

## A Statistical Comparison of a Series of Isotypic Structures as Determined by the Powder Method

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(Received 26 February 1973; accepted 28 February 1973)

The differences between the structural parameters of a series of hydrated and dehydrated *X* and *Y* zeolites with varying Si/Al ratio and saturated with potassium, as reported in previous studies, are examined statistically. Indications are found of larger framework distortions in the dehydrated state, as compared to the hydrated state. The changes in the occupancy factors of the different ion-exchange sites in the samples with varying aluminum content are valid, but the population figures must be treated carefully.

### Introduction

Several changes of the properties of faujasite-type zeolites are reflected in the structural parameters. Although essentially the same framework and cation positions are reported, some differences in the parameters appear to be correlated with these special properties. The extent of these differences could more easily be appreciated by comparing them with the standard deviations of the individual parameters. However, this procedure does not compare the structure as a whole. On the other hand, the standard deviations reported can be too small. This frequently occurs when full-matrix methods are not used in the least-squares refinement, especially when in this way high correlations are bypassed. It is therefore difficult to compare the parameter vectors of two structures, and make some probability statements about the extent of those differences. In earlier work (Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972), the structures of a series of potassium *X* and *Y* zeolites with varying Si/Al ratio were investigated in the hydrated as well as in the dehydrated state. On a statistical basis we shall try to draw some conclusions about the equality of the framework parameters and about the change of the parameters of the different ion-exchange sites.

### The statistical treatment

A full-matrix approximation for the estimation of the parameter vector is not always possible when high correlations exist between the parameters, or when some parameters are obtained by methods other than the least-squares method.

The present discussion is based mainly on the work of Geller (1961), and on the book by Mood & Graybill (1963). For completeness, the following definitions are given.

The multiple regression and Taylor expansion of the *i*th general function  $F_i^q(u_1, u_2, \dots, u_p) = F_i^q(u)$  of *p* parameters, for which the *i*th observed value is  $F_i^q$  with

weight  $w_i$ , produces in matrix notation the observational equations

$$Y = X\beta + e$$

where

$$Y = [y_i] = [\sqrt{w_i} \Delta F_i] = [\sqrt{w_i} (F_i^q - F_i^c)]$$

$$X = [x_{ij}] = \left[ \sqrt{w_i} \frac{\partial F_i^q(u)}{\partial u_j} \right]$$

and

$$\beta = [\beta_j] = [du_j].$$

For *e*, we assume a mean zero, and a covariance matrix  $\sigma^2(I)$ . The least-squares estimate  $\hat{\beta}$  of  $\beta$  is then obtained as  $\hat{\beta} = S^{-1}X'Y$ , where  $S = X'X$  (*S* is the  $p \times p$  matrix of the coefficients of the normal equations), and a least-squares estimate of  $\sigma^2$  by

$$\hat{\sigma}^2 = \frac{(Y - X\hat{\beta})'(Y - X\hat{\beta})}{n - p}$$

which equals

$$s^2 = \frac{\sum (\sqrt{w_i} \Delta F_i)^2}{n - p}$$

when convergence has been reached.  $\hat{\beta}$  and  $\hat{\sigma}^2$  are independent. If we assume normally distributed errors, the distribution of  $\hat{\beta}$  and  $\hat{\sigma}^2$  can be obtained. The estimate  $\hat{\beta}$  has a multivariate normal distribution with mean  $\beta$ , and covariance matrix  $\sigma^2 S^{-1}$ . For a subset of *q* parameters, the inverse of  $\sigma^2 S_1^{-1}$  (*S*<sub>1</sub> is the matrix of the coefficients of the normal equations) is the covariance matrix in the conditional distribution of those parameters, given the other  $p - q$  parameters. The vector of the differences of two independent estimates of  $\beta$ , *i.e.*  $\hat{\beta}_1$  and  $\hat{\beta}_0$ , has the same density function, but with mean zero, and covariance matrix  $2\sigma^2 S^{-1}$ . For a subset of *q* parameters, *S* may be replaced by *S*<sub>1</sub>, if no correlations exist between the parameters, or when the remaining  $p - q$  elements of the vector are zero. Since the first case is certainly not fulfilled, the density function described gives the conditional den-

sity function for the differences of  $q$  parameters, given that the other  $p - q$  parameters, which were not considered, are identical.

The quadratic form in the density function of the multivariate normal distribution has a  $\chi_q^2$  distribution.  $q$  is the size of the vector of random variables. Consequently, we may write for  $q$  parameters  $(\hat{\beta}_1 - \hat{\beta}_0)' \times S_1(\hat{\beta}_1 - \hat{\beta}_0)/2\sigma^2 = \chi_q^2$ , and since

$$\frac{n-p}{\sigma^2} \hat{\sigma}^2 = \chi_{n-p}^2$$

or after convergence

$$\frac{n-p}{\sigma^2} s^2 = \chi_{n-p}^2,$$

we obtain

$$Q = \frac{(\hat{\beta}_1 - \hat{\beta}_0)' S_1(\hat{\beta}_1 - \hat{\beta}_0)}{2qs^2} = F_{q, n-p}(\alpha). \quad (1)$$

This expression can be used to test the hypothesis:  $\hat{\beta}_1 = \hat{\beta}_0$ , by comparing  $Q$  with  $F_{q, n-p}(\alpha)$ . If  $Q > F_{q, n-p}(\alpha)$ , we may reject the equality of the two parameter vectors, with probability  $\alpha$  of taking a wrong decision, *i.e.* that the hypothesis really is true. Without obtaining the full matrix of normal equations, it is therefore possible to test the differences between a subset of the parameter vectors, with the restriction that the test is performed on a conditional basis.

### Results

We were interested in the influence of the Si/Al ratio and the dehydration of the samples on the structure parameters, and especially on the parameters of the framework. A comparison of the parameter differences with the standard deviations is not possible, because of the block-diagonal approximation, and the exclusion from the refinement of the scale factor and the radii of the spheres of statistically distributed matter (Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972).

If we accept as null hypothesis that the framework parameters, or the cation parameters or both, are obtained from the same population, it is possible to test this hypothesis with equation (1), since we dispose of completely independent samplings.

The matrix  $S_1$  was obtained by a full-matrix refinement of 15 framework parameters together with the positional and occupancy factors of the cations. The weight  $w_i$  was calculated for each reflexion from the standard deviation of the four independent measurements of each peak according to a single  $N (= h^2 + k^2 + l^2)$  value. The general functions in the refinement were the 128 intensities, sampled for each  $N$  value, up to  $N = 396$ , and no attempt was made to separate those intensities for the several  $hkl$  values in a single  $N$  value. The program used was a modified version of *POWOW* (Hamilton, 1962).

To make sure that convergence was sufficient, the

matrix  $S_1$  was taken from the second cycle following the previous refinement (Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972). The decrease of  $wR_I$  from the first to the second cycle was about 1 to 5% and reached 7% in one case. The final  $wR_I$  values are given in Table 1, together with the  $R_I$  values obtained by the previous refinement, and the total number of parameters  $p$ . Sometimes slightly different parameters are obtained with the full-matrix approximation, as compared to *FD3MPLS*. *FD3MPLS* is the program written especially for our purposes. The refinement was based on the structure factors. A block-diagonal approximation was used to solve the matrix of normal equations. The parameters  $x$ ,  $y$ ,  $z$  and  $B$  for the individual framework parameters were taken in separate blocks. The parameters of the exchangeable cations were taken together in another single block, refining alternately positional and temperature factors and occupancy factors in order to eliminate as far as possible the close correlation between the population factors and the temperature factors. The weighting scheme was also different from that of *POWOW*. We used the weighting scheme suggested by Cruickshank *et al.* (Lipson & Cochran, 1966) for  $|F_c| > |F_o|_{\min}$ , *i.e.*  $w_i = 1/(2|F_o|_{\min} + |F_o| + 2|F_o|^2/|F_o|_{\max})$ . Otherwise a zero weight was used (Dunning & Vand, 1969). For other features of the refinement method, we refer to the previous published work (Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972). Some differences between the parameters obtained by both programs are shown for the occupancy factors of the cation sites in Table 2. These differences do not affect the conclusions of the previous work on the cation distribution. Moreover, on the basis of difference Fourier calculations the results obtained with the program *FD3MPLS* are considered to be more reliable.

We used for  $\hat{\beta}_1$  the parameters reported earlier (Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972) and for  $\hat{\beta}_0$  the parameters obtained

Table 1. *Residuals and the number of parameters*

Hydrated	$wR_I(a)$	$R_I(b)$	$p$
KF48·2	0·1603	0·1992	31
KF54·7	0·2096	0·1616	33
KF69·8	0·0825	0·1629	33
KF86·5	0·3415	0·2030	33
Dehydrated			
KF48·2	0·1029	0·1983	27
KF54·7	0·0470	0·1967	27
KF69·8	0·1156	0·2018	27
KF86·5	0·1615	0·1958	27

(a)

$$wR_I = \left[ \frac{\sum w_i(kI_o - I_c)^2}{\sum w_i(kI_o)^2} \right]^{1/2}$$

(b)

$$R_I = \frac{\sum |kI_o - I_c|}{\sum kI_o}$$

Table 2. *POWOW* and *FD3MPLS* occupancy factorsThe standard deviations (*POWOW*) are indicated in brackets.

Hydrated		KF48·2	KF54·7	KF69·8	KF86·5
Site I	(1)	—	0·08	0·44	0·56
	(2)	—	0·09 (7)	0·45 (7)	0·60 (6)
Site I'	(1)	0·43	0·41	0·38	0·22
	(2)	0·53 (3)	0·41 (3)	0·50 (4)	0·45 (4)
Site II	(1)	0·57	0·63	0·76	0·73
	(2)	0·51 (3)	0·58 (4)	0·78 (2)	0·67 (3)
Dehydrated		KF48·2	KF54·7	KF69·8	KF86·5
Site I	(1)	0·40	0·34	0·52	0·57
	(2)	0·40 (4)	0·34 (3)	0·51 (4)	0·43 (6)
Site I'	(1)	0·44	0·57	0·52	0·43
	(2)	0·49 (2)	0·62 (3)	0·66 (4)	0·41 (4)
Site II	(1)	0·82	0·84	0·90	0·78
	(2)	0·77 (2)	0·76 (2)	0·92 (2)	0·94 (3)

(1) *FD3MPLS*(2) *POWOW*

from the second cycle of the *POWOW* refinement which, together with the variance-covariance matrix for the same vector  $\hat{\beta}_0$ , determine the confidence region for the sample considered. The  $Q$  values [equation (1)] for 15 framework parameters or for the 15 framework plus 5 cation parameters are given in Tables 3 and 4. For KF48·2 hydrated only 4 cation parameters were included. These values must be compared with  $F_{15, (n-p)}(\alpha)$  and  $F_{20, (n-p)}(\alpha)$  respectively [ $F_{19, (n-p)}(\alpha)$  for sample KF48·2]. Since  $(n-p)$  varies only from 95 to 101, and since the corresponding  $F_{q, (n-p)}(\alpha)$  values show only minor differences, we include in Tables 3 and 4 only a list of  $F_{15, 100}(\alpha)$  and  $F_{20, 100}(\alpha)$ . Those cases are italicized for which no significant difference is found between the parameter vectors with a probability of 0·99. The samples are named as indicated previously (Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972), where F stands for 'faujasite', K for potassium, and where 48·9, 54·7, 69·8 and 86·5 indicate the number of Al atoms per unit cell. KF54·7 is a zeolite Y, KF86·5 is a zeolite X.

## Discussion

Let us consider the differences in the framework parameters. In Table 3 the  $\hat{\beta}_1$  values are those obtained with *FD3MPLS*,  $\hat{\beta}_0$  those obtained with *POWOW*. Apart from the different weighting schemes, the same observations have been used in both programs: therefore we would expect  $\hat{\beta}_1$  to equal  $\hat{\beta}_0$ . [It must be mentioned that the two parameter estimates for the same sample are not independent. Strictly speaking equation (1) is not completely valid in this case.] Considering the diagonal terms in Table 3 we see that this is not the case for all samples. Therefore we reject the samples KF48·2 and KF69·8 hydrated and also KF54·7 dehydrated as a basis for comparison, because the confidence region of those, obtained with *POWOW*, does not include the parameter vector obtained with *FD3MPLS*. The different weighting scheme in the two programs may be the reason for this significant difference. For this reason the values in brackets cannot be used in the discussion.

Although the hydrated samples have a broad confidence region (because of the less well determined structure, especially for KF86·5), some interesting conclusions can be drawn. With only one exception (KF69·8 hydrated compared to KF86·5 hydrated) the framework parameters of the hydrated samples do not differ significantly from each other. When the dehydrated samples are compared to the hydrated ones, the framework parameters are significantly different except for KF86·5 dehydrated. A similar conclusion can be drawn when the dehydrated samples are used as the reference for the hydrated material. Note that the hydrated structures have a lower  $wR_f$  value which results in a narrower confidence region. Thus we conclude that the framework parameters of the hydrated samples are similar to each other but differ significantly from those of the dehydrated material. This can be ascribed to framework distortions occurring

Table 3. Comparison based on 15 framework parameters

	Hydrated					Dehydrated			
	(b)	(a) KF48·2	KF54·7	KF69·8	KF86·5	KF48·2	KF54·7	KF69·8	KF86·5
Hydrated	KF48·2	(2·66)	1·08	(11·63)	1·64	6·68	(34·90)	4·64	3·21
	KF54·7	(9·36)	1·37	(8·54)	2·02	7·20	(21·07)	3·40	5·73
	KF69·8	(3·59)	1·64	(7·33)	2·26	5·87	(11·97)	7·10	6·04
	KF86·5	(2·82)	2·03	(7·33)	1·13	6·39	(24·10)	5·86	2·51
	KF48·2	(3·40)	3·31	(8·39)	2·60	2·03	(27·46)	2·98	5·52
Dehydrated	KF54·7	(5·71)	3·00	(5·92)	2·48	3·42	(30·00)	5·21	6·88
	KF69·8	(12·40)	4·33	(39·01)	2·86	7·79	(64·45)	1·18	4·53
	KF86·5	(4·70)	1·92	(10·37)	1·66	3·71	(42·66)	3·09	1·55
					$\alpha$	$F_{15, 100}(\alpha)$			
(a)	Reference structure ( $\hat{\beta}_0$ ):					0·10	1·56		
	$\hat{\beta}_0$ was obtained with <i>POWOW</i> .					0·05	1·78		
					0·025	1·98			
(b)	Compared structure ( $\hat{\beta}_1$ ):					0·01	2·24		
	$\hat{\beta}_1$ as reported in previous work					0·005	0·44		
	(Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972).								

Table 4. Comparison based on 20 structure parameters

		Hydrated				Dehydrated			
(b)		KF48·2	KF54·7	KF69·8	KF86·5	KF48·2	KF54·7	KF69·8	KF86·5
Dehydrated	Hydrated	(4·14)	1·03	(29·92)	(8·18)	10·11	(80·03)	21·08	(17·04)
	KF54·7	(13·47)	1·18	(22·35)	(6·07)	9·62	(48·88)	18·54	(17·14)
	KF69·8	(12·68)	3·10	(4·24)	(3·07)	7·33	(6·57)	12·17	(19·29)
	KF86·5	(11·82)	6·56	(9·96)	(2·84)	9·33	(22·31)	12·31	(26·00)
	KF48·2	(9·36)	4·85	(9·39)	(3·33)	1·68	(28·97)	5·94	(9·86)
	KF54·7	(13·01)	4·95	(20·16)	(3·85)	2·64	(43·38)	5·38	(11·84)
	KF69·8	(19·90)	9·83	(83·52)	(4·50)	8·35	(178·51)	1·77	(11·24)
KF86·5	(11·77)	6·57	(52·89)	(2·37)	6·94	(77·65)	7·52	(28·00)	
						$\alpha$	$F_{20,100}(\alpha)$		
(a)	Reference structure ( $\hat{\beta}_0$ ):					0·10	1·50		
	$\hat{\beta}_0$ was obtained with <i>POWOW</i> .					0·05	1·69		
						0·025	1·86		
(b)	Compared structure ( $\hat{\beta}_1$ ):					0·010	2·09		
	$\hat{\beta}_1$ as reported in previous work					0·005	2·26		
	(Mortier & Bosmans, 1971; Mortier, Bosmans & Uytterhoeven, 1972).								

during the dehydration of the samples. Smith (1971) states that the greatest distortions occur in the dehydrated form. This was inferred from the T–O–T bond angles which have a smaller spread in the hydrated samples, and from the changes in the diameters of the framework rings. The exception of KF86·5 dehydrated can be understood if it is assumed that the coordinates of its framework ions are closer to the mean position (those of the hydrated series) than those of the other dehydrated structures. This could be the consequence of a partial ordering of the Al atoms, established by Olson (1970) for NaX, which would not allow distortions leading to a large deviation of the coordinates from the mean position. This also indicates that the framework differences between zeolites X and Y are mainly due to factors such as the presence of cations and sorbed molecules rather than to the Al content.

For a similar treatment with 20 structure parameters (framework and cations) only KF54·7 hydrated and KF48·2 and KF69·8 dehydrated can be used as a reference (see Table 4). Moreover, it is seen in Table 2 that the occupancy factors of the cation location sites obtained with *POWOW* and *FD3MPLS* are comparable for these samples, and more divergent for the others.

From the data in Table 4 it may be concluded that, on a statistical basis, no distinction can be made between KF54·7 and KF48·2 hydrated. However KF54·7 hydrated differs significantly from the hydrated samples KF69·8 and KF86·5. In the dehydrated state all the structures for which comparison can be made are significantly different from each other and from the hydrated samples.

The changes in the parameters indicate that care must be taken when parameters are derived from powder data. Fixing of the scale factor yielded good convergence in our case. However, Geller (1961) indicated that by this procedure, errors in the intensity measurement are easily absorbed by the temperature

factor, which is highly correlated with the scale factor. Since for powder data, the errors associated with the intensity measurement can be large (e.g. partially overlapping peaks), unrealistic values of the temperature factors, which have no physical significance can be expected. A supplementary indeterminacy is created when different results are obtained by different weighting methods, as was found here.

It is clear that not all the differences between our structures are significant. This would be even more pronounced if we could use the marginal distribution of the parameters and if correlations between the observations were included in the refinement. Finally, the structure is essentially indeterminate if high correlations between the parameters exist, and the standard deviations alone are not sufficient to describe the uncertainty in the parameters. Before drawing conclusions, it is worthwhile testing these differences, albeit on a conditional basis.

From a single structure analysis based on powder data, it is very difficult to draw far-reaching conclusions. However, when a series of structures is investigated, with the data treated in the same manner, it is possible to obtain some information about the influence of certain factors, such as the Si: Al ratio and the dehydration; but care must be taken when the absolute figures of the parameter vector are considered.

The author is indebted to the 'Belgisch Nationaal Fonds voor Wetenschappelijk Onderzoek', for a research grant as 'aspirant', to Professor H. J. Bosmans for his interest and to Professor J. B. Uytterhoeven for valuable help with the preparation of the manuscript. We acknowledge support from the Belgian Government (Dienst voor Programmatie van het Wetenschapsbeleid).

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*Acta Cryst.* (1973). **A29**, 477

## Thermal Expansion of NaF, KBr and RbBr and Temperature Variation of the Frequency Spectrum of NaF

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(Received 12 December 1972; accepted 25 January 1973)

Coefficients of thermal expansion of NaF, KBr and RbBr are determined at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. Equations are given for the variation of lattice constants with temperature. The temperature dependence of the thermal expansion at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The energies of formation of Schottky pairs in the three halides are estimated and are found to be consistent with those deduced from ionic-conductivity studies. The halides are found to obey the 'law of corresponding states' established by Pathak & Vasavada [*Acta Cryst.* (1970), **A26**, 655–658]. The geometric mean of the frequency spectrum of NaF is found to decrease by about 14% between room temperature and 1000°K.

### Introduction

The thermal expansion of NaF, KBr and RbBr has been investigated by many workers both by the X-ray and macroscopic methods, notably by Eucken & Dan-nöhl (1934), Gott (1942), Connell & Martin (1951), Pathak & Pandya (1960), Deshpande (1961), Deshpande & Sirdeshmukh (1961), Pathak, Pandya & Ghadiali (1963).

On examination of the results of the various workers it is found that although the results agree at lower temperatures, there are wide discrepancies at higher temperatures. This can be seen from Tables, 1, 2 and 3.

One of the aims of the present experiments was, therefore, to determine accurate values of the thermal expansion of these salts especially at high temperatures.

### Experimental

The experimental observations were taken with the Philips X-ray unit PW 1009 with an external voltage stabilizer, diffractometer, chart recorder and a specially designed furnace having a large volume of uniform temperature in which the powder specimen was placed. The details of measurements are described in an earlier paper (Pathak & Vasavada, 1970, hereafter called Paper I). The accuracy of the results is estimated to be about ½%.

### Results and discussion

The lattice constants of the different alkali halides were found to vary with temperature according to the follow-

ing equations. The equations were obtained with the help of an IBM 1620 computer.

NaF:

From 0 to 750°C,

$$a_t = 4.6295 + 1.5432 \times 10^{-4}t + 5.727 \times 10^{-8}t^2 + 6.35 \times 10^{-12}t^3 \quad (1)$$

from 700 to 930°C,

$$a_t = 4.7677 + 2.4400 \times 10^{-4}(t - 700) + 7.363 \times 10^{-8} \times (t - 700)^2 + 2.236 \times 10^{-10}(t - 700)^3 \quad (2)$$

KBr:

From 0 to 550°C,

$$a_t = 6.5709 + 2.5138 \times 10^{-4}t + 6.8369 \times 10^{-8}t^2 + 4.892 \times 10^{-11}t^3 \quad (3)$$

from 500 to 700°C,

$$a_t = 6.7198 + 3.5602 \times 10^{-4}(t - 500) + 11.1013 \times 10^{-8}(t - 500)^2 + 6.0796 \times 10^{-10}(t - 500)^3 \quad (4)$$

RbBr:

From 0 to 500°C,

$$a_t = 6.8610 + 2.6423 \times 10^{-4}t + 8.5322 \times 10^{-8}t^2 + 4.143 \times 10^{-11}t^3 \quad (5)$$

from 450 to 650°C,

$$a_t = 7.0010 + 3.6538 \times 10^{-4}(t - 450) + 8.793 \times 10^{-8}(t - 450)^2 + 7.4760 \times 10^{-10}(t - 450)^3 \quad (6)$$