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The crystal structure of synthetic zeolite *F*

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Auszug

Die Kristallstrukturen von zwei Varianten des synthetischen Zeoliths K-*F*, nämlich von Na^{ex}K-*F* und Rb-*D*, wurden aus Daten von Pulveraufnahmen bestimmt. Die Strukturen beruhen auf einem Gerüst des Edingtonit-Typs, welches sich aus Ketten, ähnlich den beim Natrolith gefundenen, aufbaut.

Na^{ex}K-*F* wurde auf der Grundlage einer primitiv-tetragonalen Zelle mit den Gitterkonstanten $a = 10{,}056$ Å und $c = 6{,}68$ Å indiziert und seine Struktur in der Raumgruppe $P\bar{4}2_1m$ bis zu $R_I = 0{,}17$ verfeinert. Die Zelle von Rb-*D* erwies sich als tetragonal-raumzentriert mit $a = 9{,}978$ Å und $c = 13{,}215$ Å. Die Strukturverfeinerung erfolgte in der Raumgruppe $I222$; Endwert von R_I war 0,14. Beide Strukturen sind pseudosymmetrisch; die wahre Symmetrie muß geringer als hier angegeben sein. Die Kationen befinden sich in zwei verschiedenen Lagen. Im Rb-*D* wurde beträchtliche Unordnung der Kationenverteilung beobachtet. Zur Erklärung der Entstehung von Unordnung wird ein Mechanismus vorgeschlagen; es wird angenommen, daß die Unordnung ihrerseits die beobachtete Pseudosymmetrie verursacht.

Abstract

The crystal structures of two variants of the synthetic zeolite K-*F*, namely Na^{ex}K-*F* and Rb-*D*, were solved using powder data. The structures are based on the edingtonite-type framework, which is built from chains similar to those found in natrolite.

Na^{ex}K-*F* has been indexed on a tetragonal primitive unit cell with parameters $a = 1.0056$ nm and $c = 0.668$ nm. The structure was refined in space group $P\bar{4}2_1m$ to an $R(I)$ value of 0.17. The Rb-*D* cell was found to be tetragonal body centred with cell dimensions $a = 0.9978$ and $c = 1.3215$ nm. However, space group $I222$ had to be used for the structure refinement, which proceeded to an $R(I)$ value of 0.14. Both structures are pseudosymmetric and their true symmetry must be still lower.

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The cations are located in two different sites. In Rb-*D* considerable disorder was observed in these cation positions. A mechanism is proposed for the occurrence of this disorder, which in turn is thought to be mainly responsible for the observed pseudosymmetry.

Introduction

In 1956 BARRER and BAYNHAM reported the synthesis of a new synthetic potassium zeolite, termed K-*F*, which had no apparent natural counterpart. Since then a large number of different synthetic species have been identified as variants of K-*F* by means of their powder diffraction patterns. The species N and O of BARRER, HINDS and WHITE (1953), for example, were shown by BARRER and MARCILLY (1970) to be KCl- and KBr-bearing phases of K-*F*. BARRER, COLE and STICHER (1968) identified the zeolite Rb-*D* reported by BARRER and MCCALLUM (1953) as a variant of K-*F*. Additionally, zeolite *F* can be prepared from systems containing mixed bases. A summary of the different crystallization fields in which variants of zeolite *F* are obtained was given by BARRER and MAINWARING (1972). The diversity of these syntheses made zeolite *F* one of the most important synthetic zeolite species whose structure had not then been determined.

The first step towards solving the crystal structure of this zeolite was taken by MAINWARING (1970). He was able to index the pattern of Rb-*D* on the basis of a body-centred tetragonal unit cell with dimensions $a = 0.998$ nm and $b = 1.323$ nm. Because these dimensions resemble those of natural edingtonite, MAINWARING (1970) suggested that the structure might be based on the edingtonite-type framework. This proposal was taken as the starting point for the present structural investigation, in which the following three cationic forms were examined: $\mathrm{Na}^{\mathrm{ex}}$ K-*F*, Rb-*D* and to a lesser extent K-*F*.

Experimental

It had been shown (BARRER, BAYNHAM, BULTITUDE and MEIER, 1959) that K-*F* tends to crystallize with a Si/Al ratio of 1. Similarly, Rb-*D* prepared by Dr. D. E. MAINWARING had an oxide formula of

$$\mathrm{Rb_2O,\ Al_2O_3,\ 2SiO_2,\ 2.6\ H_2O}\ .$$

Its density was found to be 2.75 g/cm³. The Na-exchanged form of K-*F* was obtained by ion exchange with a 1 M NaCl solution at 80 °C. It can be inferred from the broadening of the powder lines that some break-up of crystals occurred during the exchange. All samples were equilibrated over a saturated calcium nitrate solution (relative humidity 51% at 24 °C) for at least two weeks. The water content of species $Na^{ex}K$-*F*, Rb-*D* and K-*F* was determined with a Stanton Thermobalance and found to be 18.5%, 10.3% and 12.3% respectively.

The *d* values were obtained from a Guinier photograph, taken with Cu$K\alpha$ radiation. Lead nitrate ($a = 0.78404$ nm) was used as internal standard. The indexing resulted in the following refined cell parameters:

$Na^{ex}K$-*F*: tetragonal primitive with
$a = 1.0056 \pm 0.0002$ nm
$c = 0.6680 \pm 0.0002$ nm

Rb-*D*: tetragonal body centred with
$a = 0.9978 \pm 0.0001$ nm
$c = 1.3215 \pm 0.0002$ nm

K-*F*: orthorhombic primitive with
$a = 1.3921 \pm 0.0004$ nm
$b = 1.4011 \pm 0.0004$ nm
$c = 1.3136 \pm 0.0004$ nm

Two weak lines of the $Na^{ex}K$-*F* pattern can only be indexed on the basis of a cell with a doubled *c* dimension. The pattern of K-*F* was successfully indexed on an orthorhombic unit cell which is four times as large as that of the Na-exchanged form. All reflections requiring the enlargement are weak or very weak. From the above results the following ideal unit cell contents can be calculated for the three forms:

$$Na_5Al_5Si_5O_{20} \cdot 9\,H_2O$$

$$Rb_{10}Al_{10}Si_{10}O_{40} \cdot 13\,H_2O$$

$$K_{20}Al_{20}Si_{20}O_{80} \cdot 25\,H_2O$$

Because the *a* and *b* cell parameters of K-*F* are almost identical, a large number of reflections overlap so closely that their intensities cannot be resolved. However, their resolution is vital for a successful structure determination. In addition to this, many of the important reflections which require the doubling of the unit-cell parameters are so weak that they can hardly be observed in the relatively high background of the powder pattern. Therefore, it was not found possible to determine the structure using the powder method. Attempts to grow larger crystals for single-crystal analysis by the method of CHARNELL

(1971) were only partly successful. Strong twinning and break-up made the crystals unsuitable for single-crystal analysis. Nevertheless, it was possible to confirm the indexing of the powder pattern by oscillation and Weissenberg photographs. However, there was some indication that the true *a* and *b* parameters may be as large as 1.96 nm.

The x-ray powder patterns were obtained with a Philips PW 1050/25 powder diffractometer using Co$K\alpha$ radiation for the $\mathrm{Na^{ex}K}$-*F* and Cu$K\alpha$ for Rb-*D*. A numerically controlled step-scan device (Frost and Whitehead, 1970) was used, which punched the output on paper tape. With the aid of the computer program CUFIT (Thoeni, 1972) partially overlapping peaks were resolved. For the least-squares refinement individual weights have been assigned to the intensities according to the counting rate and the degree of overlapping. A total of 84 reflections was obtained for both the $\mathrm{Na^{ex}K}$-*F* and the Rb-*D* form, and of these 28 and 14 reflections respectively had to be classified as unobserved. No absorption correction was applied.

Structure determinations

The rare mineral edingtonite has the idealized chemical composition $\mathrm{Ba_2Al_4Si_6O_{20}\cdot 8H_2O}$. It is reported to have either tetragonal or orthorhombic cell parameters with *a* and *b* about 0.96 nm and $c = 0.653$ nm (Hey and Bannister, 1934). The structure has been determined by Taylor and Jackson (1933). They used the tetragonal space group $P\bar{4}2_1m$ but pointed out that the true symmetry of edingtonite was probably $P2_12_12$. A stereoscopic drawing of the framework is presented in Fig. 1. The structure is built up from chains similar to those found in natrolite and thomsonite. These chains are joined together and rotated in such a way that perpendicular to *c* (chain axis) a boat-shaped eight-membered ring is formed. From a topological point of view there are two different (Si,Al) positions [marked T(1) and T(2)] and three different oxygen atoms [designated O(1), O(2) and O(3)]. In natural edingtonite the $\mathrm{Ba^{2+}}$ ion is located in position C(1) in front of the eight-membered ring.

The main reasons why it was thought that the structure of zeolite *F* is based on the edingtonite-type framework are as follows:

(*i*) All variants of K-*F* which have been indexed have a pseudocell of roughly $1.0\times 1.0\times 0.65\ \mathrm{nm^3}$. This is in good agreement with the lattice constants of edingtonite. The *c* parameter of 0.65 nm is an especially strong indication that the structure could be based on the so-called natrolite chain.

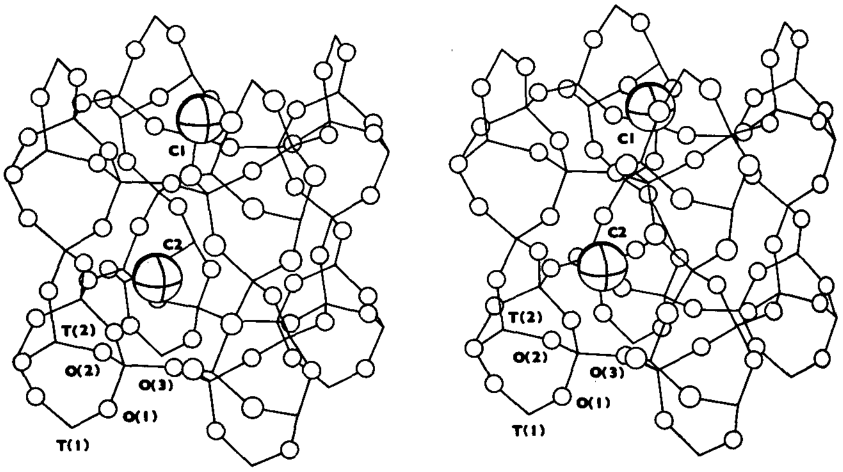

Fig. 1. Stereoscopic drawing of the edingtonite-type framework structure. The principal cation positions C(1) and C(2) are also shown

(*ii*) HEY and BANNISTER (1934) prepared the potassium exchanged form of edingtonite and found that each cell parameter was at least doubled. This is similar to the doubling of the unit cell found for K-*F*.

(*iii*) The powder pattern of the Ba-exchanged form of K-*F* is strikingly similar to that of natural edingtonite. Additionally, the K-exchanged form of synthetic (Ba,Li) edingtonite (BARRER, COLLELA and BEAUMONT, 1972, private communication) is almost identical with that of K-*F* (Fig. 2).

(*iv*) BARRER and BAYNHAM (1956) carried out some sorption experiments on various cationic forms of K-*F*. They found no uptake of oxygen or argon at 90 °K. This is consistent with the behaviour expected of a zeolite with the edingtonite-type framework.

(*v*) Ion exchange experiments by BARRER and MUNDAY (1971) showed that K-*F* has a high selectivity for Ba^{2+}. The Ba^{2+} ions are trapped in the crystal and they cannot be exchanged under mild hydrothermal conditions. This preference for the Ba^{2+} ions is in line with the composition of natural edingtonite.

Refinement of $\mathrm{Na^{ex}K}$-*F*

The sodium exchanged form of K-*F* was chosen for the initial structure determination. It has the smallest unit cell and since the contri-

Table 1. *Parameters of hydrated* Na^{ex} K-*F*, *based on space group* $P\bar{4}2_1m$

Atom	Position	Occupancy factor[a]	x	y	z	B[b]
(Si,Al)(1)	2*a*	1.0	0	0	0	0.045 nm^2
(Si,Al)(2)	8*f*	1.0	$0.127 \pm 0.002_5$	$0.134 \pm 0.002_5$	0.375 ± 0.003	0.010
O(1)	8*f*	1.0	0.099 ± 0.005	$0.093_5 \pm 0.005_5$	$0.133_5 \pm 0.005_5$	0.027
O(2)	8*f*	1.0	-0.018 ± 0.006	$0.184_5 \pm 0.004$	$0.466_5 \pm 0.009$	0.037
O(3)	4*e*	1.0	$0.240 \pm 0.004_5$	0.260	0.389 ± 0.009	0.009
I	4*e*	0.78	0.242 ± 0.005	0.258	-0.059 ± 0.010	0.019
IIa	4*e*	0.92	-0.101 ± 0.006	0.399	$0.324_5 \pm 0.009$	0.026
IIb	2*c*	0.60	0	1/2	0.325 ± 0.022	0.004
IIIa	4*e*	0.50	0.147 ± 0.010	0.353	-0.272 ± 0.016	0.017
IIIb	4*e*	0.52	$0.112_5 \pm 0.010$	0.387_5	$-0.054_5 \pm 0.015$	0.018
IV	2*c*	0.36	0	1/2	-0.181	0.018

[a] Estimated standard deviation of the order of 0.08 for the non-framework atoms.

[b] Estimated standard deviation of 0.005—0.015 nm^2 and 0.02—0.04 nm^2 for the framework atoms and sites I—IV, respectively.

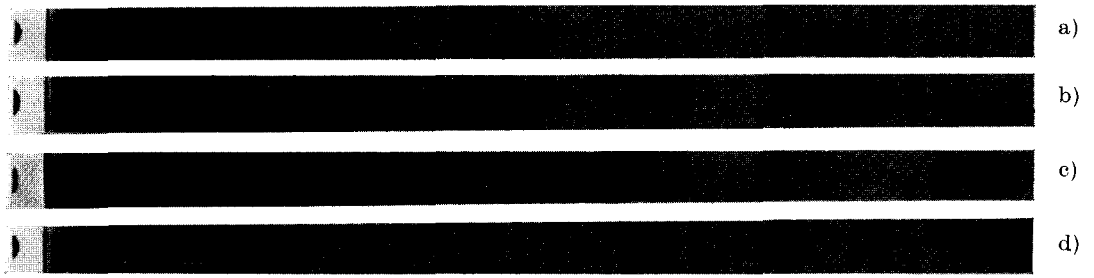

Fig. 2. Guinier photographs of a) Rb-*D*, b) K-*F*, c) K^{ex}-(Ba,Li) edingtonite and d) edingtonite

bution of the cation is small, it was expected that the framework structure could be determined unambiguously.

In the structure refinement space group $P\bar{4}2_1m$ was assumed. This space group does not allow a distinction between Si and Al. Initial framework coordinates were calculated with the aid of the distance least-squares program DLS (MEIER and VILLIGER, 1969) using a mean T—O distance of 0.1681 nm. The satisfactory agreement of the DLS refinement indicated that the above symmetry assumption was acceptable.

Difference Fourier maps revealed the peaks I to IV in the channels, some of which were overlapping. Initially these were refined together with the framework atoms by means of F_o and F_c maps. For the non-framework atoms the scattering factor of O^- was used. The convergence of the refinement was relatively slow, but an $R(I)$ value* of about 0.22 was eventually reached. The least-squares refinement was then commenced and after several cycles the $R(I)$ value dropped to 0.17. A plot of the observed and calculated powder diffractograms is shown in Fig. 3

Table 2. *Some interatomic distances in* $Na^{ex}K$-*F*

T(1)—O(1)	0.163 nm	I —O(1)	0.255 nm
T(2)—O(1)	0.169 nm	IIa—O(2)	0.25 nm
—O(2)	0.166 nm		
—O(2)	0.168 nm	IIIa—O(2)	0.295 nm
—O(3)	0.170 nm	—O(3)	0.26 nm
mean	0.166 nm	IIIb—O(1)	0.32 nm

The final atom parameters are listed in Table 1 and the interatomic distances which are of interest in Table 2. The estimated standard deviation is around 0.01 nm for the T—O distances and 0.015—0.02 nm for the distances involving non-framework atoms.

Refinement of Rb-*D*

Rb-*D* had been indexed on a body-centred unit cell. In order to fit the edingtonite-type framework into this cell, its chains have to be twisted in such a way that, looking along the chains, alternate O(3) atoms (Fig. 1) point in opposite directions. At first sight it may seem that this twisting of the chains will result in a considerable distortion of the TO_4 tetrahedra. However, it was possible to show by DLS calcu-

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* Defined as $R(I) = \frac{\Sigma|I_o - I_c|}{\Sigma I_o}$, where $I_c = \Sigma m_i F^2_{c,i}$, m = multiplicity.

lations that an acceptable agreement between prescribed and calculated distances can be obtained, even when assuming the highest possible symmetry $I\bar{4}2m$.

This space group was used to start the refinement. The first difference Fourier map showed two peaks near the positions C(1) and C(2) (Fig. 1). The peak at C(2) was elongated along [110] and could not be attributed to one atom position only. It was interpreted as an overlap of two or more positions caused by the assumption of too high a symmetry. But it was decided not to reduce the symmetry at this stage and instead to refine the Fourier peak with three partially occupied Rb positions. Including these positions together with the Rb position at site C(1) reduced the $R(I)$ value from 0.70 to 0.38. Several Fourier cycles were calculated during which a second position near C(1) was located, overlapping with the first one. This and the unusually slow convergence of the refinement were taken as strong indication that the symmetry had to be reduced. Unfortunately, the data would only allow a symmetry reduction of the order of two at the most.

The twisting of the chains in the structure, imposed by the body centering of the lattice, is somewhat unexpected. Therefore, the feasibility of indexing the pattern on the basis of a primitive cell was tested. It was found that only about 10 reflections of the pattern with $h + k + l = 2n + 1$ were clearly separated from other reflections. Since these odd reflections could be accidentally extinct or very weak, it was thought worthwhile to try to refine the structure on the assumption of a primitive space group. Space groups $P\bar{4}2_1m$ and $P\bar{4}2_1c$ were used for this test. However, the refinement did not proceed satisfactorily in either case. Some of the unobserved odd reflections had persistently large calculated intensities. These could only be made small by rotating the chains in such a way that the angle at O(3) approached 180°. This behaviour can be interpreted as indicating that after all the chains are twisted. Since in addition to this the elongated peaks could not be resolved and the number of variables was unacceptably high, the refinement in the primitive space groups was abandoned.

In a final attempt the symmetry was reduced to $I222$. However, in order to keep the number of parameters within reasonable limits, the mirror plane along [110] was retained for the framework atoms, thus imposing the original symmetry $I\bar{4}2m$ on the framework. This compromise was thought to be justified, since deviations of the heavier Rb^+ ions from the higher symmetry have a greater effect on the intensities than do deviations of the lighter framework atoms. With this symmetry assumption a satisfactory agreement was reached after several Fourier and least-squares cycles. However, the overlapping positions could not be resolved. The final $R(I)$ value was 0.14.

Table 3 lists the observed and calculated values of the corrected intensities. The atom parameters of the last cycle are shown in Table 4 and some of the interatomic distances in Table 5. The estimated standard deviation of the T—O distances lies between 0.008 and 0.013 nm. For the Rb—O distances it is around 0.011 nm. An F_0 Fourier section based on the phases calculated from the final parameters is presented in Fig. 4. It shows the electron distribution along the pseudo-mirror plane.

Table 3. *Observed and calculated intensities of* Rb-*D* ($I_c = \Sigma m_i F^2_{c,i}$)

h k l	I_c	I_o
1 0 1 0 1 1	1	1
1 1 0	55	54
0 0 2	12	12
2 0 0 0 2 0	9	9
1 1 2	10	7
2 1 1 1 2 1	29	27
1 0 3 0 1 3	8	10
2 0 2 0 2 2	29	18
2 2 0	413	412
0 0 4	57	55
3 0 1 0 3 1	11	24
3 1 0 1 3 0 2 1 3 1 2 3 2 2 2	1343	1430
1 1 4	1277	1391
3 1 2 1 3 2	1797	1552
2 0 4 0 2 4	93	129
3 2 1 2 3 1	17	63
3 0 3 0 3 3	2	12
1 0 5 0 1 5	17	<7
4 0 0 0 4 0	7	<8
2 2 4	21	29
4 1 1 1 4 1	32	16
3 3 0 3 2 3 2 3 3 4 0 2 0 4 2	131	171
3 1 4 1 3 4 2 1 5 1 2 5	350	359
4 2 0 2 4 0	2	22
3 3 2 0 0 6	85	93
4 1 3 1 4 3 4 2 2 2 4 2	106	119
1 1 6	1	17
3 0 5 0 3 5	4	<12
2 0 6 0 2 6	83	56
4 0 4 0 4 4	82	66
5 0 1 0 5 1 4 3 1 3 4 1	40	46
5 1 0 1 5 0	84	83
3 3 4 3 2 5 2 3 5	116	124
5 1 2 1 5 2	43	70
2 2 6	295	292
1 0 7 0 1 7 4 2 4 2 4 4	88	61
5 2 1 2 5 1	30	41
5 0 3 0 5 3 4 3 3 3 4 3	114	105
3 1 6 1 3 6	137	161
4 1 5 1 4 5	32	<15
4 4 0	758	790
2 1 7 1 2 7	22	<16
5 3 0 3 5 0 5 2 3 2 5 3 4 4 2	243	267
5 1 4 1 5 4	206	199
6 0 0 0 6 0 5 3 2 3 5 2 0 0 8 4 0 6 0 4 6	401	398
3 0 7 0 3 7	82	<18
6 1 1 1 6 1	30	<18
6 0 2 0 6 2 1 1 8 3 3 6	360	428
5 0 5 0 5 5 4 3 5 3 4 5	86	111
6 2 0 2 6 0	100	113
2 0 8 0 2 8 4 2 6 2 4 6	438	505
3 2 7 2 3 7 4 4 4	99	149
5 4 1 4 5 1	46	45
6 1 3 1 6 3 6 2 2 2 6 2	158	199
5 3 4 3 5 4 5 2 5 2 5 5	488	479
2 2 8	176	158
4 1 7 1 4 7 6 0 4 0 6 4 6 3 1 3 6 1	101	72
5 4 3 4 5 3 3 1 8 1 3 8 5 1 6 1 5 6	286	292
1 0 9 0 1 9	44	<24
6 2 4 2 6 4 7 0 1 0 7 1	261	257
7 1 0 1 7 0 5 5 0 6 3 3 3 6 3	77	<11
2 1 9 1 2 9 6 1 5 1 6 5	25	<12
6 4 0 4 6 0 7 1 2 1 7 2 5 5 2 4 0 8 0 4 8 4 4 6	258	274
5 0 7 0 5 7 4 3 7 3 4 7	48	<12
7 2 1 2 7 1	92	75
7 0 3 0 7 3 6 4 2 4 6 2 3 3 8 5 3 6 3 5 6	51	16
3 0 9 0 3 9 5 4 5 4 5 5	60	<13
4 2 8 2 4 8 6 0 6 0 6 6	105	118
5 2 7 2 5 7 0 0 10	31	26
7 3 0 3 7 0 7 2 3 2 7 3	104	98
1 1 10 7 1 4 1 7 4 5 5 4 3 2 9 2 3 9 6 3 5 3 6 5	485	502
7 3 2 3 7 2 6 2 6 2 6 6	414	527
2 0 10 0 2 10 6 4 4 4 6 4 6 5 1 5 6 1	217	449
5 1 8 1 5 8	251	450
4 1 9 1 4 9 7 0 5 0 7 5 8 0 0 0 8 0	125	129
6 1 7 1 6 7 2 2 10	169	283
8 1 1 1 8 1 7 4 1 4 7 1 6 5 3 5 6 3 8 0 2 0 8 2	206	113
3 1 10 1 3 10 7 3 4 3 7 4 7 2 5 2 7 5	173	178
8 2 0 2 8 0 4 4 8 5 4 7 4 5 7	199	192
1 0 11 0 1 11 8 1 3 1 8 3 7 4 3 4 7 3 8 2 2 2 8 2 5 3 8 3 5 8 7 1 6 1 7 6 5 5 6 5 0 9 0 5 9 4 3 9 3 4 9	316	324
6 6 0 6 0 8 0 6 8 6 4 6 4 6 6	61	56
6 3 7 3 6 7 4 0 10 0 4 10 8 0 4 0 8 4	28	<21
8 3 1 3 8 1 2 1 11 1 2 11 7 5 0 5 7 0 6 6 2 3 3 10 5 2 9 2 5 9 6 5 5 5 6 5	278	172
7 5 2 5 7 2 6 2 8 2 6 8	196	283
7 0 7 0 7 7 4 2 10 2 4 10 8 2 4 2 8 4	115	108
3 0 11 0 3 11 8 3 3 3 8 3	65	<22

Table 4. *Parameters of hydrated* Rb-*D*, *based on space group* $I222$[a]

Atom[b]	Position	Occupancy factor[c]	x		y		z		B[d]
T(1)	$2b$	1.0	1/2		0		0		0.025 nm^2
T(1)′	$2d$	1.0	1/2		0		1/2		0.025
T(2)	$8k$	1.0	0.356	± 0.002	− 0.124_5	± 0.002	0.313_5	± 0.001_5	0.031
T(2)′	$8k$	1.0	0.375_5		0.144		0.186_5		0.031
O(1)	$8k$	1.0	0.385_5	0.004_5	0.076	0.003_5	0.076_5	0.002_5	0.065
O(1)′	$8k$	1.0	0.424		0.885_5		0.423_5		0.065
O(2)	$8k$	1.0	0.294	0.003	− 0.004	0.008_5	0.240_5	0.004	0.066
O(2)′	$8k$	1.0	0.496		0.206		0.259_5		0.066
O(3)	$8k$	1.0	0.254	0.005_5	0.254		0.182	0.003	0.014
Rb(1a)	$4i$	0.49	0		0		0.205	0.003_5	0.089
Rb(1b)	$4i$	0.26	0		0		0.331	0.006	0.124
Rb(2a)	$8k$	0.18	0.122_5	0.004	0.165	0.003_5	0.445_5	0.003_5	0.020
Rb(2b)	$8k$	0.34	0.219	0.003	0.225	0.003	0.433_5	0.002	0.022
Rb(2c)	$8k$	0.33	0.323	0.004	0.319_5	0.004_5	0.428	0.003_5	0.080
$H_2O(1)$	$8k$	0.38	0.147	0.009_5	0.098	0.011	0.011_5	0.010	0.010
$H_2O(2)$	$8k$	0.30	0.43	0.02	0.46	0.02	0.040	0.015	0.030

[a] Framework atoms were refined with symmetry $I\bar{4}2m$.

[b] Atoms which are equivalent in $I\bar{4}2m$ are marked with a prime.

[c] Estimated standard deviation 0.02 and 0.06 for the Rb and H_2O positions, respectively.

[d] Estimated standard deviation 0.005 to 0.01 nm^2 for the framework atoms and cation positions and 0.03 nm^2 for the H_2O positions.

Table 5. *Interatomic distances in* Rb-*D*

T—O distances

T(1)—O(1)	0.170 nm
T(2)—O(1)	0.161 nm
—O(2)	0.166 nm
—O(2)′	0.183 nm
—O(3)	0.164 nm
mean	0.169 nm

Rb—O distances (expected value 0.29 nm)		*Some Rb—Rb distances* (expected value > 0.42 nm)	
Rb(1a)—O(2)	0.297 nm	Rb(1a)—Rb(2a)	0.38 nm
—O(3)	0.359 nm	—Rb(2b)	0.43 nm
		—Rb(2c)	0.44 nm
Rb(1b)—O(2)	0.317 nm		
—O(3)	0.348 nm	Rb(1b)—Rb(2a)	0.26 nm
		—Rb(2a)	0.36 nm
Rb(2a)—O(1)	0.311 nm	—Rb(2b)	0.34 nm
—O(2)	0.325 nm	—Rb(2c)	0.42 nm
—O(3)	0.345 nm		
		Rb(2a)—Rb(2a)	0.28 nm
Rb(2b)—O(1)	0.295 nm	—Rb(2a)	0.36 nm
—O(2)	0.350 nm		
—O(3)	0.330 nm	Rb(2b)—Rb(2b)	0.47 nm
Rb(2c)—O(1)	0.305 nm	Rb(2c)—Rb(2c)	0.40 nm
—O(2)	0.305 nm		
—O(3)	0.340 nm		

Discussion

The first objective of the crystal-structure determination of $\mathrm{Na^{ex}K}$-*F* was to confirm that the structure of K-*F* is based on the edingtonite-type framework as proposed by MAINWARING (1970). Although the final $R(I)$ value is not as low as might have been expected, the agreement between observed and calculated intensities is satisfactory (see Fig. 3). Also, the result of the refinement conforms with crystal-chemical requirements. The mean T—O distance of 0.166 nm is, within the limit of error, in good agreement with the expected value of 0.1681 nm for a Si/Al ratio of 1 (RIBBE and GIBBS, 1969). All distances between framework oxygen atoms and non-framework atoms are also within the expected range (0.23 nm for Na—O and about 0.29 nm for O—H · · · O distances).

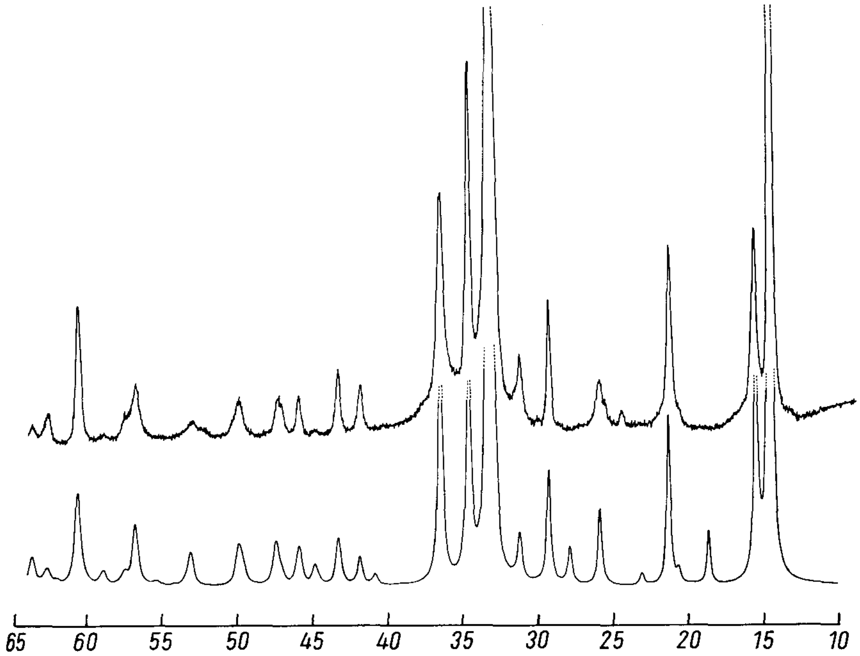

Fig. 3. Observed (upper curve) and calculated powder diffractograms of $\mathrm{Na^{ex}K}$-*F*

The reasons for the somewhat high *R*(*I*) value are twofold. The crystals of K-*F* tend to break up during the K→Na exchange, which is indicated by the broadening of the x-ray lines of the Na-exchanged form. This makes the detection of weaker reflections and also the resolution of overlapping peaks more difficult. The second cause is the assumption of too high a symmetry for the refinement. Symmetry restrictions imposed by such an assumption have a much greater effect in flexible frameworks than in more rigid ones. For these reasons a more detailed discussion of the atom position and interatomic distances is not feasible. This is especially true for the non-framework positions. Therefore, an assignment of cations or water molecules to these sites is highly speculative. However, considering the result of the Rb-*D* refinement, it seems likely that sites I and II are occupied by $\mathrm{Na^+}$.

The structure refinement of Rb-*D* was hampered mainly by the limited amount of data available. The final result establishes that the structure is based on the edingtonite-type framework, but there is still considerable doubt as to its true symmetry. The final coordinates show that the chains are virtually untwisted and the angle at O(3) is almost 180 °. This angle is unlikely and is thought to be due to the wrong symmetry assumption. As a further consequence of this, the TO_4 tetrahedra appear to be distorted as is indicated by the large variations in the T—O distances.

The Rb^+ ions are located in the two principal sites C(1) [Rb(1) positions] and C(2) [Rb(2) positions] of Fig. 1. Their distances to the framework atoms are given in Table 5. The relatively large Rb(1)—O(3) distances are due to the unreal atom coordinates obtained for O(3). The total occupancy of the sites C(1) and C(2) corresponds with 3 Rb and 6.5 Rb per unit cell, which agrees well with the 10 Rb found by chemical analysis. Roughly one third of the cations is thus located in site C(1) and two thirds in site C(2). This is also in good agreement with the results obtained by BARRER and MUNDAY (1971). These authors showed that most cation exchange isotherms of K-*F* could be interpreted in terms of two different cation sites which had cation populations in the ratio of 2:1. The result also compares well with the findings of TAYLOR (1935) in his structural examination of Tl and K-exchanged edingtonites. The Tl^+ and K^+ ions occupy similar positions to those found for the Rb^+ and TAYLOR states that the best agreement between observation and calculation is obtained with a uniform distribution of the cations over all available positions.

This partial occupancy of the two sites is thought to be one of the reasons why the overlapping positions occur. In the pseudo cell a total of six locations [two C(1) and four C(2) positions] for cations are available, but only five monovalent cations are needed for the neutralization of the framework charge. In a framework with a Si/Al ratio of 1 each oxygen atom has a formal charge of 0.25 *e*, counterbalanced either by direct contact with a cation or by a cation-water bridge. A cation in position C(1) is coordinated by O(2) and O(3) oxygen atoms, whereas a cation in C(2) has the oxygen atoms of types O(1) and O(2) as its nearest neighbours. Distance calculations using the Rb-*D* cell parameters showed that the ideal cation positions for the Rb^+ ions would be near site Rb(1a) and roughly halfway between Rb(2b) and Rb(2c). If all sites were fully occupied there would be no obvious reason why the cell should be doubled (except for Si,Al ordering) or why cation positions should overlap. Since however only 5 cations per pseudo unit cell are required, one location has to be empty. This means that depending on which site is unoccupied either two O(3) or two O(1) oxygen atoms are not in direct contact with a cation. Consequently their charge has to be counterbalanced via a water molecule. If, for instance, the position labelled Rb(1a) in Fig. 4 was unoccupied, a water molecule in site $H_2O(1)$ could form such a charge transfer between the Rb(2b) and O(3) positions. To make a charge transfer effective, it may be necessary for the Rb^+ ion to move some way along the pseudo-mirror plane. Such a shift is quite easily achieved, since it does not significantly alter the distances to the O(1) and O(2) oxygen atoms. A displacement from the 'ideal' position is also possible for the Rb(1) cations.

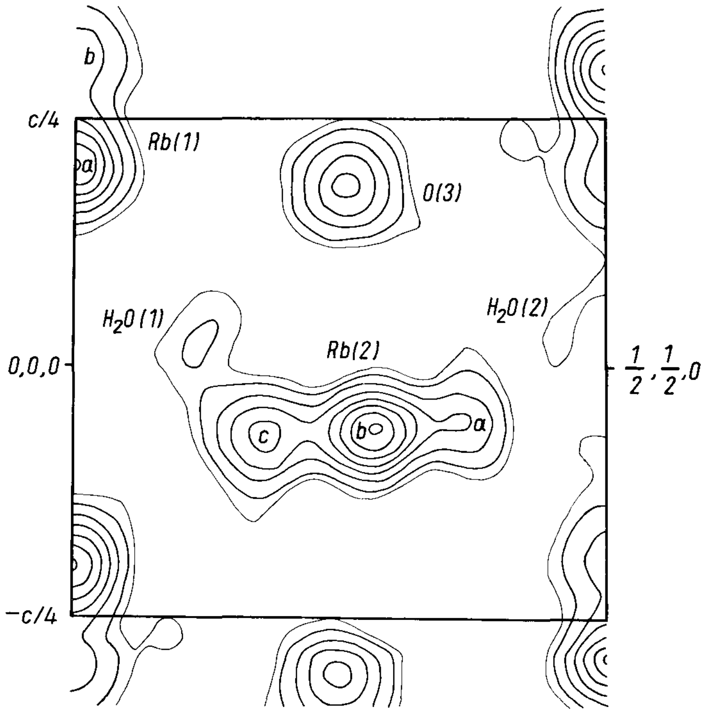

Fig. 4. Electron-density distribution along the (110) plane of Rb-*D*. The contours are at equal intervals, the thinner outside ones at half that interval. The zero line is not shown

Another feasible explanation for the observed cation peaks is the following. The Rb(1) cations may be slightly displaced from the centre of the eight-membered ring. This could be indicated by the relatively large temperature factors of the Rb(1) positions and may be necessary in order to achieve more satisfactory interatomic distances to O(2). If such a displacement occurred, the nearest cation in site C(2) would also have to move away because of electrostatic repulsion. However, this mechanism alone could not fully explain the refined cation positions. It is likely that the true answer to the problem is a combination of both the proposed mechanisms. If these explanations are correct it is easily understood why it was not possible to resolve the overlapping Fourier peaks.

As might have been expected, the determination of the water positions is very incomplete. Since the cation positions appear as overlapping partially occupied positions, the same must be true for the water positions. This will make them undetectable. Nevertheless, two Fourier peaks have been refined which might be partially occupied water positions and which account for about half the number of water molecules in the structure.

All investigated variants of K-*F* are to a greater or lesser degree pseudosymmetric. This is especially true for the potassium form. Since the framework is rather flexible various distortions of the ideal structure are possible. It could, for instance, be shown by DLS calculations that the T(1) atoms can be shifted away from the chain axis without introducing too much strain. The resulting chain is then zig-zagged. The phenomenon of pseudosymmetry is not uncommon in zeolites in general and particularly among the members of the group of fibrous zeolites. Edingtonite itself is pseudotetragonal. Natrolite, which is face-centred orthorhombic with cell dimensions $1.83 \times 1.86 \times 0.66$ nm^3 (Meier, 1960), has a pseudotetragonal body-centred cell of $1.3 \times 1.3 \times 0.66$ nm^3. The pseudosymmetry of zeolites is frequently due to Si,Al ordering. However, it can also be caused by the cation distribution as is clearly demonstrated by the doubling of each cell dimension of K-exchanged edingtonite (Hey and Bannister, 1934).

The structure determination of K^{ex} edingtonite (Taylor, 1935) did not permit any suggestion as to the reason why its true unit cell was eight times as large as that of Ba edingtonite. Unfortunately, the present investigation of the synthetic variants of edingtonite does not provide much additional information. Nevertheless, it is thought that a further clue is provided by the observed elongated peaks in Rb-*D*. A mechanism similar to that proposed for the Rb$^+$ ions may also apply for the cations in K-*F* and the other variants. An ordered distribution of the unoccupied cation location could, for instance, be the cause of the observed framework distortion.

Conclusions

The evidence presented here establishes that the structure of zeolite *F* is based on the edingtonite-type framework. This structure not only explains satisfactorily the observed x-ray intensities, but is also in agreement with other physicochemical properties of this zeolite. The strong twinning observed in most zeolite-F preparations can also be easily understood. However, it was not possible to determine the structure in great detail. In particular the reasons for the observed pseudosymmetry are still mostly unknown. Further work is in progress on zeolite K-*F* in order to clarify these questions.

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