING, MARTIN and LEVY (1964). Table 3 shows the observed powder line intensities, the calculated intensities and the values of $\pm F$.

Description of the structure

Framework

The building units of the aluminosilicate framework of zeolite L are the cavities found in cancrinite (JARCHOW, 1965), erionite and offretite (BENNETT and GARD, 1967; STAPLES and GARD, 1959). The cavities are linked through their two nearly planar six-membered rings, forming hexagonal prisms with the planes of the six-membered rings normal to the c axis (Fig. 1). The columns formed thereby are joined by single oxygen bridges, which are part of the planar twelve-membered rings that circumscribe the main channels running parallel to the c axis (Fig. 7*b*). Clearly these channels cannot be blocked by simple stacking faults as is possible in cancrinite, offretite and gmelinite. The channels are made by the stacking of sections 7.5 \AA high each of which encloses an estimated free volume of 610 \AA^3 . Any section is joined top and bottom to identical sections by shared twelve-membered ring windows having minimum and maximum free diameters of 7.1 and 7.8 \AA . The largest free diameter of a section (which is midway between the twelve-membered rings) is about 13 \AA . The unit-cell volume is 2205 \AA^3 so that 610 \AA^3 corresponds to a free

volume of 28% or of 0.15 cm³/g which is in agreement with the water content of 15.3% found at 14 Torr partial pressure.

The main channels are connected with each other through a less important two-dimensional channel system along the a_1 and a_2 axes as well as the enclosed mirror plane. The openings are formed by nonplanar eight-membered rings (Fig. 1) with a limiting aperture dimension of 1.5 Å. They are probably too small to represent diffusion paths especially since they are partly blocked by cations K(2).

All the figures given refer to the hydrated form and may be subject to changes upon dehydration of the crystals. The aperture dimensions were calculated using the coordinates in Table 1 and assuming an oxygen radius of 1.40 Å.

Cations

Cations are present in at least four different sites denoted A, B, C and D (Fig. 1*b*). Site A , (Na, K), which was refined assuming partial occupancy by sodium, is located in the middle of the hexagonal prism. The cation-oxygen distance of 3.0 Å (Table 2) for six framework oxygen atoms together with twelve others within 3.6 Å suggests that this position could well be occupied by a potassium ion. This assumption is in agreement with the chemical analysis of 9 cations per unit cell, whereas the number of cations calculated from occupancy factors

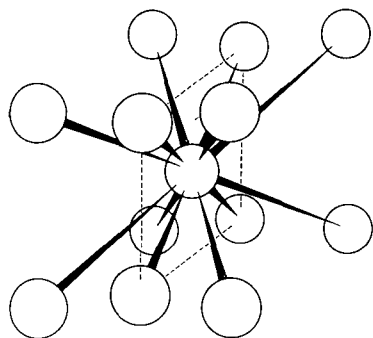


Fig. 4

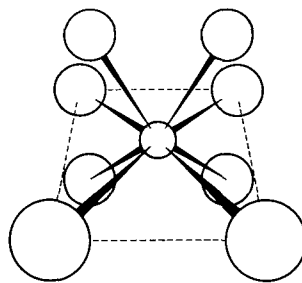


Fig. 5

Fig. 4. Environment of K(2) on site C . K(2) and oxygen atom O(5) lie in the outlined plane which is perpendicular to the a axis. The remaining oxygen atoms are of type O(5)

Fig. 5. Environment of Na(2) on site D viewed along the a axis. H₂O(7) in front, Na(2) in the centre and O(6) at the rear lie in the outlined mirror plane at $z = 0$. The remaining oxygen atoms above and below are of type O(4)

gives 9.7. Assuming (Na,K) to be in fact a potassium ion, the number of cations found by means of x-ray analysis would be ~ 9.1 .

Site *B* is the centre of the cancrinite cavity and is fully occupied by K(1). Twelve framework oxygen atoms form the coordination shell as indicated in Table 2. The O atoms lie in two planes above and below the potassium. Site *C*, containing K(2) is located midway between the centres of two adjacent cancrinite cavities, and has a fractional occupancy of 0.9. Figure 4 shows the framework oxygen environment of this site. Site *D*, partially occupied by Na(2) is the only cation position found in the main channel. Its location is best understood by reference to Figs. 1*b* and 5. As mentioned earlier, this site is occupied by K in the potassium-enriched form as is shown by the two difference Fourier maps of Fig. 3. The cations on site *D* seem to be virtually the only exchangeable ones at room temperature (see experimental section). On dehydration one would expect cations smaller than potassium on this site to withdraw from the channel to the more symmetric coordination position *E* (Fig. 1*b*) located midway between adjacent sites *A*. The next position most likely to be exchanged is site *C*. Hence this material could show interesting ion-exchange behaviour.

Zeolitic water

The zeolitic water was found to fill the free space in the main channel. The rather long framework-oxygen-water distances (Table 2) suggest that the water is only loosely bound. The water molecules seem to form a succession of clusters with partial regularity, although it was not possible to ascribe a definite arrangement to a cluster because of the many sites which statistically are only partially occupied (Table 1). H₂O(8) in particular lies in a position only 2.0 Å from Na(2) and is thought to be present only when Na(2) is absent. This distance was therefore not included in Table 2. The water positions are not resolved near the centre of the channel and also possess very high temperature amplitudes according to Table 1. The number of water molecules based on occupancy factors is 20.8 and agrees very well with the value of 21 found by means of thermogravimetric analysis.

Si,Al distribution

The highest possible symmetry of the framework is $P6/mmm$ with statistical distribution of silicon and aluminium. The structure has been refined in this space group, because the limited number of

measurements available did not permit an increase in the number of variables for the least-squares refinement. Zeolite L, however, evidently prefers a Si:Al ratio of 3.0 (BRECK and FLANIGEN, 1967, reported a range of 2.5 to 3.5). Assuming an ordered Si,Al distribution with a ratio of 3.0, one finds $P3$ as the highest possible symmetry. Four most symmetric arrangements of Si and Al can be obtained in this space group, but even in this case building units (cancrinite cavities) with a different Si:Al ratio would have to alternate in the a_1, a_2 plane. Overall ordering of Si and Al, together with identical building units requires an even further lowering of the symmetry. Another alternative would be to double the c constant. However no evidence of a doubled unit cell was found in the powder patterns. The many partially occupied water positions could also indicate a lower symmetry, as mentioned by SMITH, RINALDI and GLASSER (1963) in their work on hydrated chabazite. According to the estimated standard deviation of the observed intensities it was hoped to refine the structure to an $R(I)$ value of 0.10. The assumption of pseudo-symmetry due to neglecting possible order in the Si,Al distribution could account for the higher $R(I)$ value obtained, since the mirror planes in $P6/mmm$ impose very severe restrictions upon the positions of framework oxygen atoms.

Hypothetical structures related to zeolite L

Figures 1 and 2 show that both our original proposals contain the same type of chain running parallel to the c axis. The nature of these chains made from four-membered rings can most easily be described by stating the positions of the so far unconnected oxygen atoms. Taking as reference system a general n -fold axis, the two unlinked oxygen atoms at the same height are either near (N) or far (F) from the reference axis (Fig.6). Any type of n -fold, screw, or inversion axis can serve as an operator. Since this paper is concerned with a hexagonal structure we restrict our consideration to three-fold operators. The type of chain is described by stating the sequence of N and F atoms within one identity period. The number of F or N atoms following each other directly may only be one or two since a three-fold repetition would otherwise lead to unlikely arrangements such as treble hexagonal rings. The lengths of the identity period is not restricted. It is however not likely that a complicated pattern could be strictly maintained. Thus the longer the identity period the more likely are frequent stacking faults. For this reason

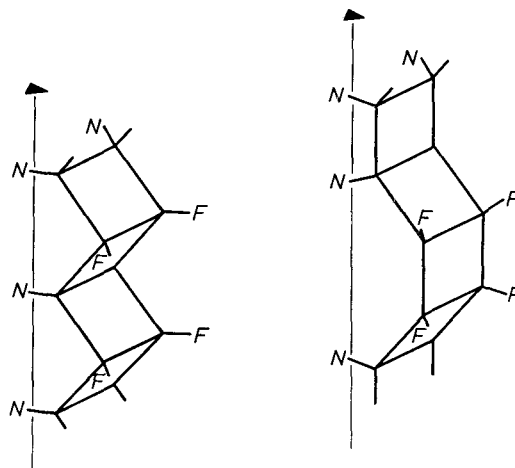


Fig. 6. NF chains in relation to three-fold operators. The left-hand side shows a chain of type NF and the right-hand side of type NFFF. The latter is also a chain of type UDD as described by SMITH and RINALDI (1964)

we limit our consideration to not more than eight tetrahedra corresponding to a c constant of about 20 Å.

By linking the chains generated by the three-fold operator using the oxygen atoms near to the axis, the characteristic columns of this group of structures are formed.

There are three ways of extending the network in the plane perpendicular to the operator axis using the oxygen atoms far from the axis as links:

1. The chain considered is *shared* by two operators,
2. The chain considered is linked to a second chain belonging to another operator, in such a way that,
 - a) the two chains connected do *not face* each other (Fig. 7),
 - b) the two chains are *facing* each other (Fig. 8). Table 4 and Figs. 7 and 8 illustrate the above statements.

Structures of the kind illustrated in Fig. 8 and Table 4, column 5, if they can be synthesized, may be of special significance. Both in respect of accessibility of intracrystalline pores and of total porosity (~ 0.6 of crystal volume) they would be well above any crystal hitherto known.

The columns 3 to 5 in Table 4 assemble structures with nearly the same a constant and free diameter of the main channel. The members with $n = 2, 3$ and 4 in each column will show quite different properties (e.g. ion-exchange) due to the different forms of their cavities. Those properties will gradually approach each other as

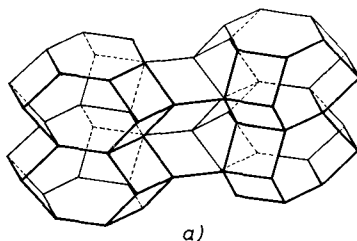


Fig. 7a. Hypothetical structure of type NF, in which the chains are *not facing* each other

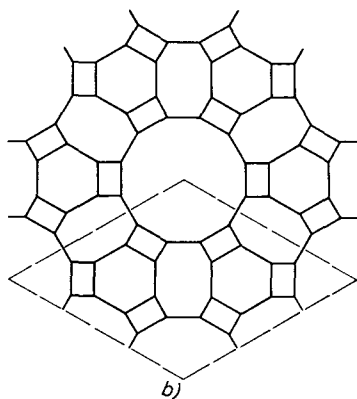
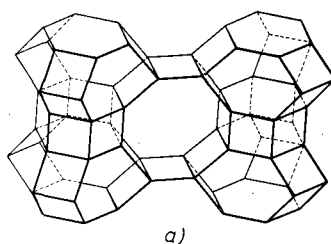


Fig. 7b. Corresponding projection down the c axis, showing the channel circumscribed by twelve-membered rings. This projection is appropriate for all structures listed in column 4 of Table 4

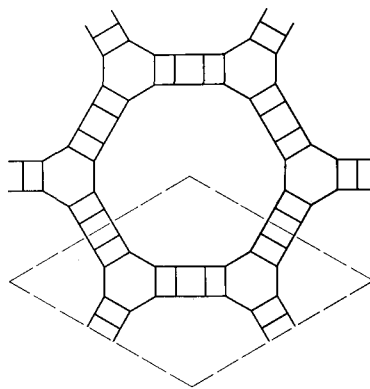
n increases. Structures lying in a row will be related in so far as they consist of the same secondary structural building units. Up to the present time it has been customary to identify any zeolite by merely stating the d spacings, sometimes together with information about the powder-line intensities. Quite different structures, such as proposals 1 and 2 as well as any member in the columns in Table 4 with equal n , have more or less the same cell parameters and hence the same d spacings. This makes it clear that it is not possible completely

to identify many zeolites on the basis of a range of composition and a powder pattern without a detailed structure analysis. The column headed "chain shared" in Table 4 contains certain members of the chabazite group minerals listed by MEIER (1967). They can be described equally well in terms of the stacking of layers of either single or double six-membered rings, and involving only sequences of layers



a)

Fig. 8a. Hypothetical structure of type NNF, in which the chains are *facing* each other



b)

Fig. 8b. Corresponding projection along the *c* axis, showing in section the channel circumscribed by eighteen-membered rings. This projection is appropriate for all structures listed in column 5 of Table 4

such that every third layer is superposed on the first. The remaining known members of the chabazite group, namely sodalite, erionite, chabazite and levynite, as well as hypothetical structures such as those suggested by KOKOTAILO and LAWTON (1964), can be generated by applying 6_3 and $\bar{3}$ axes as operators. It is however also easy to think of them as indicated for group *A* below.

The way in which hypothetical and known structures have been presented enables one to extend and subdivide the chabazite group.

Table 4

Some actual and hypothetical structures based on NF chains of four-membered rings

		Operator: ▲		
		Chain shared	Chain not shared	
<i>n</i>	Type of chain		not facing	facing
2	NF	canerinite	unknown ¹	unknown
3 a	NNF	} offretite	zeolite L ²	unknown ⁴
b	FFN		unknown ³	unknown ⁵
4	NFFF	gmelinite	unknown	unknown ⁵
5 a	NFFNF	} unknown	unknown	unknown ⁵
b	FNNFN		unknown	unknown
6	NNFNFF	unknown	unknown	unknown ⁵
7 a	NFNFNFN	} unknown	unknown	unknown
b	FNFNFNF		unknown ⁵	
c	NNFNFFF	} unknown	unknown	unknown ⁵
d	FFNNFNN		unknown ⁵	
8 a	NFNFFNFN	unknown	unknown	unknown ⁵
b	NFNFFNFF	} unknown	unknown	unknown ⁵
c	FNFNNFNN		unknown	
a_{hex}		12.8 to 13.7 Å	~ 18.5 Å	~ 22 Å
<i>c</i>		$n \times 2.5 \text{ Å}$	$n \times 2.5 \text{ Å}$	$n \times 2.5 \text{ Å}$
Free diameter of main channel		6.5 Å	7.5 Å	15 Å
Number of tetrahedra per ring		12	12	18
Stacking faults		block main channel	do not block main channel	do not block main channel

¹ Fig. 7.² Fig. 1.³ Fig. 2.⁴ Fig. 8.⁵ FF leads to very distorted double four-membered rings.

Group *A* comprises structures in which layers of single six-membered rings and layers of hexagonal prisms are stacked in sequences using various permutations of the three layer positions characteristic of hexagonal close packing. Groups *B*, *C* and *D* correspond to structures listed in columns 3, 4 and 5 in Table 4.

Acknowledgements

Thanks are due to Prof. W. M. MEIER and Prof. D. ROGERS and Dr. I. S. KERR for helpful discussions, to Miss R. OSBORN of the University of London Intercollegiate Research Service for diffractometer measurements and to Mrs. G. VILLIGER-JÄGGI for intensity measurements. One of us (H.V.) is indebted to the Science Research Council for a grant which enabled him to take part in this work.

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