parison of population parameters may be better achieved by a transformation to uncorrelated linear combinations of population parameters, as described in the last section of this article. The comparison of the electron density maps shows clearly that neither INDO, nor STO-3G minimal basis set calculations give an adequate representation of the electron density in the bonding regions of the cyanuric acid molecule.

The authors would like to thank Professor R. F. Stewart for making the results of his unpublished theoretical calculation on the cyanuric acid molecule available. They gratefully acknowledge support of this work by the National Science Foundation.

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Determination of a Probable Reflexion Symmetry by Counting Statistics shown in the Example of the Zeolite, NaPl

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(*Received* 8 *June* 1972)

The deviation of symmetry equivalent intensities from their mean values was used to determine a probable reflexion symmetry for the zeolite NaPl. The method of investigation is based on the χ^2 test and compares the measured deviation with the one expected from counting statistics. The lattice dimensions of zeolite NaPl are cubic, but it was suspected that its symmetry is tetragonal and that the crystal is multiply twinned, thus simulating a near cubic X-ray pattern. Cubic symmetries were clearly rejected by the test and it was shown that reflexion symmetry *mmm* is a good approximation for the observed intensities.

1. Introduction

Schulz & Huber (1971) described a method by which X-ray intensities, obtained with a single-crystal diffractometer, can be tested for significant deviation from an assumed reflexion symmetry. The method is based on the χ^2 test. In this paper its application will be explained using as an example the synthetic zeolite NaPl. A brief description of the background of the NaPl problem is given below. A more detailed account of it can be found elsewhere (Baerlocher & Meier, 1972).

Zeolite NaPl crystallizes, normally as spherulitic aggregates of 1–2μ diameter, from sodium aluminosilicate gels under hydrothermal conditions. The powder pattern can be indexed on a body-centered cubic unit cell with an a dimension of 10·04 Å. An interesting framework structure with $Im3m$ symmetry was proposed but the refinement with powder data did not proceed satisfactorily. Further evidence then indicated that the NaPl structure may be based on the gismondine framework, which has similar cell dimensions. However, this framework possesses only a maximum symmetry of $I4_1/amd$ and the powder data were clearly insufficient for a structure analysis based on this framework. A larger crystal of NaPl was synthesized and precession photographs showed a body-centred cubic lattice. Optical examination of the crystal indicated multiple twinning. It was suspected that the individual sections of the crystal are related to each other by a rotation of 90° around their a or b axis

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thus simulating a cubic X-ray pattern. Provided that the three different orientations of these sections do not have the same abundance, a deviation from the cubic reflexion symmetry should be detectable. If such a deviation was observed with certainty, the cubic proposal could be discarded. A refinement based on the gismondine type framework would then appear worthwhile.

2. Experimental features

The crystal of NaPl, which was enclosed in a sealed glass capillary, was approximately spherical. From 19 measurements the average diameter of the sphere was determined as

$$d=244\mu \quad \sigma(d)=17\mu.$$

An on-line Picker diffractometer with Nb-filtered Mo radiation was used for the intensity measurements. The lattice parameters were found to be $a=b=c=$ 10·04 Å. The relative intensities of reflexions obeying the conditions $h+k+l=2n$ were collected up to $\theta=$ 15°, covering half the reciprocal space. About 600 of the recorded intensities had a counting rate larger than their threefold standard deviation calculated from the count rates. Only these measurements were used for the statistical analysis.

The linear absorption coefficient is equal to 7·45 cm^{-1} for Mo radiation.

To correct for the long time drift of the diffractometer, a control reflexion correction was applied to the intensities as described by Schulz (1971, § 2).

3. Statistical analysis of the intensity measurements

3.1 *Description of method of investigation*

The statistical analysis of the data set was carried out with the procedure described by Schulz & Huber (1971) and Schulz (1971). This procedure is based on the χ^2 test. The test compares estimated errors calculated from the intensity differences of symmetry equivalent reflexions with standard deviations calculated from the count rates.

The main steps of the analysis are as follows:

(1) The single measurements are arranged in groups of symmetrically equivalent reflexions (*S*-groups).

(2) The *S*-groups are divided into property groups (*P*-groups). In our case the appearance in one of the four property groups (*P*1–*P*4) is governed only by the relative standard deviation $\sigma(I)/I$. The ranges of these relative standard deviations for each *P*-group are listed in Table 1.

(3) The χ^2 value and the degree of freedom is calculated for each *S*-group.

(4) The χ^2 values and the degrees of freedom of all the *S*-groups belonging to a *P*-group are summed. These sums are designated $X^2(P)$ and G respectively. $X^2(P)$ belongs to a normally distributed totality with the expected value G and the variance $2G$.

(5) The quotient $Q=X^2(P)/G$ is calculated for each

Table 1. *Quantities used for the statistical analysis*

Columns I: number of single reflexions forming a *P*-group.
Columns II: number of *S*-groups of a *P*-group.
Columns III: degrees of freedom of $X^2(P)$.
Columns IV: Q values.
Columns V: $Q_{\pm 1}$ values.

$\sigma(I)/I$		*P*1 (counts/measurement < 10^3) 0·50–0·23				*P*2 (counts/measurement ~ 5 . 10^3) 0·23–0·06				*P*3 (counts/measurement ~ 1 . 10^5) 0·060–0·055				*P*4 (counts/measurement ≥ 2·5 . 10^4) 0·055–0·051			
		I	II	III	IV	V	I	II	III	IV	V	I	II	III	IV	V	
Investigation steps	1.	214	17	197	1·32	0·80–1·20	240	23	217	2·09	0·81–1·19	92	8	84	2·83	0·69–1·31	56	9	47	3·46	0·59–1·41
	2.	213	29	184	1·36	0·79–1·21	244	33	211	2·18	0·81–1·19	79	11	68	3·01	0·66–1·34	56	11	45	3·24	0·58–1·42
	3.	132	44	88	1·38	0·70–1·30	212	71	141	1·57	0·76–1·24	78	26	52	1·38	0·61–1·39	42	14	28	0·76	0·46–1·54

P-group. It has the expected value 1 (*cf.* step 4) and belongs also to a normally distributed totality. The standard deviation of Q is:

$$\sigma(Q)=\frac{\sigma[X^2(P)]}{G}=\frac{\sqrt{2G}}{G}=\sqrt{\frac{2}{G}}.$$

(6) If the Q values lie within the aim range of $Q_{\pm l}=1\pm 2\sigma(Q)$, the probability of agreement between the errors of the intensity measurements and the expected errors is 0·94 and the assumed reflexion symmetry can therefore be accepted. If the Q values are outside their aim ranges, a measure of the degree of their deviation can be obtained by comparing the difference $Q-1$ with $\sigma(Q)$.

3.2 *Statistical investigation*

Because the crystal shape is not ideal the standard deviations of the individual measurements were increased to allow for differences in absorption. The increase in the standard deviation was calculated using equation (3) of Jeffrey & Rose (1964) which is valid for crystals with $\mu r<0{\cdot}4$. From this equation the relative standard deviation $\sigma(I)/I=0{\cdot}059$ was obtained using a $\sigma(d)/d$ of 0·086 for the crystal diameter. The recalculated standard deviation of the intensity measurements was used for all calculations. For each P group the extremes of $\sigma(I)/I$ are listed in Table 1. The values of $\sigma(I)/I$ decrease from about 0·3 for $P1$ to about 0·055 for $P3$ and $P4$.

The first reflexion symmetry tested was *m3m*, because this was the symmetry indicated by precession photographs. It was also the symmetry of the original structure proposal. Additionally, the lower cubic symmetry *m*3 was checked. Assuming that the crystal shows mimetic twinning, the highest possible Laue symmetry in the case of the tetragonal structure proposal would be *mmm*. Therefore a final test was made using this symmetry. The results of the statistical analysis for the three symmetries are assembled in Table 1. It lists for each property group the number of measurements, the number of *S*-groups and the degree of freedom G of $X^2(P)$. Lastly, it embodies the Q values and their aim ranges of $Q_{\pm l}$.

4. Discussion

It can be seen from Table 1 that for all *P*-groups the Q values calculated with the two cubic symmetries are larger than their upper limiting value Q_{+l}. For $P1$ the deviation from the expected value 1 equals only three times the standard deviation $\sigma(Q)$ but for the other 3 groups the differences $Q-1$ are at least 15 times the respective $\sigma(Q)$ values. This means that the cubic symmetries are clearly rejected.

In the next step the reflexion symmetry was reduced to *mmm*. Now, the Q values of $P3$ and $P4$ lie within their aim ranges. For $P1$ the deviation of Q from 1 is less than $3\sigma(Q)$, which could still be regarded as a sufficient agreement. Only Q of group $P2$ deviates almost by $5\sigma(Q)$ from 1. Nevertheless, the agreement of symmetrically equivalent reflexions is significantly better for the symmetry *mmm* than for the cubic symmetries. [A change of $2\sigma(Q)$ of a Q value should be regarded as significant.] The agreement reaches the limit at which the assumed symmetry may be accepted as correct, but the deviation of Q of group $P2$ suggests a further symmetry reduction.

Because our crystal is multiply twinned such a reduction would reveal no further information about the true symmetry of the structure. Nevertheless, from the above analysis the following conclusions can be drawn. The structure of the zeolite NaPl is not in agreement with the cubic proposal. It could be based on the gismondine-type framework. Space group *I*4 */amd* could be used as an approximation. It is however likely that the true symmetry of the crystal is lower. (These conclusions have been proved correct by the subsequent structure analysis (Baerlocher & Meier, 1972)]. Table 1 also shows that the Q values of the property group with the smallest intensity mean values ($P1$) are not significantly affected by different reflexion symmetries. This means that the deviation of symmetrically equivalent reflexions from their mean value is due only to the counting statistics. The test is based on the assumption that the variance of a single measurement is equal to its expected value. However, counting rates measured with a single crystal diffractometer do not follow the relation exactly. Counting rates with low probability are measured too often. This was shown by Schulz (1971) for the diffractometer used in his measurements and it is probably also true in the case considered here. Approximately, this effect can be compensated by multiplying the expected variance by a factor, estimated by Schulz at 1·15. All Q values of $P1$ lie within the aim range if this factor is applied, that is if the Q values are divided by 1·15.

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