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J. Appl. Cryst. (2013). **46**, 1017–1023



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Using *FOCUS* to solve zeolite structures from three-dimensional electron diffraction data

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The program *FOCUS* [Grosse-Kunstleve, McCusker & Baerlocher (1997). *J. Appl. Cryst.* **30**, 985–995] was originally developed to solve zeolite structures from X-ray powder diffraction data. It uses zeolite-specific chemical information (three-dimensional 4-connected framework structure with known bond distances and angles) to supplement the diffraction data. In this way, it is possible to compensate, at least in part, for the ambiguity of the reflection intensities resulting from reflection overlap, and the program has proven to be quite successful. Recently, advances in electron microscopy have led to the development of automated diffraction tomography (ADT) and rotation electron diffraction (RED) techniques for collecting three-dimensional electron diffraction data on very small crystallites. Reasoning that such data are also less than ideal (dynamical scattering, low completeness, beam damage) and that this can lead to failure of structure solution by conventional direct methods for very complex zeolite frameworks, *FOCUS* was modified to accommodate electron diffraction data. The modified program was applied successfully to five different data sets (four ADT and one RED) collected on zeolites of different complexities. One of these could not be solved completely by direct methods but emerged easily in the *FOCUS* trials.

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1. Introduction

Zeolites are crystalline aluminosilicate framework materials with large internal surface areas that are widely used in industry as catalysts, adsorbents and ion exchangers. Their open framework structures are built from corner-sharing TO_4 tetrahedra, where T is a tetrahedrally coordinated atom such as Si or Al. The bond distances and angles of the framework atoms are generally well defined, but the connectivities of the T atoms differ from one framework type to the next.¹ The different connectivities lead to very different pore systems, and these in turn have a profound effect on the properties of the zeolite. Therefore, the determination of the framework structure of any new zeolite is fundamental to its characterization.

Unfortunately, many zeolites and related porous materials crystallize in polycrystalline form, so the framework structure determination often has to be performed using X-ray powder diffraction (XPD) data. This means that the analysis is complicated by the fact that reflections with similar d spacings overlap in a powder diffraction pattern, so their individual intensities cannot be determined. As a result, conventional

single-crystal methods of structure determination, which rely on having accurate intensities, often fail.

The program *FOCUS* was conceived and written to address just this problem (Grosse-Kunstleve *et al.*, 1997, 1999). It proved to be possible to compensate for the reflection overlap problem, at least in part, by including some crystal chemical information common to all zeolite structures (three-dimensional 4-connected framework structure with known $T-O$ distances and $O-T-O$ and $T-O-T$ angles) in an automated structure determination procedure. The algorithm takes a dual-space approach that involves (1) generating electron density maps by combining the (partially ambiguous) reflection intensities extracted from the powder diffraction pattern with (random) starting phases and (2) interpreting those maps by using the crystal chemical information supplied. A Fourier recycling procedure is then applied to improve the maps and thereby their interpretation. This use of real-space information to compensate for the poor quality diffraction intensities proved to be most effective. As might be expected, the closer the intensities are to those of the single crystal, the better the algorithm works.

Another way of adding information to supplement the XPD data in the *FOCUS* program was explored by Gramm *et al.* (2006). They derived some phase information from high-resolution transmission electron microscopy (HRTEM)

¹ 206 framework types have been recognized by the International Zeolite Association and assigned three-letter codes to date (<http://www.iza-structure.org/databases/>; Baerlocher, McCusker & Olson, 2007).

images and used this in the *FOCUS* starting phase sets with considerable success. Indeed the complementarity of electron crystallography [the use of electron diffraction (ED) reflection intensities or HRTEM images, and the Fourier transform thereof, for crystal structure determination] and XPD techniques has now been exploited for zeolite structure determination in several instances (McCusker & Baerlocher, 2013a). Traditionally, ED data are measured as two-dimensional patterns along single low-index zone axes. Such data are generally incomplete and suffer from dynamical scattering effects, so they are not very well suited for structure determination by themselves. However, in combination with XPD data, they have been shown to be very effective (Xie *et al.*, 2008).

Recent advances in the computer control of electron microscopes have led to the development of automated diffraction tomography (ADT; Kolb *et al.*, 2007) and rotation electron diffraction (RED; Zhang *et al.*, 2010). Both methods allow high-quality and high-coverage three-dimensional ED data to be collected on tiny crystallites (down to 30–50 nm in size) automatically. As these data are collected on single crystallites, they are conceptually comparable to single-crystal X-ray diffraction data, in terms both of completeness and of three-dimensional information. These three-dimensional ED data are collected avoiding low-index zone patterns. In such a way the dynamical scattering is reduced, even if not completely eliminated. Although the origin of the diminished quality of the reflection intensities for ED data (dynamical scattering) is different from that of XPD data (reflection overlap), it was thought that perhaps the use of chemical information to compensate for the deficiency in the ED data might work in the same way. Therefore, *FOCUS* was modified to accommodate ED data and tested on a series of three-dimensional ED data sets collected on zeolitic materials.

2. Electron diffraction tomography

Electrons have a few distinct advantages over X-rays. The key difference is that electrons interact much more strongly with matter, so even very tiny crystallites, with dimensions as small as a few tens of nanometres, can be measured. The advantage of this for a polycrystalline material is that single crystallites can be targeted, so there is no problem with reflection overlap and impurities can be avoided. However, there are also some significant disadvantages: the intensities are dynamical in nature and therefore difficult to interpret, beam damage is much more severe, and specific crystallite shapes (platelets, needles) can exacerbate the problem of incomplete data (Mugnaioli & Kolb, 2013).

ADT data were collected with a TECNAI F30 transmission electron microscope working at 300 kV. The ADT method consists of the sequential acquisition of nano electron diffraction (NED) patterns in steady steps of 1° around the primary tilt axis of the microscope goniometer (tilt α). Using a tomographic holder, it is possible to reach a tilt range of $\pm 60^\circ$. A condenser aperture of 10 μm and mild illumination settings were used in order to produce a semi-parallel beam of 50 nm

in diameter and to minimize the electron dose rate on the sample (Kolb *et al.*, 2007). Owing to the low illumination, the crystal position was tracked in microprobe dark-field scanning transmission electron microscopy (STEM) mode. ADT was coupled with precession electron diffraction (PED; Vincent & Midgley, 1994) in order to further reduce the dynamical effects and to improve reflection integration (Mugnaioli *et al.*, 2009). A stack of two-dimensional diffraction patterns was recorded, neglecting any crystallographic orientation, and then reconstructed in a three-dimensional diffraction volume using the *ADT3D* software (Kolb *et al.*, 2008). Data on ITQ-43 were collected at 115 K to further reduce the beam damage of the sample, while all the other materials were investigated at room temperature.

RED data (Zhang *et al.*, 2010) were collected with a JEOL2010 transmission electron microscope working at 200 kV. The RED method is conceptually similar to ADT, but combines rough mechanical tilt steps with fine beam tilt steps, and usually in this way a finer sampling of reciprocal space is achieved. However, in this measurement only mechanical tilt steps of 0.2° could be used, because the beam tilt function was not working with the older microscope at the time. Thus this acquisition equates to ADT using selected-area electron diffraction (SAED) mode and TEM imaging instead of nano diffraction mode and STEM imaging (Gorelik *et al.*, 2011). In total, 500 SAED patterns were collected for 2 s each. The crystal position was tracked in TEM mode. Three-dimensional reconstruction and intensity integration were performed using the *RED* software (Wan *et al.*, 2012).

3. FOCUS

The dual-space approach to zeolite framework structure determination that is implemented in *FOCUS* (Grosse-Kunstleve *et al.*, 1997, 1999) uses *a priori* crystal chemical information to supplement the powder diffraction data. The only chemical information needed, beyond the chemical formula per unit cell, is the minimum distance to be allowed between the different types of atoms in the structure. The *T* atoms of a zeolite form a three-dimensional tetrahedrally connected network with bridging O atoms and a *T*–O–*T* angle of approximately 145° , so the distance between the node atoms is about 3.1 Å for an aluminosilicate.

A flowchart of the algorithm is shown in Fig. 1. It begins by generating an electron density map by assigning starting (usually random) phases to structure factor amplitudes derived from the X-ray powder diffraction pattern, essentially generating a random structure. For centrosymmetric structures, this means approximately half of the phases will be correct, and that is a good starting point for structure determination. The highest peaks in the map are stored in a list, sorted by peak height. Those that fulfill the criteria, are marked as potential ‘node’ atoms. At this point, an attempt is made to construct a structural model. There are two options:

(a) Atom recycling. Atoms are assigned to the peaks in the asymmetric unit on the basis of peak height (*i.e.* the heavier scatterers in the chemical formula are assigned to the highest

peaks) in a conventional manner. However, atom types are assigned only if the peak position does not violate the user-defined minimum distances. Independently, a framework search is also performed on a user-defined number of the highest peaks in the unit cell. If a full framework structure is found, it is recorded in the output file.

(b) Framework recycling. A full framework search is performed on all potential node peaks based on the pre-defined framework geometry. This is done using a specialized backtracking algorithm. Atoms are assigned according to the largest framework fragment found. Whenever a full framework is found, it is recorded in the output file.

It has been found that alternating between the atom and framework recycling procedures is the most effective strategy for structure solution. The assigned atoms are then used to generate a new set of phases, which are used together with the measured amplitudes in a Fourier recycling procedure to generate a new electron density map. The framework search is by far the most time-consuming part of the program, but this identification of potential framework structures is the key to the success of the program. Any complete framework structure found is classified and stored. A trial ends when the phases have converged or a pre-set number of cycles has been reached. Then a new set of starting phases is generated to start a new trial. This loop is repeated as often as needed to generate a sufficient number of possible framework solutions.

FOCUS takes a statistical approach to structure solution. The topology of each complete framework found is classified by computing the coordination sequence of each of the *T*

atoms in the asymmetric unit. This set of numbers acts as a fingerprint of the framework (Brunner, 1979) and can also be compared with those in a database of known framework types. Once *FOCUS* has finished, the number of times each classified topology has been found is output as a histogram and the topology occurring most frequently is most likely to be the correct one. Only the positions of the *T* atoms are reported, so bridging O atoms are then added and the framework geometry optimized using distance least squares (*DLS-76*; Baerlocher *et al.*, 1976) to give the best possible starting point for structure refinement.

Numerous zeolites of medium to high complexity have been solved using this method (McCusker & Baerlocher, 2013b). The *FOCUS* framework search routine was specifically designed for zeolites but is not limited to them. Any framework material containing nodes with well defined coordination geometries can be tackled.

The zeolite-specific information in *FOCUS* appears to compensate well for the information lost as a result of reflection overlap in XPD data, and it was hoped that it could also compensate for the incompleteness and dynamical scattering problems in ED data, and perhaps for intensity perturbations produced by crystal degradation under beam damage. Therefore, analytical scattering factors for electron diffraction, based on Table 4.3.2.2 of *International Tables for Crystallography* Vol. C (Cowley *et al.*, 2006), were included in the *FOCUS* code. A new keyword, `ScatteringFactorTable`, which tells the program which scattering factor table to use, was added to the input options. Two choices are available: `X-ray` tells the program to use the default analytical scattering factors for X-rays based on tables as derived by Waasmaier & Kirfel (1995), and `electron` tells the program to use the aforementioned Table 4.3.2.2. Data are treated with the kinematic approximation, *i.e.* intensities are considered to be proportional to the square of the structure factor amplitudes.

4. Application to test cases

For testing purposes, ADT data collected on the zeolites natrolite (framework type **NAT**²), ZSM-5 (**MFI**), ITQ-43 and IM-5 (**IMF**) (Mugnaioli & Kolb, 2013; Jiang *et al.*, 2011) were used. RED data collected on SSZ-45 were kindly provided by D. Xie (Chevron, USA). For comparison purposes, synchrotron X-ray powder diffraction data were collected on a sample of SSZ-45 on the Materials Science beamline at the Swiss Light Source (wavelength 1.0000 Å, Mythen II detector).

A summary of the samples and their structure solutions with *FOCUS* can be found in Table 1 and the corresponding histograms in Fig. 2. For the data presented, the input parameters for *FOCUS* were slightly optimized (*i.e.* by tweaking the selectivity of the framework search through `MaxPeaksFwSearch` and `MaxPeaksFwFragmentSearch`) in order to obtain better statistics and a cleaner result (Table 2). Naturally, in all cases the overlap factor was set to 0 and the

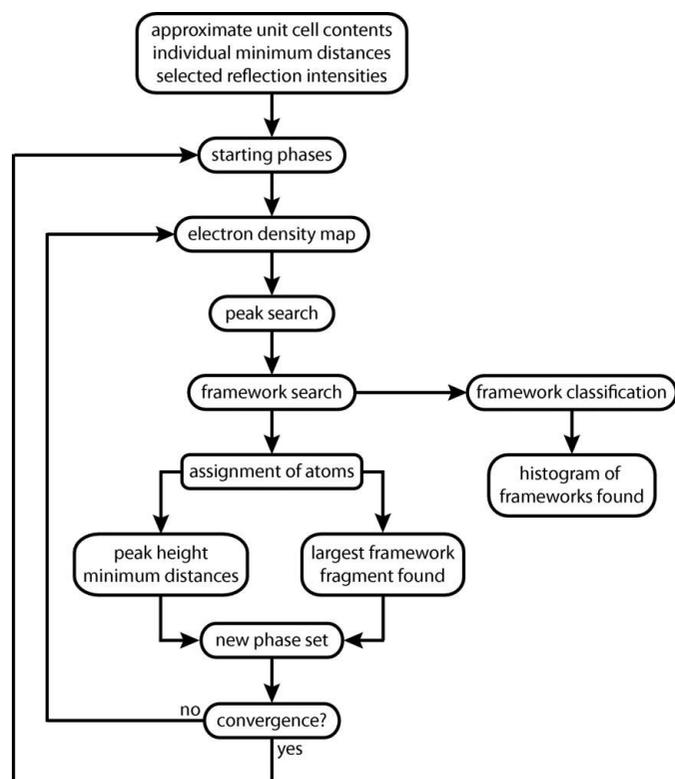


Figure 1
Flowchart illustrating the *FOCUS* method.

² The three-letter code for a known framework type will be given in parentheses when the zeolite is first mentioned.

Table 1
Crystallographic data and *FOCUS* structure solution details for the five zeolites.

Sample	Natrolite	ZSM-5	ITQ-43	ITQ-43	ITQ-43	IM-5	IM-5	IM-5	SSZ-45	SSZ-45
Measurement										
Data collection	ADT	RED	XPD							
Data set†	–	–	1 + 2	1	2	1 + 2	1	2	–	–
Total reflections	4432	22423	13032	7982	7532	32541	23342	22653	4326	982
Unique reflections	743	5285	2735	2461	2314	8489	7725	7829	708	982
Crystal data										
Space group	<i>Fdd2</i>	<i>Pnma</i>	<i>Cmmm</i>	<i>Cmnm</i>	<i>Cmmm</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Fmmm</i>	<i>Fmmm</i>
<i>a</i> (Å)	18.293	20.100	26.411	26.411	26.411	14.209	14.209	14.209	13.6	13.7129
<i>b</i> (Å)	18.640	19.924	41.399	41.399	41.399	57.237	57.237	57.237	21.7	22.1253
<i>c</i> (Å)	6.586	13.424	12.839	12.839	12.839	19.994	19.994	19.994	35.03	35.1924
Crystal size (nm)	500 × 500	500 × 300	–	200 × 90	250 × 140	–	300 × 200	300 × 200	–	100 × 100
Independent <i>T</i> atoms	3	12	11	11	11	24	24	24	10	10
<i>FOCUS</i>										
Reflections used	200	200	200	200	200	200	200	200	200	200
<i>d</i> _{min} (°)	1.00	1.14	1.19	1.17	1.19	1.16	1.16	1.13	1.05	1.18
Completeness (%)‡	100	81	98	89	87	95	92	92	53	100
<i>N</i> _{trials}	2000	2815	16156	40000	20554	100000	100000	100000	8000	155147
<i>N</i> _{solutions}	3938	311	1898	2326	2470	595	908	409	351	238
<i>N</i> _{correct}	2340	300	1791	2043	2319	587	894	372	142	108
Percentage (%)	60	96	94	88	94	98	98	91	40	45
Total CPU time	6 min	6 h	4 h	5.5 h	5.5 h	24 h	28 h	35 h	80 min	20 h
Rate (<i>N</i> _{corr} min ⁻¹)	390	0.83	7.5	6.2	7.0	0.41	0.53	0.18	1.8	0.09

† Data sets labeled (1) and (2) represent the individual unmerged data sets for ITQ-43 and IM-5. ‡ Completeness of the full data set up to *d*_{min} corresponding to the reflections used.

electron scattering factors from Table 4.3.2.2 of *International Tables for Crystallography Vol. C* (Cowley *et al.*, 2006) were used. For the natrolite, ZSM-5 and IM-5 data sets, high coverage was achieved by merging data from two different acquisitions. All structures, except for that of SSZ-45, were known beforehand, so the framework topologies generated

could be verified easily by comparing their coordination sequences with the known ones.

All five structures could be solved and identified relatively easily using the modified *FOCUS* program (Fig. 2). The most difficult part proved to be tweaking the framework search parameters in order to obtain a statistically significant solution

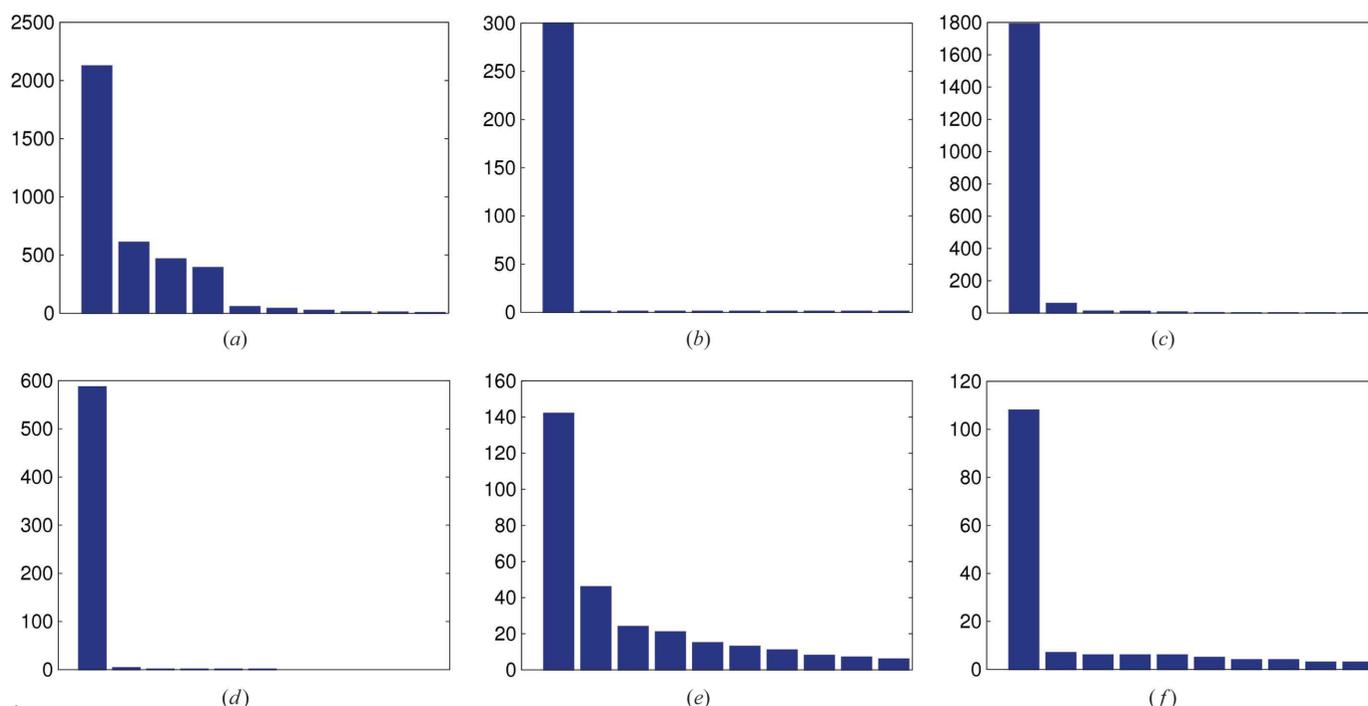


Figure 2
Histograms showing the distribution of the ten most frequently found frameworks for (a) natrolite, (b) ZSM-5, (c) ITQ-43, (d) IM-5, (e) SSZ-45 (RED), and (f) SSZ-45 (XPD).

Table 2

Overview of the input parameters most relevant to the framework search and selectivity of the algorithm for *FOCUS* structure solution.

Sample	Natrolite	ZSM-5	ITQ-43	IM-5	SSZ-45
MaxPotentialAtoms	120	130	270	1200	300
MaxRecycledAtoms	40	96	180	300	200
MaxPeaksFwSearch	1000	500	1080	900	800
MaxPeaksFwFragmentSearch	800	200	250	400	400
MinNodeDistance	2.6	2.6	2.6	2.6	2.6
MaxNodeDistance	3.6	3.8	3.7	3.8	3.8

within a reasonable amount of time. *FOCUS* has several parameters that guide the selectivity of the algorithm, and these have the power to alter the statistical outcome of the procedure significantly. A short overview of some of the reasoning used to adjust these parameters is given below.

It was found that the maximum node–node distance for the topology search was best increased from 3.6 to 3.8 Å in order to increase the number of frameworks found. For aluminosilicates, a MaxNodeDistance value of 3.8 Å seems to be better than 3.6 Å for detecting valid *T–T* connections. Higher values resulted in larger numbers of incorrect frameworks. Only the *T* atoms were used in the recycling procedure, so MaxRecycledAtoms could be set to the number of *T* atoms and MaxPotentialAtoms was set to a value somewhere between 1.2 and 3.0 times the number of *T* atoms.

The input parameters MaxPeaksFwSearch and MaxPeaksFwFragmentSearch were found to be very difficult to balance. Low values tended to make the framework search faster, at the cost of fewer solutions per trial, whereas high values resulted in much longer trials but, on average, more solutions per trial, both correct and incorrect. Reasoning that, as long as correct solutions are found, a reduced time per trial is preferable to a larger number of solutions per trial in terms of total efficiency, the lower value option was favored. As a general rule for a starting value, MaxPeaksFwSearch was set to 4.5–6.0 times and MaxPeaksFwFragmentSearch to 1.5 times the number of *T* atoms.

For each data set, the 200 reflections with the largest structure factor amplitudes (mF , where m is the multiplicity of the reflection) were used for structure solution. For each structure solution, the resolution was well below the minimum *T–O* distance of 1.4 Å.

Structure solutions were performed in parallel on a 2010 Mac Pro equipped with a dual 2.4 GHz Quad-Core Intel Xeon processor. The reported times are the single-CPU equivalents. Although some of the examples presented here took up to 35 h to complete in order to test the method thoroughly, correct frameworks were often found in a matter of minutes.

4.1. Test case 1: natrolite (NAT)

Natrolite is a simple natural zeolite, whose structure was first deduced by Pauling (1930). Its framework consists of three independent *T* atoms (one Al, two Si) with Na⁺ and H₂O in the pores. Because of its simplicity and the high completeness of the data set, natrolite served as an ideal test case to

check and validate the modified *FOCUS* structure solution procedure. The structure had been solved from ADT data previously using the direct methods algorithm implemented in *SIR2008* (Burla *et al.*, 2007), and all ten non-H atoms could be located and correctly assigned (Mugnaioli & Kolb, 2013).

Structure solution with *FOCUS* was straightforward and no optimization of the input parameters was necessary in order to find the correct framework. Optimizing the input parameters led to an increase in selectivity towards the correct structure. The most frequently found solution represents 60% of all solutions. Because the structure is a simple one, the solution is very fast and efficient. At the same time, the simplicity allows a large number of alternative framework structures to be generated by *FOCUS*. No attempt was made to distinguish between Al and Si, because their electron scattering factors are nearly identical. In contrast to direct methods, *FOCUS* only looks for a framework that matches the specified criteria. The location of the atoms in the pores and the distribution of Al and Si over the *T*-atom sites have to be determined subsequently during the course of the structure refinement.

4.2. Test case 2: ZSM-5 (MFI)

The structure of ZSM-5 was first solved by model building using single-crystal X-ray diffraction data (Kokotailo *et al.*, 1978). Its solution from ADT data more than 30 years later using direct methods was straightforward (Mugnaioli & Kolb, 2013). All Si and O atoms could be located, despite the fact that the coverage was relatively low (79%) and all *h*00 reflections were missing.

The framework was easily deduced using *FOCUS*, once it was recognized that MaxNodeDistance should be relaxed from the conventional 3.6 to 3.8 Å.

4.3. Test case 3: ITQ-43

ITQ-43 is an interesting silicogermanate with a huge cloverleaf-shaped pore (21.9 × 19.6 Å), delimited by 28 *T* atoms, and a low framework density of 12.8 T per 1000 Å³. The structure was first solved using direct methods on ADT data and was then refined with X-ray powder diffraction data (Jiang *et al.*, 2011). These ADT data allowed us to test the ability of *FOCUS* to deal with very large pores and low framework densities.

Two data collections on different crystals (with the same tilt range) were merged to produce a single data set with increased completeness (98%). The data were collected on a sample that still had the organic structure directing agent (SDA) used in the synthesis in the pores, because removing the SDA by calcination in the atmosphere destroyed the framework. Nonetheless, all 20 independent Si/Ge atoms and 24 of the 42 O atoms could be found *ab initio* by direct methods in the space group *C222*.

There are three aspects of this material that made the structure determination with *FOCUS* challenging:

(1) The zeolite pores are populated with 16 SDA molecules {(2*R*,6*S*)-2,6-dimethylspiro[isoinoline-2,1-iperidin]-1-ium hydroxide} per unit cell. These were approximated by including

$16 \times C_{15}N$ as non-framework atoms in the *FOCUS* input file to make the scaling more correct.

(2) There are $Q^3 T$ atoms in the framework, and for structure solution using *FOCUS*, it is essential that this be specified *via* the *NodeType* instruction. No solutions were found until the presence of 3-connected *T* atoms was indicated in the *FOCUS* input file. In this case, the structure was known, so $Q^3 T$ atoms were included. For a material of unknown structure, this information could be derived from magic angle spinning NMR spectra.

(3) The *T*-atom positions are partially occupied by Ge and Si, with an expected Si/Ge ratio of 2 (supplementary material of Jiang *et al.*, 2011). To improve the structure determination procedure, the scattering factor for the *T* atoms was calculated as a linear combination of 0.35 Ge and 0.65 Si.

It took several attempts to find suitable input parameters for *FOCUS* for this structure. Although it was found that specifying the *SDA* and customizing the scattering factor for the *T* atoms improved the results, these modifications were not strictly necessary for structure solution. On the other hand, knowing that $Q^3 T$ atoms were present was essential. The final input parameters are as general as possible and provide a convincing result for the determination of the framework structure of ITQ-43; of the retrieved frameworks, 94% were correct. In view of the large number of solutions found, *MaxNodeDistance* was reduced to 3.7 Å in an attempt to filter out more of the incorrect frameworks. Indeed, the resulting histogram of solutions showed that the algorithm was more selective towards the correct solution, but as a consequence also generated fewer solutions in total. Structure solution was repeated using the unmerged data sets, but the reduced completeness of 89 and 87% did not affect the structure solution significantly.

4.4. Test case 4: IM-5 (IMF)

The structure of IM-5 was first solved using a complicated procedure involving the charge-flipping algorithm in combination with X-ray powder diffraction and high-quality HRTEM data (Baerlocher, Gramm *et al.*, 2007). With 24 independent Si atoms and a total of 288 Si and 576 O atoms in the unit cell, IM-5 is one of the most complex zeolite structures known. Because of its complexity, the structure has been used as a test case in methodology development and has since been solved from HRTEM data alone (Sun *et al.*, 2010) and from XPD data alone (Xie *et al.*, 2011). From ADT data, it was only possible to solve the structure partially using direct methods (Mugnaioli & Kolb, 2013).

FOCUS was first applied to a data set created by merging two data sets collected on the same crystallite with tilt angles of 106 and 102°, each covering different areas of reciprocal space. In this way, a rather complete data set with a coverage of 95% could be obtained. However, all reflections in the *h*00 direction are missing. Over a period of 24 h, *FOCUS* was able to generate 587 correct framework solutions in a very straightforward manner. The procedure was then repeated on the unmerged data sets, which are slightly less complete and

less accurate. The same input file was used and the framework structure was recovered easily using either data set. The simplicity with which *FOCUS* is able to solve this structure from ADT data is remarkable. With optimized parameters, the most frequently found solution is the correct one and represents nearly all solutions found. This example shows that *FOCUS* is able to solve a very complex structure from ADT data, despite the missing *h*00 reflections.

4.5. Test case 5: SSZ-45

The SSZ-45 test case was an interesting one for several reasons: (1) the data were collected using the RED method, (2) they only had a completeness of 53%, (3) synchrotron XPD data were available on the same sample, so the different data types could be compared directly, and (4) the structure was unknown. The structure of SSZ-45 was first solved in our group independently using *FOCUS* and XPD data. That framework structure was later identified as being the same as the one reported for ERS-18, which had been solved earlier using *FOCUS* on XPD data (Zanardi *et al.*, 2011).

The XPD pattern could be indexed with an orthorhombic unit cell ($a = 13.7129$, $b = 22.1253$, $c = 35.1924$ Å), but the space group was ambiguous (*Fmmm* or one of several *C*-centered space groups: *C222*, *Cmmm*, *C2mm*, *Cm2m*, *Cmm2*). Intensities and peak half-widths were extracted using the Pawley (1981) profile fitting procedure in the program *TOPAS* (Coelho, 2007) for all of these space groups. However, only with *Fmmm* was structure solution successful. A total of 155 147 trials were performed with *FOCUS* over 16 h of total computing time, yielding 238 framework solutions. The most frequent solution is the expected one and represents 108, or 45%, of the total number found. Refinement of the structure is presently in progress.

The RED data did not show any violations of the *F*-centering condition, so *Fmmm* was assumed. However, the RED data set is only 53% complete up to a resolution of 1.05 Å. Nonetheless, the correct topology could be produced easily. Exactly the same input parameters as those used for the XPD data were applied, with the exception that the overlap factor was set to 0 and electron diffraction scattering factors were used. Eight thousand trials were found to be sufficient to produce 351 possible frameworks in 80 min, out of which the correct solution is the most frequent one, occurring 142 times (40%). The relatively low percentage of correct frameworks compared to the ADT examples can probably be attributed to the low completeness of the data. Coincidentally, the percentage of correct solutions found is similar for the XPD and RED data and highlights one of the advantages of using three-dimensional electron diffraction data in combination with *FOCUS*. The solutions with RED data were produced in only 80 min, while those for XPD data took 16 h.

5. Conclusion

The test cases presented in this paper show how a program like *FOCUS*, which is based on using *a priori* crystal chemical

data specific to zeolite structures together with less-than-ideal diffraction data, can be used to solve even very complex framework structures of zeolites from three-dimensional electron diffraction data.

These results show that imposing chemical and geometrical restraints on a structure can be of great benefit in structure solution. While the reflection intensities derived from three-dimensional electron diffraction data are not affected by the overlap problem, they do suffer from dynamical scattering effects, so the intensities are not directly proportional to the square of the structure factor. The results presented here show that this does not pose any problem for structure solution with *FOCUS*. Indeed from the comparison of the two types of data in the case of SSZ-45, the inaccuracies introduced *via* dynamical scattering in ED data and the incompleteness of this data set appear to be less obstructive than those arising from reflection overlap in XPD data.

The use of *FOCUS* with three-dimensional electron diffraction data offers a major improvement in both the time and the effort required to solve a zeolite framework structure, as long as the sample allows the ED data to be collected in the first place. In fact, process automation and reduction of electron dose on the sample are major requisites for tomographic ED data acquisition on zeolite samples.

In each of these test cases, one solution was clearly found preferentially (Fig. 2), and this always proved to be the correct structure. Of course, in a true structure determination, the model would still have to be validated by Rietveld refinement using the XPD data.

The program package, including several useful tools, is available for download free of charge on the web site of the Structure Commission of the International Zeolite Association (<http://www.iza-structure.org/>) under 'Software'.

We thank the beamline scientists at the Swiss Light Source in Villigen, Switzerland, for their assistance with the powder diffraction measurement and Dan Xie for the RED data collection. Funding from the Swiss National Science Foundation and Stiftung Rheinland Pfalz für Innovation is gratefully acknowledged.

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