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The Crystal Structure of Synthetic Zeolite K–*F*

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The crystal structure of a synthetic zeolite K–*F*, $K_{13}(OH)_3(H_2O)_{13}Si_{10}Al_{10}O_{40}$ ($Z=1$) has been solved using powder data. Zeolite K–*F* has been indexed on a tetragonal primitive cell with parameters $a=9{\cdot}896\pm0{\cdot}004$ and $c=13{\cdot}154\pm0{\cdot}006$ Å ($c/a=1{\cdot}329$). As a starting point for the structural investigation, the edingtonite type framework was used. Difficulties in refining the structure in the experimental space group $P\bar{4}2_1c$ forced us to lower the symmetry to orthorhombic space group *Ccc*2, with $a'\simeq b'=13{\cdot}995$ Å $=a\sqrt{2}$, and $c=13{\cdot}154$ Å. Two types of flattened channels were found. One of the channel types, supposed to contain the OH^- ions, had a much higher content of exchangeable potassium ions. The refinement proceeded to an R_I value of 0·22 after assumption of double positions for some of the potassium ions, of which the occupancies appeared to complement each other to a value of *ca* 1·0.

Introduction

Zeolite K–*F* was first described by Barrer & Baynham in 1956 during an exploratory synthesis in the system K_2O–Al_2O_3–SiO_2–H_2O. Later on, two patents were taken out on zeolite *F*: firstly by Milton in 1961 on its synthesis, secondly by Breck in 1973 for its application to waste-water cleaning because of its high selectivity for uptake of NH_4^+. In addition the synthesis of structural analogues of zeolite K–*F* has been realized in mixed-base systems (Borer, 1969; Barrer & Mainwaring, 1972; Bosmans, Tambuyzer, Paenhuys, Ylen & Vancluysen, 1973). Barrer & Marcilly (1971) also prepared salt-bearing analogues of zeolite K–*F* with KCl, KBr or KI contained in the cages. Zeolite K–*F* shows a high base-exchange capacity (5·3 meq/g) and a very high temperature stability (to above 1050°C) even without stabilization by means of salt in the cages.

Although zeolite K–*F* was an early found and easily synthesized zeolite, its structure remained unsolved. According to Barrer & Marcilly (1971) the strong selectivity of zeolite K–*F* for Ba^{2+} ions would indicate that a naturally occurring variant of zeolite K–*F* might be found in a Ba^{2+}-rich zeolite. Baerlocher (1973) informed us of the close similarity of the X-ray powder pattern of the Ba^{2+}-exchanged K–*F* with that of the rare natural Ba^{2+} zeolite edingtonite. At that time he submitted a paper on the structure of a Na^+-exchanged K–*F* and its Rb^+ analogue (Baerlocher & Barrer, 1974). This similarity was confirmed in our laboratory and so the topological edingtonite framework was the starting point for the structure investigation of zeolite K–*F*.

Experimental

Zeolite K–*F* has been obtained as a white powder by hydrothermal synthesis under many different conditions (Bosmans *et al.*, 1973), but a very pure and well crystallized sample was found by crystallization from a mixture with a relative oxide composition of 20% SiO_2, 10% Al_2O_3 and 70% K_2O (in formula %) and initially 97 formula % of H_2O (against 3 formula % of oxides) kept at 90°C for 10 days and concentrated by slow evaporation until nearly dry. This sample consisted of lath-like crystals with a cross-section of 0·5–3μm as seen by the scanning electron microscope. Attempts to prepare mountable single crystals of zeolite K–*F* using triethanolamine in the mixture (following Charnell, 1971) or by seeding (following Kerr, 1966) were unsuccessful.

Chemical analysis was made after equilibration over a saturated $CaCl_2$ solution (32% relative humidity at 20°C) and gave as oxide formula

$$1{\cdot}32\ K_2O\ ,\quad 1{\cdot}00\ Al_2O_3\ ,\quad 2{\cdot}01\ SiO_2\ ,\quad 3{\cdot}34\ H_2O$$

and only very small amounts of Na_2O and CaO. The large excess of 0·32 K_2O in the formula suggests that OH^- groups are present in the unit cell as in the case of hydroxysodalite which has a similar excess of Na_2O in its structure (Löns & Schulz, 1967). The fact that zeolite K–*F* can be prepared with salt inclusions, as can sodalite polymorphs, adds argument to this evidence. In addition zeolite K–*F* crystallizes in the same composition field of the potassium system as hydroxysodalite in the sodium system of the mixed oxides M_2O–Al_2O_3–SiO_2–H_2O. Sodalite type structures are known to accommodate free anions (Cl^-, CO_3^{2-}, SO_4^{2-}, S^{2-} or OH^-) in the cages of their Si–Al–O framework which can neutralize the excess of exchangeable cations.

X-ray powder diffraction diagrams of zeolite K–*F* were recorded at room temperature on a Philips PW 1050/25 powder diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The indexing of the diagram ($\frac{1}{8}$° 2θ per min) with a Fortran IV program for automatic indexing of powder diagrams (Taupin, 1968) yielded a tetragonal unit cell. The parameters of K–*F* were calculated by least-squares refinement on 27 of the best 2θ values with the program *PARAM* (X-RAY 72 System, 1972) and are given in Table 1.

Table 1. *Comparison of crystallographic parameters* (Å) *and powder data*

	a	*b*	*c*
Zeolite K–*F* (this paper)	9·896 (4)	9·896 (4)	13·154 (6)
Zeolite K–*F* (other sample, Bosmans *et al.*, 1973)	9·82 (1)	9·82 (1)	13·09 (1)
Ca^{2+} exch. K–*F*	9·849	9·849	13·101
Na^{+} exch. K–*F*	10·071	10·071	6·690
Ba^{2+} exch. K–*F*	9·827	9·827	6·570
Edingtonite (ASTM 12-577 recalculated)	9·594	9·588	6·506
Edingtonite (Taylor & Jackson, 1934, recalc.)	9·79 (1)	9·76 (1)	6·58 (2)
Edingtonite (Hey & Bannister Böhlet, 1934)	9·56	9·68	6·53

Powder data (new cell) for this sample of K–*F* (*hkl*=*khl*)

d_o	d_c	hkl	d_o	d_c	hkl	d_o	d_c	hkl
-	9.8960	110		2.6360	333	-	2.0044	226
7.9282	7.9080	111	2.5432	2.5472	423	1.9783	1.9792	550-710
7.0141	6.9976	200		2.5425	115		1.9770	444
6.5830	6.5771	002	2.5356	2.5330	512		1.9755	623
5.4914	5.4776	112	2.4754	2.4740	440	1.9605	1.9645	316
-	4.9480	220	2.4295	2.4314	441	1.9550	1.9572	551-711
4.8010	4.7924	202	2.3983	2.4001	530	1.9442	1.9408	640
4.6562	4.6312	221		2.3962	404		1.9387	534
4.4350	4.4256	310	2.3655	2.3612	531	1.9217	1.9200	641
4.2025	4.1946	311	2.3266	2.3325	600	1.9032	1.9025	604
4.0131	4.0088	113		2.3289	334		1.8992	515
3.9585	3.9540	222		2.3265	513		1.8953	552-712
3.6776	3.6718	312		2.3229	225	1.8600	1.8614	642
3.5052	3.4988	400	2.3151	2.3156	442		1.8578	406
3.2903	3.2987	330	2.2648	2.2670	424	-	1.8462	117
	3.2885	004		2.2614	315	1.8386	1.8376	730
	3.2816	223		2.2547	532		1.8359	624
3.2023	3.1996	331	2.2168	2.2128	620	1.8275	1.8259	336
3.1157	3.1294	420	2.1941	2.1984	602	1.8173	1.8200	731
	3.1207	114		2.1924	006	1.8005	1.8039	553-713
	3.1148	313	2.1809	2.1822	621		1.8023	445
3.0935	3.0889	402	-	2.1547	443		1.7956	426
3.0480	3.0444	421	2.1365	2.1405	116	1.7744	1.7747	643
2.9785	2.9762	204	2.1071	2.1072	514		1.7731	535
2.9402	2.9486	332		2.1054	533		1.7699	732
2.8287	2.8258	422	2.0918	2.0973	622	-	1.7567	227
2.7410	2.7447	510		2.0921	206	1.7523	1.7494	800
	2.7388	224	-	2.0568	335	-	1.7297	317
2.6913	2.6868	511	-	2.0138	425	1.7127	1.7130	516
2.6390	2.6396	314						

To check the reliability of the indexing, de Wolff's (1968) criterion was applied, and resulted in $M_{20}=Q_{20}/(2\bar{\varepsilon}N_{20})=1250/(2\times2\cdot5\times22)=11\cdot4$, which means that the indexing is essentially correct. Zeolite K–*F* and its exchanged forms have unit-cell parameters comparable to those of edingtonite, allowance being made for the *c* parameter which in the original K–*F* and the Ca^{2+}-exchanged forms is double that in edingtonite and the Ba^{2+}-exchanged and Na^{+}-exchanged K–*F* forms, as seen from the presence of peaks which are not otherwise indexable.

For this K–*F* sample an experimental density of 2·44 g cm^{-3} was found with the pyknometer method. The idealized chemical composition of the unit cell of zeolite K–*F* is therefore $K_{13}(OH)_3(H_2O)_{13}Si_{10}Al_{10}O_{40}$. A theoretical density of 2·57 g cm^{-3} for $Z=5$ was calculated. Zeolite K–*F* thus has a low water content of about one H_2O for each K^+-ion. Because the Si/Al ratio is unity, ordering of Si and Al atoms is assumed according to the rule of Loewenstein (1954).

The complete X-ray diffraction pattern gives 78 reflexions (up to 70° 2θ, *i.e.* $\sin\theta/\lambda=0\cdot37$). In order to evaluate the relative intensity of all peaks as accurately as possible, these peaks were recorded three times at a step-scanning rate of 0·04° (2θ) min^{-1} and a chart speed of 300 mm h^-,^{1} redrawn on tracing paper of homogeneous density and weight. The mean of three recordings was then taken as the observed intensity. Because the background was relatively high, the intensity of a less-than-background reflexion was defined as $\frac{2}{3}$ of the smallest intensity found.

The observed intensities were corrected for the Lorentz–polarization and geometric effects for powder specimens. No absorption correction was needed, because a flat specimen of sufficient thickness was used, so that this factor was the same for all peaks (Cullity, 1967).

Structure determination

The unit cell of zeolite K–*F* always contains a multiple of 10 *T* (=Si+Al) atoms. Suitable structural models were found first in a cuborhombododecahedral Si–Al–O framework structure, which also has been described as the δ (001–664) framework by Shoemaker, Robson & Broussard (1973), and in the different combinations of the natrolite motif. A structural calculation on the first model appeared untenable (Tambuyzer, 1972). Further calculations were based on one of these combinations of the natrolite motif, *i.e.* the edingtonite topological framework as suggested by Baerlocher & Barrer (1974). Its structural unit, the natrolite motif, is a group of five tetrahedra joined to form four, four-membered rings and is connected to similar groups along their $\bar{4}$ axes, thus giving chains with a repeat distance of *ca* 6·6 Å. This defines the typical *c* parameter. The unsaturated *T* atoms at the four corners of the units in the chains can only be linked parallel to the *ab* plane in three ways to form the framework types of natrolite, thomsonite and edingtonite (Taylor, 1934).

Edingtonite is a rare natural Ba-zeolite known since 1825, with a chemical composition $Ba_2(H_2O)_8Al_4Si_6O_{20}$. Taylor & Jackson (1933) described the structural type of edingtonite. Here the *T* atoms at the four corners of the natrolite motif are connected at the same height to corresponding *T* atoms of other motifs so as to realize, parallel to the *ab* plane, series of boat-shaped eight-membered rings linking four motif chains. This framework in its most symmetrical form belongs to the tetragonal space group $P\bar{4}2_1m$ (*International Tables for X-ray Crystallography*, 1965, No. 113) if no ordering of Si and Al atoms is assumed, and its unit cell has $a=b\simeq 9{\cdot}8$ and $c\simeq 6{\cdot}6$ Å.

In the case of zeolite K–*F*, however, a double *c* axis of about 13·1 Å is always observed. In addition the extinctions for *hhl* with $l\neq 2n$ indicate a *c* glide plane. Also a 2_1 screw axis is possible because the few independently observed *h*00 have all $h=2n$. The corresponding space group is $P\bar{4}2_1c$ (No. 114). The double *c* axis and this symmetry are necessary requirements if ordering of Si and Al atoms is taken into account. Since the difference in electron density between Si and Al, and the displacement of the oxygens by ordering are in general not sufficient to explain the doubling of the *c* axis and the particular symmetry, more important changes such as the positions of the K^+ ions and the rotation of the motif chains must be involved.

Distance least-squares (DLS) refinement (Meier & Villiger, 1960) was applied to find the ideal atomic positions compatible to the space group requirements. The distances used were the best averages found in silicate structure determinations (Baur, 1971; Brown, Gibbs & Ribbe, 1969; Ribbe & Gibbs, 1969; Shannon & Prewitt, 1969; Smith & Bailey, 1973). The atomic positions found by the DLS procedure gave distances agreeing to within 0·01 Å of the ideal ones. The framework of the space group needs 22 parameters, one of which is fixed by taking the origin at one Al atom. Four possible positions of K^+ were found from difference Fourier syntheses. The atomic scattering factors used were those of Si^{2+}, Al^{2+}, O^- and K^+ (*International Tables for X-ray Crystallography*, 1962).

In order to give a distinct intensity to each reflexion, the observed intensity of a peak containing more than one reflexion was distributed over the reflexions in the peak in proportion to the intensities from the preceding cycle, and this was done with a program, especially designed for such powder problems, combined with X-RAY 72. Difference Fourier was used as a criterion to follow the progress of the refinement. Full-matrix least-squares refinement of the described model ($P\bar{4}2_1c$) lowered the R_I index [defined as $R_I=\sum|I_o-I_c|/\sum I_o$, where $I_c=\sum_n (I_c')_n$ with n = number of *hkl* in one observed peak] from 0·86 to 0·51 after six cycles, after the introduction of the four K^+ positions and even after the introduction of one H_2O position found in a difference Fourier synthesis. However, incorrect interatomic distances and the difficulties in further refinement led us to look for other space groups. Because no other tetragonal space group with a *c* glide plane was found satisfactory, analogous space groups of lower symmetry were tried (as is found with other zeolites). The orthorhombic space group *Ccc*2 (No. 37) has the same glide planes as $P\bar{4}2_1c$. The fourfold inversion axis has to be replaced by a twofold axis. The description of the space group also needs a 45° rotation about the **c** direction so as to give an orthorhombic cell with $a'\simeq b'=13{\cdot}995\pm0{\cdot}006\text{Å}=a\sqrt{2}$ and $c=13{\cdot}154\pm0{\cdot}006$ Å. This space group allows more free rotation of the natrolite motif chains. The unit-cell content is doubled to $K_{26}(OH)_6(H_2O)_{26}Si_{20}Al_{20}O_{80}$.

The edingtonite framework in this space group needs three silicon and three aluminum positions, one of the three being a special position with one variable parameter, and ten oxygens in general positions. The aluminum in the special position is chosen as the origin, thus fixing one variable, giving a total of 43 variables for the framework. Satisfactory initial coordinates were calculated with the distance least-squares program DLS as before. The R_I for the thus calculated intensities was 0·80. As a result of the analysis of Fourier and difference Fourier maps (X-RAY 72) made at this point, five K^+ positions with estimated occupancies were introduced. The R_I fell to 0·55. A series of full-matrix least-squares cycles was then applied to the intensities and when over-divergent Si–O or Al–O distances were observed, the oxygen positions were corrected by DLS, before continuing with parameter refinement. In this way, R_I was reduced to 0·38.

The 43 framework parameters together with the 11 K^+ ion positional parameters and five site occupancy parameters give 59 parameters compared to the 95 independent data (78 observed reflexions and 17 so-called less-than-background reflexions) and 288 possible *hkl* values for this non-centrosymmetric space group *Ccc*2. This low ratio of observations to parameters explains

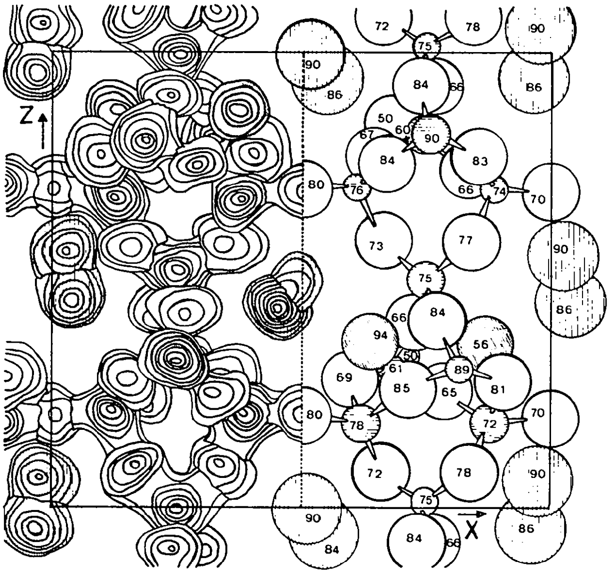

Fig. 1. The unit cell of zeolite K–*F* (outlined by a full line) is represented half as given by a Fourier synthesis, half on the basis of the final atomic positions. Only the upper half of the cell in the *y* direction is shown with heights given in hundredths. K(1), K(2), K(2′) and K(5) positions are left out for the sake of clarity. In the sphere representation, silicon and aluminum (horizontal shading) are shown with radii proportional to the 'crystal radii' given by Fumi & Tosi (1964), while K (vertical shading), H_2O or OH (oblique shading) and O (unshaded) have only $\frac{2}{3}$ of the 'crystal radii'.

why full-matrix least-squares methods are not very efficient in this case and may lead to false minima. Repeated difference Fourier syntheses were therefore necessary to enable us to overcome this difficulty. Thöni (1973) showed that a minimum of twice as many observations as variables is necessary to obtain correct positions with the least-squares method. A greater number of data has little effect on the positions but diminishes their standard deviations.

For these reasons we tried to lower the number of variables by introducing complete tetrahedral SiO_4 groups, calculated by DLS, instead of the individual atoms, together with free Al and K^+. This was justified because it is known that Si–O distances and O–Si–O angles are constant (Baur, 1971; Brown, Gibbs & Ribbe, 1969; Ribbe & Gibbs, 1969; Shannon & Prewitt, 1969; Smith & Bailey, 1973) while Si–O–Al angles may vary rather strongly. The group refinement procedure (X-RAY 72) was used for this and we thus lowered the number of framework variables from 43 to 24. At this point of the refinement, difference Fourier methods forced us to consider double positions for three of the five potassium ions. The refinement of the occupancies of these double K^+ positions always led to a sum of about 1·00. One H_2O or OH^- position was also introduced. In this way the R_I value decreased

Table 2. *Atomic positions and their standard deviations* (Å)

	x	y	z	Occupancy
Si(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·5132 (40)	
Si(2)	0·3880 (21)	0·2403 (21)	0·2045 (38)	
Si(3)	0·1798 (18)	0·1118 (18)	0·8076 (46)	
Al(1) = origin	$\frac{1}{4}$	$\frac{1}{4}$	0	
Al(2)	0·3777 (17)	0·2195 (15)	0·6840 (22)	
Al(3)	0·2437 (16)	0·1010 (15)	0·3238 (23)	
O(1)	0·3388 (48)	0·2697 (43)	0·0881 (50)	
O(2)	0·3341 (39)	0·1556 (38)	0·2449 (54)	
O(3)	0·1386 (38)	0·1682 (37)	0·2738 (47)	
O(4)	0·2644 (35)	0·1620 (41)	0·4284 (47)	
O(5)	0·3407 (47)	0·2784 (43)	0·5779 (47)	
O(6)	0·2864 (37)	0·1467 (42)	0·7673 (52)	
O(7)	0·4027 (39)	0·3072 (39)	0·7766 (48)	
O(8)	0·2273 (36)	0·1594 (39)	0·9096 (44)	
O(9)	0·5008 (56)	0·2006 (33)	0·6994 (49)	
O(10)	0·1755 (34)	−0·0062 (45)	0·3431 (47)	
K(1)	0	$\frac{1}{2}$	0·6855 (45)	0·82 (4)
K(2)	0·2283 (16)	0·4998 (22)	0·5645 (37)	0·82 (3)
K(2′)	0·2723 (40)	0·5384 (39)	0·6324 (61)	0·26 (4)
K(3)	0·4547 (16)	0·1598 (17)	0·4448 (42)	0·81 (3)
K(3′)	0·0121 (46)	0·4011 (36)	0·4974 (62)	0·25 (3)
K(4)	0·0375 (19)	0·1387 (20)	0·4535 (44)	0·57 (3)
K(4′)	0·4763 (28)	0·3977 (23)	0·5561 (48)	0·46 (4)
K(5)	0	0	0·7398 (58)	0·55 (11)
OH	0·1309 (32)	0·4410 (33)	0·8651 (58)	1·00 (8)

Table 3. *Interatomic distances and standard deviations* (Å)

Al(1)–O(1)	1·72 (7)	Si(1)–O(4)	1·67 (7)	K(1)–OH	3·10 (8)	K(5)–O(7)	3·06 (6)
Al(1)–O(8)	1·77 (6)	Si(1)–O(5)	1·58 (7)	K(1)–O(9)	2·81 (5)	K(5)–O(3)	3·08 (5)
Al(2)–O(5)	1·70 (8)	Si(2)–O(1)	1·73 (8)	K(1)–O(2)	3·28 (6)	K(5)–O(10)	2·81 (6)
Al(2)–O(6)	1·89 (7)	Si(2)–O(2)	1·50 (7)	K(2)–O(5)	3·48 (7)	K(2′)–O(6)	3·17 (9)
Al(2)–O(7)	1·76 (7)	Si(2)–O(3)	1·61 (7)	K(2)–O(6)	3·27 (8)	K(2′)–O(2)	2·66 (9)
Al(2)–O(9)	1·75 (8)	Si(2)–O(9)	1·65 (8)	K(2)–O(4)	2·89 (7)	K(2′)–O(3)	2·88 (9)
Al(3)–O(4)	1·64 (9)	Si(3)–O(6)	1·70 (6)	K(2)–O(10)	3·21 (8)	K(2′)–O(10)	2·93 (10)
Al(3)–O(2)	1·81 (7)	Si(3)–O(7)	1·67 (6)	K(2)–O(2)	3·33 (7)	K(2′)–O(8)	3·38 (9)
Al(3)–O(3)	1·87 (6)	Si(3)–O(8)	1·64 (8)	K(2)–O(8)	3·09 (7)	K(2′)–O(1)	2·90 (8)
Al(3)–O(10)	1·80 (7)	Si(3)–O(10)	1·55 (7)	K(2)–OH	3·07 (8)		
mean	1·77 (7)	mean	1·63 (7)	K(4)–O(3)	2·79 (8)	K(4′)–O(5)	2·54 (7)
K(3)–O(5)	2·89 (7)	K(3′)–O(5)	3·42 (9)	K(4)–O(4)	3·21 (6)	K(4′)–O(7)	3·33 (8)
K(3)–O(9)	3·46 (8)	K(3′)–O(9)	3·02 (10)	K(4)–O(10)	3·15 (7)	K(4′)–O(9)	3·36 (7)
K(3)–O(2)	3·12 (8)	K(3′)–O(4)	3·37 (8)	K(4)–O(5)	2·63 (8)	K(4′)–O(1)	3·17 (7)
K(3)–O(4)	2·67 (5)	K(3′)–OH	2·71 (9)	K(4)–O(7)	3·09 (8)		
K(3)–O(9)	3·34 (8)	K(3′)–OH	3·27 (9)	K(2)–K(2′)	1·21 (8)		
K(3)–OH	3·45 (6)			K(3)–K(3′)	1·19 (7)		
K(3)–OH	3·03 (6)			K(4)–K(4′)	1·46 (8)		

relatively quickly to 0·29 and, after releasing the group condition, to 0·22 ($R_F=0\cdot12$).*

To keep the number of variables low, only an overall temperature factor was refined. This general temperature factor was set to 2·0 Å^2 and during refinement, the equation $\ln F_o^2/F_c^2=\ln 1/C-2B(\sin\theta/\lambda)^2$ (C=scale factor) was used to correct it. The final value was $B=1\cdot20\pm0\cdot20$ Å^2. Four different weighting schemes were tried out on the basis of observed standard deviations, or on the basis of equations used in the programs *WTLSSQ* and *WTANAL* (X-RAY 72). Another weighting scheme was tested with individual weights given to the observed peaks depending on the number of reflexions they contained, the intensity of the peak, and the standard deviation of the intensity. All tested schemes gave a worsening rather than an improvement of the refinement so that it seemed better to give unit weights to all reflexions. The fact that at the end of the refinement only a small residual background noise was found in the difference Fourier synthesis, indicates that the refinement had reached a satisfactory level. The final atomic parameters are shown in Table 2 and the most important interatomic distances in Table 3.

Discussion

The framework of zeolite K–*F* is similar to that of edingtonite. The pseudotetragonal configuration of the unit cell (Fig. 1) ensures that the distances between the central Si and Al atoms in the chains are the same in the **a** and the **b** direction. However, the twisting of the units creates flattened channels along the *c* axis, so that neighbouring channels are alternately oriented along the **a** and the **b** directions. This is found in the structure of Ba^{2+} edingtonite (Taylor & Jackson, 1933) but not in the Rb^+ and Na^+ analogues of synthetic zeolite *F* (Baerlocher & Barrer, 1974). In zeolite K–*F* however the channels with a flattening following one direction (*A* channels) differ from those flattened following the other direction (*B* channels), both in configuration and in content.

The best agreement is found for a structure in which the *A* channels have about double the potassium ion content of the *B* channels. Although OH^- ions or H_2O molecules have much lower electron densities than the potassium ions, difference Fourier methods allowed us to introduce one set of supposed OH^- ions into the *A* channels (eight positions compared with about six reported OH^- ions and 20 reported H_2O molecules). The presence of these OH^- ions explains the relative excess of potassium in the *A* channels as well as the excess in the complete structure (*cf.* sodalite) as shown by chemical analysis (26 K^+ ions against 20 Al atoms).

The double positions for the potassium ions may be considered as an indication that the filling of the channels is not the same in the whole structure. This can be interpreted in the following way. In about 80% of the structure the *A* channels have two central K(1) ions (occupancy=0·82) together with four K(2) ions (0·82) and four K(3) ions (0·81) near the walls of the channels. In about 20% of the structure the central K(1) ions are absent so that the four K(3′) (double) positions (0·25) move nearer to the centre of the channel and the K(2′) (double) positions (0·26) withdraw somewhat from this centre. In the *B* channels two central K(5) (0·55) are found in about half of the structure and four K(4) (0·57) near the walls in the long direction of the channel. In the other half of the structure, the central K(5) ion is absent and the K(4′) (double) position (0·46) moves towards the centre. The presence of double positions has also been found for Rb^+ in the Rb^+ analogue of zeolite *F* (Baerlocher & Barrer, 1974).

Although the interatomic distances are in general in relatively good agreement with the accepted values, some less satisfactory distances for some oxygens may be due to unresolved double positions associated with the double potassium positions.

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Samenvatting

De kristalstruktuur van een synthetisch zeoliet K–*F*, $K_{13}(OH)_3(H_2O)_{13}Si_{10}Al_{10}O_{40}$ ($Z=1$) werd ontrafeld uitgaande van poedergegevens. Zeoliet K–*F* werd geïndexeerd als een tetragonale primitieve cel met parameters $a=9{,}896\pm0{,}004$ en $c=13{,}154\pm0{,}006$ Å. Als uitgangsbasis voor de verfijning werd het edingtonietskelet aangenomen. Moeilijkheden bij de verfijning in de experimentele ruimtegroep $P\bar{4}2_1c$, dwongen ons de symmetrie te verlagen tot de orthorhombische ruimtegroep *Ccc*2, met $a'\simeq b'=13{,}995$ Å$=a\sqrt{2}$ en $c=13{,}154$ Å. Twee types afgeplatte kanalen werden bekomen. Eén dezer kanaaltypes, waarvoor een OH^--ionenbezetting aangenomen werd, bevatte ook heel wat meer uitwisselbare Kaliumionen. De verfijning vorderde zo tot een R_I-eindwaarde van 0,22 mits aanname van dubbelplaatsen voor sommige Kaliumionen, waarvoor een complementaire bezetting van ongeveer 1,0 gevonden werd.

References

Baerlocher, C. (1973). Private communication.

Baerlocher, C. & Barrer, R. M. (1974). *Z. Kristallogr.* **140**, 10–26.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31549 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Barrer, R. M. & Baynham, J. W. (1956). *J. Chem. Soc.* pp. 2882–2891.
Barrer, R. M. & Mainwaring, D. E. (1972). *J. Chem. Soc. Dalton*, pp. 2534–2546.
Barrer, R. M. & Marcilly, C. (1971). *J. Chem. Soc.* (*A*), pp. 2735–2745.
Baur, W. D. (1971). *Amer. Min.* **56**, 1573–1589.
Borer, H. (1969). *Synthese von Zeolitischen Alumosilikaten im System* Li_2O–Na_2O–Al_2O_3–SiO_2–H_2O, Thesis, Diss. no. 4308, ETH, Zürich.
Bosmans, H. J., Tambuyzer, E., Paenhuys, J., Ylen, L. & Vancluysen, J. (1973). *Advanc. Chem. Ser.* **121**, 15, 179–188.
Breck, D. W. (1973). *Process for Removal of Ammonia from Waste Water Streams* USP 3, 723, 308 Mar. 27, 1973.
Brown, G. E., Gibbs, G. V. & Ribbe, P. M. (1969). *Amer. Min.* **54**, 1044–1061.
Charnell, J. F. (1971). *J. Cryst. Growth*, **8**(3), 291–294.
Cullity, B. D. (1967). *Elements of X-Ray Diffraction*, 3rd ed., pp. 188–190. Reading, Mass.: Addison-Wesley.
Fumi, F. G. & Tosi, M. P. (1964). *J. Phys. Chem. Solids*, **25**, 31.
Hey, M. H. & Bannister Böhlet, F. A. (1934). *Miner. Mag.* **23**, 144, 483–494.
International Tables for X-ray Crystallography (1965). Vol. I, 2nd ed. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III, 201–212. Birmingham: Kynoch Press.
Kerr, G. T. (1966). *J. Phys. Chem.* **70**, 1047.
Loewenstein, W. (1954). *Amer. Min.* **39**, 92.
Löns, J. & Schulz, H. (1967). *Acta Cryst.* **23**, 434–436.
Meier, W. M. & Villiger, H. (1969). *Z. Kristallogr.* **129**, 411–423.
Milton, R. M. (1961). *Crystalline Zeolite F*, USP 2, 996, 358 Aug. 15, 1961.
Ribbe, P. M. & Gibbs, G. V. (1969). *Amer. Min.* **54**, 85–94.
Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* B**25**, 925–946.
Shoemaker, D. P., Robson, M. E. & Broussard, L. (1973). Proc. Third Int. Conf. Mol. Sieves, Zürich, edited J. B. Uytterhoeven, Univ. of Leuven.
Smith, J. V. & Bailey, S. W. (1963). *Acta Cryst.* **16**, 801–811.
Tambuyzer, E. (1972). *Onderzoek naar de struktuur van de synthetische zeolieten F, W, J, H en V*, Thesis, K.U. Leuven.
Taupin, D. (1968). *J. Appl. Cryst.* **1**, 178.
Taylor, W. H. (1934). *Proc. Roy. Soc.* A**145**, 80–103.
Taylor, W. H. & Jackson, R. (1933). *Z. Kristallogr.* **86**, 53–64.
Thöni, W. (1973). *Methodische Aspekte der Strukturanalyse mittels Pulverdaten*, Thesis, Diss. no. 5038, ETH, Zürich.
Wolff, P. M. de (1968). *J. Appl. Cryst.* **1**, 108.
X-RAY 72 System (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Hydroxyl Orientations in Gibbsite and Bayerite

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The hydrogen positions in bayerite and gibbsite [both $Al(OH)_3$] have been determined by minimizing the electrostatic energy as a function of hydroxyl orientation for a fixed O–H distance. The hydrogen positions in gibbsite are known from an accurate X-ray refinement and one of the H–H distances is short (2·122 Å). The point charge model (fully ionized atoms) separates these hydrogens resulting in deviations from the observed OH orientations of approximately 18°. Several models with reduced charges on the ions were refined with no improvement in the hydroxyl orientations. The addition of a modifying function to simulate sp^3 hybridization of the oxygens resulted in hydrogen positional parameters which are within two standard deviations (X-ray) of the X-ray refinement for 16 of the 18 positional parameters. Hydrogen positions have been determined for all six geometrically possible hydroxyl orientations and the correct one has the lowest electrostatic energy. There are three geometrically possible hydroxyl orientations for bayerite and all three have been refined. The model with the lowest energy has, between the layers, one hydroxyl nearly normal to the hydroxide layer, (001), participating in a single hydrogen bond, a second hydroxyl inclined at 58·3° to (001) participating in a single hydrogen bond and a third hydroxyl in the surface of the hydroxide layer participating in a bifurcated bond.

Introduction

The naturally occurring polymorphs of $Al(OH)_3$ are the minerals gibbsite, bayerite and nordstrandite. Gibbsite is readily found in nature; but both bayerite and nordstrandite are extremely rare and yet bayerite, and to a lesser extent nordstrandite, are readily precipitated under alkaline conditions while gibbsite forms very slowly (Schoen & Roberson, 1970). Several mechanisms have been proposed to explain the appearance of one