Development of Hybrid Methods for Solving the Structures of Polycrystalline Materials

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“What a computer is to me is it’s the most remarkable tool that we have ever come up with. It’s the equivalent of a bicycle for our minds.”

— Steve Jobs
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Abstract

For structure determination of complex polycrystalline materials, synchrotron X-ray powder diffraction (XPD) data alone is sometimes not enough. The data may be of unavoidably poor quality, the sample may contain multiple phases, the reflection overlap may be high, or the structure may simply be complex. Information from electron microscopy techniques has shown to be an effective complement to XPD data, even when structure solution seems impossible from either method by itself. The approach to solving a structure will depend on the problem. Such was the case for high-silica zeolites SSZ-45, SSZ-61, SSZ-87, and SSZ-70, where combining data from different sources was vital to success.

The program FOCUS was originally developed to solve zeolite structures from XPD 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 (ED) 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 tested successfully with four different ADT data sets and then applied to solve the structures of two new zeolites (SSZ-45 and SSZ-87) with RED data.

Previous studies had already shown that the combination of ED data collected along several zone axes with XPD data can lead to an improvement of the structure solution process. This idea was revisited with three-dimensional ED data in mind. ED intensities are dynamical and full coverage cannot always be achieved, but because single crystallites are measured, all diffraction peaks are well resolved. XPD data suffers from an ambiguity in diffraction intensities due to reflection overlap, but the data are complete, diffraction intensities kinematical, and the total intensity accurate. Although this results in unreliable reflection intensities in both cases, the data are highly complementary. By combining the three-dimensional ED and XPD data sets, the deficiencies of each could be compensated by the other, and this significantly improved the structure solution process of the four zeolite samples tested.

Determining the location of the organic structure-directing agent (SDA) inside the channel system of a zeolite is a long-standing problem in zeolite struc-
The tangible connection between the SDA used and the framework formed is of great value to our understanding of the synthesis process. However, this is often limited by the quality of the XPD pattern of the material. Furthermore, the SDA is often disordered, and does not necessarily follow the symmetry of the framework. Simulated annealing is an effective and practical tool to overcome this problem. By introducing the SDA into the model as a rigid-body, a starting location and orientation can be found using simulated annealing. Subsequent Rietveld refinement can then be used to verify the structure. To test if this method could be applied in a routine manner, synchrotron XPD data were collected on as-synthesized samples of SSZ-53, SSZ-55, SSZ-56, SSZ-58, SSZ-59, and SSZ-60, all with known framework structures. In each case, the location of the SDA was estimated originally using molecular dynamics modeling. For SSZ-56, and SSZ-59, with two-dimensional channel systems, the location of the SDA could be determined in a straightforward manner. All the others have one-dimensional channel systems, and these required more effort. For most of these zeolites, the molecular modeling results compare well with those obtained from the XPD data, but there are also some clear differences.

X-ray free electron laser (XFEL) sources provide new opportunities for analyzing difficult crystal structures. For organic/inorganic materials with unit cells much smaller than those of the macromolecular crystals that have been the focus of most XFEL studies to date, the broad-bandpass mode (4% energy bandwidth) that will be provided at SwissFEL can be used. To deal with such data, new strategies for data collection and processing are required. The crystals are destroyed by the extremely intense X-ray pulse, so only single snapshots of the sparse data can be recorded, and this makes indexing a challenge. The problems to be overcome are four-fold: (1) accurate orientations have to be retrieved from a single frame, (2) the wavelength associated with each diffraction spot is indeterminate, (3) the unit cells are small, so the number of observations per frame is limited, and (4) it would be advantageous if the orientations of multiple crystals could be determined from a single frame. Experiments mimicking a 4%-energy-bandpass mode were performed on SNBL at the ESRF on samples of the zeolite ZSM-5 (up to 15 crystals measured simultaneously), the mineral sanidine, and a cesium cyanoplatinate. Several existing methods for indexing these data were examined, assuming the unit cell to be known a priori, but most of them proved to be ill-suited. Therefore, a new strategy was developed to deal specifically with the data at hand. Candidate crystal orientations are generated either by searching for the indices that match the d-spacings and angles of two low-resolution non-collinear reflections, or with a brute force approach that tries 1.5 million roughly equally distributed rotation matrices that cover all possible crystal orientations. The idea is that only a good solution will index a large number of reflections. To index multiple patterns, the smallest subset of orientation matrices that indexed the largest number of reflections are to be identified. For each sample, the indexing routine performed admirably, and the orientations of up to 12 crystals could be determined from a single frame. While our algorithms were developed with SwissFEL in mind, they can be applied to any data collected in single snapshot mode with either monochromatic or broad-bandpass radiation.
Zusammenfassung

Zur Strukturbestimmung komplexer polykristalliner Materialien genügen Synchrotron-Röntgenpulver-Beugungsdaten (XPD) allein nicht immer. Die Daten können von nicht vermeidbaren schlechter Qualität sein, die Probe kann mehrere Phasen enthalten, die Überlappung der Reflexe kann hoch oder die Struktur einfach zu komplex sein. Informationen von Elektronenmikroskopie-Techniken sind eine effektive Ergänzung zu XPD Daten, auch wenn die Kristallstruktur mit den jeweils separaten Daten dieser Methoden nicht gelöst werden kann. Der Ansatz zur Lösung einer Struktur hängt vom Problem ab. Dies war der Fall für die high-silica Zeolithe SSZ-45, SSZ-61, SSZ-87 und SSZ-70, bei denen nur die Kombination von Daten aus verschiedenen Quellen zum Erfolg führte.


Frühere Studien hatten bereits gezeigt, dass die Kombination von XPD Daten mit zweidimensionalen ED Daten (gemessen entlang verschiedener Zone-Achsen) zu einer Verbesserung des Strukturlösungsprozesses führen kann. Diese Idee wurde nun auch auf die dreidimensionale ED Daten übertragen. ED Intensitäten sind dynamisch und eine vollständige Messung aller vorhandenen Reflexe kann nicht immer erreicht werden. Weil aber Einkristalle gemessen werden, treten – im Gegensatz zu den XPD Daten – keine Überlappungen der Beugungsintensitäten auf. Umgekehrt sind XPD Daten immer vollständig, die Beugungsintensitäten kinematisch und damit die Gesamtintensitäten genau. In beiden Fällen erhält man unzuverlässige Intensitäten für die einzelnen Reflexe. Da die Ursachen dafür aber verschieden sind, sind die Daten sehr komplexen-
tär. Durch deren Kombination kann ihre Unvollkommenheit gegenseitig etwas kompensiert werden. Dies verbesserte das Strukturlösungsverfahren bei den vier getesteten Zeolithproben.


Röntgenlaser (X-ray free-electron laser, XFEL) bieten neue Möglichkeiten für die Analyse von komplizierten Kristallstrukturen. Im Mittelpunkt der meisten XFEL Studien stehen bis heute makromolekulare Kristalle, die sehr grosse Einheitszellen haben. Für organische oder anorganische Materialien mit kleineren Einheitszellen, könnte der Breitbandmodus (4% Energiebandbreite) verwendet werden, der ab ca. 2017 am SwissFEL zur Verfügung gestellt wird. Darum mit solchen Daten gearbeitet werden kann, sind neue Strategien für die Datenerhebung und -verarbeitung erforderlich. Der Röntgenimpuls an einem XFEL ist extrem stark und zerstört die Kristalle sofort. Daher kann nur ein einziges Beugungsbild pro Kristall aufgezeichnet werden, was die Indizierung zu einer grossen Herausforderung macht. Es gibt vier Hauptprobleme: (1) die genaue Kristallorientierung muss aus nur einer Aufnahme bestimmt werden, (2) die Wellenlänge, die zu einem bestimmten Reflex gehört, ist unbestimmt, (3) die Elementarzellen sind klein, was die Anzahl der Reflexe pro Aufnahme begrenzt, und (4) die Orientierungen mehrerer Kristalle (falls vorhanden) müssten ebenfalls aus einer einzigen Aufnahme bestimmt werden. Um einen 4%-Energie-Bandpass-Modus zu imitieren, wurden an der SNBL in Grenoble entsprechende Experimente durchgeführt an Proben (1) vom Zeolith ZSM-5 (bis zu 15-Kristalle gleichzeitig im Röntgentrahl), (2) dem Mineral Sanidin und (3) einem Cäsium Cyanoplatinat. Zur Indizierung dieser Daten wurden mehrere bekannte Algorithmen unter der Annahme untersucht, dass die Elementarzelle bekannt ist. Die meisten Methoden waren aber ungeeignet für diese Art von Daten. Daher wurde eine neue Strategie entwickelt. Mögliche Kristallorientierungen werden erzeugt, entweder durch eine Suche nach den Indizes von zwei Beugungsmaxima.
mit Hilfe eines Vergleichs der $d$-Werte und des dazwischen liegenden Winkels, 
or mit einem Brute-Force-Ansatz, bei dem rund 1.5 Millionen gleichverteilte 
Kristalldorientierungen getestet werden. Die Idee ist, dass nur eine gute Lösung 
eine grosse Anzahl von Reflexen indiziert. Um mehrere, gleichzeitig vorhanden 
Beugungsbilder zu indizieren, wird die kleinste Teilmenge von Orientierungs-
matrizen identifiziert, mit der die grösste Anzahl von Reflexen indiziert werden 
kan. Für alle Proben funktionierte dieser Algorithmus hervorragend, und auch 
die Orientierungen von bis zu zwölf Kristalle pro Aufnahme konnte einwandfrei 
bestimmt werden. Obwohl unsere Algorithmen für SwissFEL entwickelt wurde, 
können sie auf alle Daten angewendet werden, die entweder mit monochromati-
scher oder Breitbandstrahlung in Einzelbild-Modus erfasst wurden.
ZUSAMMENFASSUNG
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Chapter 1

Introduction

One may ask oneself the question “what is this white powder that has formed inside my water kettle?” Although many experimental methods can give some hints as to what it could be, only crystallographic methods can give the full atomic picture. In fact, X-ray powder diffraction (XPD) is probably the most valuable experimental technique for characterizing polycrystalline materials. Information about the material, such as its chemical content, mechanical (stress, strain) and other bulk properties, and crystal structure can be uncovered by applying powder diffraction techniques. The most widespread use of powder diffraction is for phase identification, because every crystalline material produces a distinct diffraction pattern, which serves as a fingerprint for the material. Identification can be performed by comparing the measured pattern to that of a known standard or previously prepared material. The ratio between the amounts of several phases in a sample can be obtained from a single diffraction pattern. It is relatively easy, and both time- and cost-efficient, to measure a diffraction pattern, and this is why powder diffraction is used extensively in industrial and academic laboratories for identification, characterization, and quality control, whether it be for catalysts, pharmaceuticals, minerals, semiconductors, or other materials.

Crystal structure determination, a task routinely performed using single-crystal X-ray diffraction (XRD) data, is also possible from XPD data, and is usually the only option available if a material does not form large enough crystals. With XPD data, this task is complicated by the fact that the three-dimensional single-crystal diffraction pattern is collapsed into one dimension by spherical averaging, due to the random orientation of the individual crystallites. Where reflections would be conveniently separated in the single-crystal case, those with similar $d$-spacings overlap in a XPD experiment. The degree of overlap depends on the crystal symmetry and increases with Bragg angle and the size of the unit cell.

Structure determination methods can be divided in three groups. The first are reciprocal space methods, which are the traditional ones for solving crystal structures from single-crystal data. These methods try to solve the crystallographic phase problem directly from the observed data by making assumptions about phase relationships and structure factor amplitudes, and are effective for XPD data with a low degree of reflection overlap. The second group are direct space methods, which work by applying global optimization algorithms to search
for a structural model that fits the measured data. They require a priori chemical knowledge, such as molecular geometry, cell contents, and/or connectivity. The position and orientation of rigid structural fragments and/or atoms are optimized against the data directly, so the overlap problem is circumvented. The last group are dual space methods, which typically alternate between direct and reciprocal space methods, and can consequently take advantage of constraints that can be applied in either space. Methods for structure determination from XPD data continue to improve, and a large number of crystal structures can now be solved from XPD data directly (David and Shankland, 2008). Generally, reflection overlap is the fundamental obstacle hindering the use of XPD for determining and refining complex crystal structures in a routine manner. The problem can be reduced by measuring at synchrotron facilities, because the instrumental contribution to the peak width is reduced to a minimum, or by applying computational methods that use non-overlapping reflections to estimate the intensities of overlapping reflections (Jansen et al., 1992; Estermann et al., 1992). Although it is also possible to separate overlapping peaks experimentally by exploiting anisotropic thermal expansion (Shankland et al., 1997b; Brunelli et al., 2003), or preferred orientation (Baerlocher et al., 2004; Grässlin et al., 2012), such methods have not yet found widespread use.

In cases where XPD data reach their limit, researchers have turned to other experimental methods to study nano- and micro-crystalline materials. Electron crystallography implies the use of electron diffraction (ED) intensities and/or high resolution transmission electron microscopy (HRTEM) images, and the Fourier transform thereof, for crystal structure analysis (Dorset, 1995). HRTEM can be used for two-dimensional unit cell determination and provides low resolution phase information and diffraction intensities. Using the recently developed electron diffraction tomography (EDT) techniques (Kolb et al., 2007; Zhang et al., 2010), it is now possible to collect reasonably complete diffraction data that offer information similar to that obtained with single-crystal XRD, although the reflection intensities are less accurate because of dynamical scattering and beam damage. The main advantage is that electrons scatter much more strongly than do X-rays, so structural information can be obtained from small single crystallites with dimensions down to 10 nm, and thus the overlap problem can be avoided. A considerable number of crystal structures have now been solved from EDT data directly (Yun et al., 2015). Electron microscopy techniques offer information that is notably complementary to that obtained from XPD data, and can also be used to supplement XPD data in order to solve complex crystal structures (McCusker and Baerlocher, 2009, 2013).

A small number of researchers have used solid state NMR methods, generally combined with quantum chemical calculations, model-building, and diffraction or other experimental techniques, to determine the structures of materials that are difficult to solve otherwise. These efforts have led to strategies for identification (Martineau et al., 2015), structure solution (Brouwer et al., 2005; Brouwer and Horvath, 2015), and structure refinement (Brouwer, 2008) of polycrystalline materials using NMR data.

A relatively new concept for structure determination using tiny crystals is being developed by the protein community. By using new X-ray free electron laser (XFEL) sources, it is possible to collect single shot diffraction patterns from a stream of nano-sized crystals using femtosecond pulses. The idea is that the crystals diffract before they are destroyed by the very intense pulse.
Only a small number of these shots result in a useful diffraction pattern, but by collecting hundreds of thousands of shots, a data set that is complete enough to solve the structure of a macromolecule can be constructed (Chapman et al., 2011).

The aim of my Ph.D. project was to look for new ways of combining data and methods to push the limits of structure solution for polycrystalline materials a little bit further. The motivation is that determining the structure of a polycrystalline material is not a trivial task, and methods need to continue to evolve to handle more complicated materials and structures. Zeolites are an industrially important class of microporous materials that are widely used, and often can only be obtained in polycrystalline form. Their structures are complex and can be difficult to solve, and are therefore ideally suited for method development.

To put this in perspective, the history of the synthesis of zeolites, their applications, and their characterization by crystallographic methods have been summarized in Chapter 2. Some of the basic concepts of crystallography and powder diffraction are introduced in Chapter 3, and methods for structure solution in Chapter 4. In Chapter 5, I show how a program like FOCUS, a dual-space method developed specifically for solving zeolite structures from XPD data, can evolve as a result of advances in EDT. Several new zeolite structures have now been solved using FOCUS with ED data. In Chapter 6, I describe my efforts to improve on the quality of ED and XPD data by combining them, with the goal of creating a data set that is better suited for structure solution than either one by itself. Several structures of new polycrystalline materials were solved by applying different combinations of computational methods for structure determination and/or experimental methods such as HRTEM, ED, and NMR. Their structure solutions are summarized in Chapter 7. These included some samples of as-synthesized zeolites, so the problem of locating the organic structure-direction agent (SDA) also had to be faced. In Chapter 8 I describe an efficient way of tackling this problem pragmatically, and compare the results with those obtained via molecular modeling. Finally, for something completely different, I became part of an initiative to use the 4% energy-bandpass-mode that will be unique to SwissFEL, the new XFEL source being constructed at the Paul-Scherrer Institute (Villigen, CH), for structure analysis of organic and inorganic materials, using an approach similar to the one developed by the protein community. Existing methods are ill-suited to deal with such data, so as part of this project, I developed methods to index single-shot patterns of randomly oriented crystals (Chapter 9).
Chapter 2

Zeolites

2.1 History

As in every other introduction to zeolites, this one also starts with the origin of the name, which was coined about 250 years ago. It was the Swedish mineralogist Axel Fredrik Cronstedt, who noticed in 1756 that the natural zeolite stilbite started to fume when heated as the water occluded in the pores started to evaporate. He called the material a zeolite, combining the Greek ζέω (zéō; to boil) with λίθος (líthos; stone), or boiling stone.

Zeolites are a class of crystalline open-framework materials containing channels and cavities of molecular dimensions. The geometry of the atoms in zeolite frameworks is well known. The tetrahedrally coordinated atoms (commonly referred to as T-atoms) form a three-dimensional 4-connected network with bridging O atoms and a T–O–T angle of approximately 145° (Figure 2.1). The distance between neighboring T-atoms is about 3.1 Å. The channel systems can be multi-dimensional, and each channel is often classified by the number of T-atoms delimiting the smallest pore opening. Channels delimited by an 8-ring are considered small (∼4.0 Å), 10-rings medium (∼5.5 Å), 12-rings large (∼7.0 Å), and anything above that extra-large. Traditionally, zeolites are defined as aluminosilicate framework materials. Nowadays, high- or pure-silica (SiO$_2$) zeolites can also be produced, and the Si can also be replaced by heteroatoms like Ge, B, Al, Ga, Zn, Be, P, etc. To distinguish between zeolites that have the same framework, but different composition of heteroatoms, each unique and confirmed framework type is given a three-letter code by the Structure Commission of the International Zeolite Association. Figure 2.2 shows the archetypical high-silica zeolite ZSM-5 with channels delimited by 10-rings. It serves as the type material that defines the framework code MFI (ZSM-five).

A zeolite’s performance is essentially determined by its structural characteristics, such as the dimensionality of its channels, the accessible volume, the size of the pore openings, and the number and placement of extra-framework species. Zeolites have excellent hydrothermal stability, their key components (Si, Al, O) are of high natural abundance, and therefore inexpensive, and their properties can be tuned for specialized applications. For example, Al has fewer electrons in the outer shell than does Si, so it introduces a local negative charge into the framework that is compensated by exchangeable cations. An array
CHAPTER 2. ZEOLITES

Figure 2.1: Zeolite connectivity is well known.

of cations with different catalytic properties can be introduced into the zeo-
lite at this site, and this has consequences for any reaction that is acid- or
metal-catalyzed. Furthermore, the pore openings of zeolites are of molecular di-
mensions. While this makes them useful as molecular sieves, this also allows for
shape-selective catalysis by exploiting both properties to control the selectivity
of catalytic reactions. As a result, zeolites have found widespread application as
catalysts, adsorbents, molecular sieves, and ion-exchangers and are among the
most important catalysts in the oil refining, petrochemical, and fine chemical
industries. This potential was first realized in 1925, when Weigel and Steinhoff
noticed that dehydrated chabazite acted as a molecular sieve, because it ad-
sorbed small molecules like water, methanol, and ethanol, but not larger ones,
like acetone, ether and benzene (Weigel and Steinhoff, 1925).

Although the first synthetic zeolite was produced in 1862, by St. Claire-
Deville, who was able to produce the zeolite levyne (LEV) in the lab (Saint-
Claire-Deville, 1862), the origin of modern zeolite synthesis is widely credited
to Richard Barrer and Robert Milton. Barrer laid the foundations in the 1940s
with his work on the conversion of known minerals, such as analcite and leucite,
to new materials using strongly saline solutions at high temperatures (up to
270 °C). He was able to produce the first synthetic zeolites (denoted species
P and Q) with no known natural analog (Barrer, 1948; Barrer et al., 1953). These
were later found to have the KFI framework structure (Kerr, 1963). In
the mean-time, there was significant industrial interest in the use of zeolites
as molecular sieves and adsorbents. Milton, working at Union Carbide Cor-
nporation, developed methods for synthesis using more reactive materials than
did Barrer. By 1953, he and his co-workers were able to produce a score of
new zeolites, 14 of which had not been found in nature. Most notably, they
discovered zeolites A (LTA; Breck et al., 1956; Milton, 1959a) and X (FAU;
Milton, 1959b), and later zeolite Y (FAU; Breck, 1964), each of which has found
widespread industrial and commercial applications, and all three are produced
on a massive scale today.

A major breakthrough came in 1961 when Barrer and Denny described the
inclusion of organic molecules in the synthesis, with the idea that by using a
larger cation, the amount of Al in the framework could be reduced. Initially,
simple tetramethylammonium (TMA) molecules were used, but later on, as re-
searchers began to realize that the organic cations acted as excellent structure-
2.1. HISTORY

Figure 2.2: View along the $a$-axis of the archetypical zeolite ZSM-5.

directing agents (SDAs), increasingly more complicated ones were used. An important outcome of this was the discovery of Zeolite Beta (*BEA; Wadlinger et al., 1967) and ZSM-5 (MFI; Argauer and Landolt, 1972) at Mobil Oil Corporation. These two high-silica zeolites have found many applications in catalysis.

Experimenting with the SDA flourished to become a prime research interest in the 1980s (Lok et al., 1983), and a large number of new zeolites were discovered as a result. Several groups started to perform systematic studies on the effect of the charge, shape, size, and composition of the SDA on the host-guest interaction (e.g. Gies and Marler, 1992; Gies, 1994; Kubota et al., 1996; Wagner et al., 2000).

A major trend over the last decade has been the incorporation of Ge into the reaction mixture. The longer Ge–O bond distance (1.71 Å) allows for a more flexible framework geometry, and favors the formation of double 4-rings (d4r). The Corma group in particular have produced a large number of germanosilicate materials with new framework topologies (e.g. Corma et al., 2002, 2006; Sun et al., 2009; Moliner et al., 2012; Jiang et al., 2015). Incorporation of Ge into a zeolite framework typically leads to a reduction in thermal and hydrothermal stability. Some researchers have found ways to turn this to advantage, by exploiting the preferential occupation of Ge in the d4r units to invoke an inverse sigma transformation (Shoemaker, 1973) to create high-silica zeolites with new frameworks (Verheyen et al., 2012; Chlubná-Eliášová et al., 2014; Shamzhy et al., 2014). A detailed overview of the history of hydrothermal synthesis of zeolites can be found in the reviews by Cox and Cundy (2003; 2005).

At the same time as Barrer and Milton were experimenting with zeolite syn-
thesis, methods for structure determination using XRD techniques were being
developed, and these have played a key role throughout the history of zeolite
science. Of foremost interest was the elucidation of the framework structures of
new zeolites, and consequently, their channel systems. The first zeolite struc-
tures were solved by Pauling and Taylor in the early 1930s by clever consid-
eration of the crystal symmetry in combination with model building. In this
way, they were able to solve the structures of the minerals natrolite and cancri-
nite (NAT and CAN, respectively; Pauling, 1930b), sodalite (SOD; Pauling,
1930a), edingtonite (EDI; Taylor, 1930), analcrite (ANA; Taylor and Jackson,
1933), and thomsonite (THO; Taylor et al., 1933). It was 100 years after St.
Claire-Deville discovered how to synthesize levyne, that its structure could
finally be elucidated (Barrer and Kerr, 1959).

As many companies were trying to produce new zeolites, the number of new
materials discovered boomed in the 1970s. It became clear that many labs
were producing similar materials, with the same framework topology, but un-
der different names. In an attempt to bring some order into this chaos and to
categorize the zeolites, Meier and Olson produced the Atlas of Zeolite Structure
Types – a compilation of all the known framework types, each of which had been
assigned a three-letter code (Meier and Olson, 1978). For example, Zeolites X
and Y have the same framework structure as the natural mineral faujasite, and
are therefore all assigned the code FAU. The original print, featuring MFI
on the front cover (the most complicated zeolite known at the time), contained 38
codes, including wire-frame stereo drawings of the frameworks and a descrip-
tion of their crystal, symmetries, and type materials. Nowadays, the codes are
assigned by the Structure Commission of the International Zeolite Association,
which is officially recognized by IUPAC. The 6th, and latest printed version still
features MFI on the cover, although it is no longer the most complicated zeolite
known. The most up-to-date database can only be found online, and contains
229 different framework codes at the time of writing (Baerlocher et al., 2007c).

There was also a lot of interest in the distribution of extra-framework species
and cations in the zeolite channels and cavities, because these strongly affect
the physico-chemical properties of a material and impact its ion-exchange ca-
pacity, catalytic selectivity, and adsorptive qualities. This is evidenced by the
Compilation of Extra Framework Sites in Zeolites (Mortier, 1982), which in-
cludes this information for 36 framework types. The large number of entries for
the framework types FAU (69), LTA (62), and MOR (13) is an indication of
the importance of these materials, and how much man-power was focused on
producing better variants.

Equally important is the location of the organic SDA in the channel sys-
tem, because the tangible connection between the SDA used and the frame-
work formed is of great value to our understanding of the synthesis process.
Baerlocher and Meier performed a structure analysis using XPD on a synthetic
sodalite material (SOD; Baerlocher and Meier, 1969) and on Na-P1 (GIS Baer-
locher and Meier, 1970, 1972) to locate TMA within the cages. However, the
real breakthrough was to locate the tetrapropylammonium (TPA) molecule in
the channel system of ZSM-5 (Price et al., 1981, 1982) using single-crystal data.
The location of the SDA within the channel system has played an important role
in providing detailed coordinates against which theoretical molecular modeling
of the host-guest interactions can be validated (Catlow et al., 2007). Computa-
tional methods have allowed researchers to target specific zeolite structures and
properties, and constitutes a first step in the direction of the rational design of zeolite synthesis (Yu and Xu, 2010).

2.2 Industrial & commercial applications

All of this effort to develop new synthesis methods has been driven by the demand for better materials for applications in ion exchange, sorptive separation, and selective catalysis. However, development of new synthesis methods, and discovery of new materials alone is not enough. A large challenge is the scaling up of the synthesis procedure to industrial levels suitable for commercial manufacture (Zones, 2011). Production of synthetic zeolites is estimated to be 1.8 million metric tons per year (Yilmaz et al., 2012). In the 1970s, synthetic zeolites began to replace phosphate compounds in laundry detergent powders as water softeners, at first for environmental reasons, but also because of their superior ion-exchange performance. Nowadays, approximately 73% of all synthetic zeolites produced are used for this purpose, mainly LTA-type (4A, NaA), but also GIS-type (Na-P, MAP) zeolites are used. In comparison, the amount of zeolite used for catalysis (17%) is much smaller, but this accounts for 55% of the total market value. FAU-type zeolites alone account for 95% of the catalysis market, because it is the least expensive to produce and can be used to manufacture gasoline from crude oil in the fluid catalytic cracking process (Maesen, 2007). Sometimes, MFI- and *BEA-type zeolites are used as additives to optimize the yield. The remaining 10% are produced as adsorbents/dessicants. A summary of applications of synthetic zeolites is given in Table 2.1, and a more detailed overview of industrial applications is given by Sherman (1999), Maesen (2007), and Yilmaz et al. (2012).

In 2014, 2.7 million metric tons of natural zeolites were produced worldwide, with China accounting for more than 70% of consumption (Virta, 2015). 67 naturally occurring zeolites have been found (International Zeolite Association: Commission on Natural Zeolites, 2015), but only a few of those, namely analcite (ANA), chabazite (CHA), clinoptilolite (HEU), erionite (ERI), ferririte (FER), mordenite (MOR), and phillipsite (PHI) occur in large enough deposits for commercial exploitation (Virta, 2015). Although natural zeolites are typically cheap to mine, their use in industrial applications is limited, because of the variation in chemical composition and the presence of impurities, which are expensive to remove. The channel systems are typically occupied by alkaline or alkaline-earth cations and water molecules. As a result, natural zeolites find their main applications in markets where high purity and uniformity are not so important, and are sold as pet litter and animal feed supplements, and are also used for horticultural applications (soil conditioners and growth media), and wastewater treatment.
### Table 2.1: Applications for zeolites

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<td>Gas trap (e.g. removal of CO$_2$, H$_2$S)</td>
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Chapter 3

Diffraction from polycrystalline materials

3.1 Bragg’s Law

The field of XRD originated in the laboratory of William Conrad Röntgen, who discovered a new type of radiation in 1895 that he tentatively named X-rays (Röntgen, 1898). He was awarded the Nobel prize in Physics in 1901 for this discovery. About 10 years later, Max von Laue showed that exposing a small crystal of copper sulphate to X-rays resulted in discrete diffraction spots that could be measured on a photographic film (Friedrich et al., 1913). This earned him the Nobel prize in Physics in 1914. William Henry Bragg and William Lawrence Bragg then followed up on this work, and laid the foundation of modern crystallography by deriving the formula that is now referred to as Bragg’s law:

\[ n\lambda = 2d\sin \theta. \]  

(3.1)

They used this formula to calculate the lattice spacing \( d \) knowing the wavelength \( \lambda \) and the diffraction angle of a reflection \( \theta \) (Bragg and Bragg, 1913). They realized that by combining the lattice spacings of several reflections it was possible to deduce the regular three-dimensional arrangement of the atoms in a crystal. For this work, they too received a Nobel Prize in Physics in 1915.

3.2 Ewald sphere

A convenient way of visualizing Bragg’s law is via the Ewald construction (Ewald, 1969). The Ewald construction shows the relationship between the orientation of the crystal and the reflections that are in diffracting condition, such as shown in Figure 3.1. Here, point \( O \) is the origin of the reciprocal lattice, \( C \) is the center of the Ewald sphere with radius \( 1/\lambda \) and lies on the incident beam defined by \( s_0 \) (\( |s_0| = 1/\lambda \)). Point \( P \) is a reflection that lies on the Ewald sphere, and is therefore in diffracting condition, as is any spot that is in contact with the Ewald sphere (highlighted in red). The diffracted beam is in the direction \( CP \) and is defined by the scattering vector \( s \) with length \( 1/\lambda \). \( OP \) is defined as the reciprocal lattice vector \( h \) with length \( 1/d \). From this it follows
that the Bragg angle $\theta$ (angle of PDO) is given by Eq. 3.1, and that $PCO$ equals $2\theta$. In this representation, the physical center of the crystal would be at $C$, and by rotating the crystal around the normal to the paper an equivalent rotation of the reciprocal lattice is instigated around $O$, so that reflections are brought in and out of diffracting condition. The Ewald construction is used to break down the geometry of a diffraction experiment and simplify calculations. A more complete description of the Ewald construction and its implications is given in Sands (1982).

### 3.3 Diffraction intensity

If Bragg’s law determines the reflection positions and thus the dimensions of the unit cell, then their intensities describe the decoration of the unit cell via the structure factor $F_{hkl}$, which holds the information about the arrangement of the atoms in the unit cell.

$$F_{hkl} = \sum_{j=1}^{N} n_j f_j \exp[2\pi i (hx_j + ky_j + lz_j)],$$  \hspace{1cm} (3.2)$$

where $F_{hkl}$ is the sum over all atoms in the unit cell, $x_j, y_j,$ and $z_j$ are the fractional coordinates of the $j$th atom, $n_j$ is its population parameter (also referred to as occupancy), and $f_j$ is its atomic form factor. The form factor
3.3. DIFFRACTION INTENSITY

describes the shape of the observed atomic electron density:

\[ f_j = f_j^0 t_j = f_j^0 \exp[-B_j \sin^2(\theta)/\lambda^2)] \]

where \( f_j^0 \) is an empirically found function of \( \sin \theta_{hkl}/\lambda \) that describes the scattering power of an atom. It is corrected for atomic displacement \((t_j)\), which smears out the electron density because of disorder or thermal motion, where \( B_j = 8\pi^2 <u_j^2> \). Then, \(<u_j^2>\) is the mean square displacement of atom \( j \) in Å.

Since \( F_{hkl} \) is a summation over many atoms, it can be written in a more (atom-independent) general form:

\[ F_{hkl} = |F_{hkl}| \exp[i\alpha_{hkl}] \]

where \( |F_{hkl}| \) is the structure factor amplitude and \( \alpha_{hkl} \) is the phase of the diffracted beam. The intensity \( I_{hkl} \) of the diffracted beam is proportional to the structure factor multiplied by its complex conjugate:

\[ I_{hkl} \propto F_{hkl}^* F_{hkl} = |F_{hkl}|^2 \]

Although this means that the amplitudes of the structure factor can be retrieved from a diffraction experiment, the phase information contained in \( \alpha_{hkl} \) is lost. This is referred to as the phase problem in crystallography. Many methods have been developed in order to overcome the phase problem and to recover the spatial arrangement of atoms in a crystal, and some of these have been summarized in Chapter 4.

What is measured as a diffraction peak by the detector is actually an accumulation of several effects attenuating the incident and scattered radiation. The general formula for the integrated intensity is given by Giacovazzo et al. (2002, p. 178) as:

\[ I_{hkl} = I_0 k_1 k_2 L P T E |F_{hkl}|^2 \]

Here, \( I_0 \) is the flux of the incident radiation, \( k_1 = \frac{\pi^2}{m^2 c^2} \) is a constant accounting for the scattering cross-section of an electron, \( k_2 \) depends on the diffraction experiment, \( L \) is the Lorentz factor, \( P \) is the polarization factor, \( T \) is the transmission factor, accounting for the absorption of radiation passing through the crystal, and \( E \) is the extinction coefficient, which accounts for the fact that lattice planes first hit by the primary beam diffract more intensity and therefore shield deeper lattice planes from the primary beam. However, for small crystals with \( V < 10 \mu m^3 \), absorption and extinction effects are typically negligible and can be ignored.

The Lorentz factor, sometimes also called the angular-velocity factor, corrects for the time a reflection is on the Ewald sphere in a classical rotation diffraction experiment, i.e. the velocity with which it moves through the Ewald sphere. The polarization factor depends on the state of polarization of the incident X-ray beam and the scattering angle of the diffracted beam (Giacovazzo et al., 2002, p. 156). Several of these corrections depend on the technique used, the type of radiation, and whether the crystal is rotating or stationary (Zachariasen, 1945; Buras and Gerward, 1975; Kalman, 1979). The differences between the methods relevant for this project are summarized in Appendix A.
CHAPTER 3. DIFFRACTION

3.4 Powder diffraction

Shortly after the discoveries by von Laue and the Braggs in 1913, Debye and Scherrer (1916), and Hull (1917) realized that structure determination was not limited to materials that formed as nice large crystals. Independently, they devised a method for powder diffraction using conventional XRD sources, and noted the advantage of being able characterize the bulk of a material (including its impurities) with a single photograph.

XPD found applications in phase identification, accurate unit cell determinations, and line profile analysis. Although ab initio structure solution from powders was also possible, this was complicated by the fact that reflections with equal or similar \( d \)-spacings overlap in an XPD pattern, leading to an ambiguity in the assignment of the reflection intensities. This is referred to as the overlap problem in powder diffraction (Figure 3.2). Initially, the overlap problem did not pose much of a problem, because the unit cells of the materials studied were small, symmetries high (cubic, tetragonal), and the \( d \)-spacings by themselves provided enough information to recover the structures of simple materials (e.g. Iron, Magnesium, Aluminium, graphite, diamond), so diffraction intensities were not used. Others just used the unit cell parameters and model building to determine the crystal structures (i.e. Pauling, 1930b). However, in general, reflection overlap is a serious limitation in structure determination from XPD data.

In a typical powder diffraction experiment, the procedure can be divided into five steps: Data collection, finding the unit cell and space group (indexing), intensity extraction, structure solution (Chapter 4), and structure refinement. Several large crystallographic software suites now exist to perform some or all of these tasks, the most commonly used ones are probably FULLPROF (Rodríguez-Carvajal, 1993), JANA (Dušek et al., 2001), GSAS (Toby and Von Dreele, 2013), EXPO (Altomare et al., 2013), and TOPAS (Coelho, 2007, 2012), the latter of which was used for most of this Ph.D. project.
3.4. POWDER DIFFRACTION

3.4.1 Indexing

After data has been collected, it is necessary to index the pattern to determine the unit cell parameters and the space group. Although it is possible to do this by hand for simple problems (i.e. cubic lattice), it is unfeasible for structures with large unit cells or more complicated symmetries. This is why a large number of computer programs have been developed to facilitate the process. Widely used are the three classic programs for auto-indexing ITO (Visser, 1969), TREOR (Werner et al., 1985) and DICVOL (Boultif and Louër, 1991). Since each of these just requires a – not necessarily complete – list of 2θ positions, all three are built into a large number of crystallographic software suites. More recent approaches to indexing include one based on the Monte Carlo method (McMaille; Le Bail, 2004), and another one on singular value decomposition (Coelho, 2003, implemented in TOPAS). All of these programs typically generate a large number of solutions that are ranked by a figure of merit (de Wolff, 1968). Sometimes it’s not clear which unit cell is the best one, so it may be necessary to try several to find the one that gives the best fit to the data (Section 3.4.2). A clue about the space group is often provided by the auto-indexing routine, and is determined by examining the indexed data for systematic absences. It is possible that several space groups fit the data, because reflection overlap often obscures systematic absent reflections. There are generally subtle differences between similar space groups, and while not necessarily a problem, structure determination must often be attempted with each one. Only subsequent structure refinement will show whether or not the space group is correct.

3.4.2 Pattern decomposition

The next step is to extract the peak intensities from the data. Once the unit cell is known, the reflection positions can be calculated via Bragg’s law. Each reflection is assigned a function describing the peak shape and profile parameters are then refined along with the reflection intensities to fit the diffraction pattern. The general function to fit the data at point \( x_i \) is given by:

\[
y(x_i) = \sum_j A_j \phi(x_i - x_j) + b(x_i),
\]

(3.7)

where \( A_j \) is the integrated area of the \( j \)th reflection, \( \phi \) is the normalized profile function describing the reflection, and \( b_i \) is the background contribution at \( x_i \). The summation is over all reflections contributing to the intensity at \( x_i \). If the unit cell and space group are known, starting values for the reflection positions can be calculated from the unit cell parameters. The unit cell and profile parameters are optimized using a least-squares refinement program, and the values of the reflection intensities are extracted using the Pawley (Pawley, 1981) or Le Bail (Le Bail et al., 1988) profile fitting algorithms. The difference is that in the Pawley method the reflection intensities are optimized as part of the least-squares routine, whereas in the Le Bail method they are extracted in a second step. Traditionally, extracted intensities are equipartitioned, meaning that the total intensity of a peak is equally divided over the corresponding group of reflections that cannot be resolved based on the peak shape alone. Sometimes these reflection intensities prove to be good enough for structure solution. If this
is not the case, computational methods have been developed with the aim to improve the quality of the extracted intensities, by using information contained in the Patterson function (FIPS; Estermann et al., 1992; Estermann and Gramlich, 1993), relationships between structure factors derived from direct methods (DORFES; Jansen et al., 1992), or maximum-entropy methods (David, 1990). A method very similar to FIPS has been built into the full powder pattern decomposition program EXTRA (Altomare et al., 1998), which later formed the basis for the powder diffraction software suite EXPO (Altomare et al., 1999).

### 3.4.3 Rietveld refinement

Once a starting model has been found using one of the methods described in Chapter 4, Rietveld refinement is used to validate the model and to refine the structure (Rietveld, 1969). This is done by calculating the diffraction profile based on an equation similar to that used for pattern decomposition (Eq. 3.7).

\[
y(x_i) = \sum_j I_j G_j \phi(x_i - x_j) + b(x_i) .
\]

Here, \( I_j \) is the diffraction intensity described in Appendix A.2 and \( G_j \) is a function that corrects for preferred orientation. By minimizing the difference between the observed and calculated profile via a least-squares minimization algorithm, the structural parameters may be improved. There are several numerical criteria of fit that can be used in order to evaluate the state of the refinement, and to judge the quality of the fit. The profile residual, \( R_p \), indicates how well the calculated profile matches the observed one:

\[
R_p = \frac{\sum |Y_{obs,i} - Y_{calc,i}|}{\sum |Y_{obs,i}|} .
\]

The ‘weighted-profile’ agreement value, \( R_{wp} \), also takes into account the estimated standard deviation \( \sigma_i \) of each data point:

\[
R_{wp} = \left[ \frac{\sum w_i (Y_{obs,i} - Y_{calc,i})^2}{\sum w_i (Y_{obs,i})^2} \right]^{0.5} .
\]

The expected agreement value, \( R_{exp} \), gives an indication of the best possible agreement value for \( R_{wp} \) that can be obtained, assuming that counting statistics are the only source of error:

\[
R_{exp} = \left[ \frac{n - p}{\sum w_i (Y_{obs,i})^2} \right]^{0.5} .
\]

The goodness-of-fit (GoF), sometimes called chi-squared, then gives the state of the refinement in terms of the ratio between \( R_{wp} \) and \( R_{exp} \):

\[
GoF = \chi^2 = \frac{\sum w_i (Y_{obs,i} - Y_{calc,i})^2}{n - p} = \left[ \frac{R_{wp}}{R_{exp}} \right]^2 .
\]
3.4. POWDER DIFFRACTION

The Bragg agreement value, $R_1$, is also very useful, because it does not compare the profile fit, but instead compares the calculated to the observed intensities, and is therefore most comparable to agreement values obtained from conventional single-crystal refinements:

$$R_1 = \frac{\sum_j |I_j^{\text{obs}} - I_j^{\text{calc}}|}{\sum_j |I_j^{\text{obs}}|}.$$  \hspace{1cm} (3.13)

In Eqs. 3.9 to 3.12, $Y_i^{\text{obs}}$ and $Y_i^{\text{calc}}$ are the observed, and calculated profile intensities at data point $i$, $w_i$ is the weight given to each data point, conventionally taken as $w_i = 1/\sigma_i^2 = 1/Y_i^{\text{obs}}$. $I_j^{\text{obs}}$ and $I_j^{\text{calc}}$ are the observed, and calculated Bragg intensities of the $j$th reflection, $n$ corresponds to the number of observations, and $p$ to the number of refined parameters in the least-squares procedure.

Pecharsky and Zavalij (2005, Chapter 6.7) write: “Unfortunately, there are no exact thresholds for $R_p$, $R_{wp}$, and $R_1$, below which a fit is acceptable, good or excellent. To a certain degree, the ‘absolute quality’ of the result is established by the relationship between $R_{wp}$ and $R_{exp}$, i.e. the value of $\chi^2$.” The value of GoF is largely affected by the counting statistics and may be exceptionally low due to the great counting statistics obtained at synchrotron facilities, and therefore not at all represent the quality of the structural model. In theory, the value of GoF should approach unity, but in practice, this is never achieved. A more realistic goal for the value of $R_{wp}$ of the structure refinement is the $R_{wp}$ for a profile fit without the structure (i.e. a Pawley or Le Bail fit).

Unfortunately, these criteria of fit only tell part of the story, and qualitative criteria are equally, if not more, important. A visual representation of the fit, as well as a difference plot ($Y^{\text{obs}} - Y^{\text{calc}}$), can reveal problems with the profile parameters, such as peak shape, background, zero correction and sample displacement, unit cell, etc. The physical meaning of mismatches in intensities are best visualized by calculating a difference electron density map. This can be calculated by taking the Fourier transform of the difference between the observed and calculated structure factors with the phases from the structural model, and can uncover problems with the structure, or with the symmetry. The difference map is generally biased towards the model. Positive residual electron density peaks can indicate missing atoms, while negative peaks may indicate atoms that are only partially occupied or absent. A good indication of the quality of the refinement is how clean the residual density map is.

Finally, all of this is in vain if the refined structure does not make chemical sense. It is necessary to monitor the bond angles and distances, intramolecular distances, occupancies, and atomic displacement parameters during the course of the refinement to verify that they correspond to reasonable values. Only if all qualitative criteria are fullfilled, and quantitative criteria are stable and as low as possible, can the refinement be considered finished.

A concise description of many aspects of Rietveld refinement can be found in Rietveld Refinement Guidelines (McCusker et al., 1999) and the book The Rietveld Method (Young, 1993).
3.5 Electron diffraction

Electron radiation has a few distinct advantages over X-rays. The key difference is that electrons are charged and interact with all charged particles, not just the electrons as do X-rays. Therefore, the interaction of electron radiation with atoms is much stronger, so that very small crystallites with dimensions as small as 10 nm can be measured. The advantage of this is that single crystallites can be targeted, so there is no peak overlap, and impurities can be avoided. Nevertheless, there are also some significant disadvantages in electron diffraction. Sample preparation and data collection are more difficult than for XPD, beam damage is much more severe, and the crystals selected for the analysis may not be representative of the bulk material. Intensities are dynamical in nature, and therefore difficult to interpret and not as ideal for structure solution as the purely kinematical ones obtained from single-crystal XRD. Traditionally, two-dimensional diffraction patterns are collected along a single zone-axis using a parallel beam of incident radiation in an electron microscope.

Recent advances have enabled computer-controlled electron microscopes, and that led to the development of automated diffraction tomography (ADT; Kolb et al., 2007, 2008) and rotation electron diffraction methods (RED; Zhang et al., 2010), which allow automatic collection of high-quality three-dimensional diffraction data. For ADT, this involves homogeneous sampling of reciprocal space by tilting a crystal around an arbitrary axis in fixed tilt steps of \(1^\circ\) to collect non-oriented diffraction patterns. This theoretically allows for the collection of data in all reciprocal space. A part of the reciprocal space, the so-called ‘missing cone’, however, cannot be accessed by tilting around a single axis. The data may be further limited by the tilt range of the goniometer or crystal overlap at high tilt angles. This limits the completeness for low symmetry crystal systems to about 80\%. The crystal can be tilted around a second axis or another crystal with a different orientation can be found, so a second data set can be collected and merged with the first to get around this limitation. For higher symmetries, reflections in the missing cone may have symmetry equivalents that have been measured.

Another advantage of ADT over traditional methods is that dynamical scattering is significantly reduced, because each pattern is collected off-zone, and therefore fewer reflections are excited simultaneously. The precession electron diffraction technique (PED; Vincent and Midgley, 1994) can be combined with ADT by using a tilted electron beam and precessing it around the vertical axis. The resulting intensities are more suitable for structure solution, because excitation errors due to the curvature of the Ewald sphere are removed and dynamical effects reduced.

The RED method is conceptually similar to ADT, but combines larger mechanical tilt steps with fine beam tilt steps, and usually in this way a finer sampling of reciprocal space is achieved. The resulting data are single-crystal like, and therefore compatible with the rich collection of crystallographic software available, although these generally assume kinematical intensities. An up-to-date overview of methods in electron crystallography has been outlined in the books by Zou et al. (2011) and Kolb et al. (2012).
Chapter 4

Methods of crystal structure determination

Structure determination algorithms are conventionally divided into three groups: reciprocal space methods, direct-space methods, and dual-space methods. Reciprocal space methods, such as the Patterson method and direct methods (not to be confused with direct-space methods), are the classic approaches developed for solving crystal structures from single-crystal data. They work with the diffraction data in reciprocal space to overcome the phase problem. Direct-space methods are more intuitive. They optimize a structural model in real space by comparing its calculated profile with the observed one. For complicated structures or problematic data sets, using direct or reciprocal space methods is sometimes not enough. Dual-space methods work in both reciprocal and direct space, and have the advantage that constraints can be imposed in either realm. They alternate between direct and reciprocal space, dealing with the structure factor amplitudes and phases in the former and the electron density in the latter. That said, the lines have blurred somewhat, and several programs for direct methods (reciprocal space) now include some perturbation or interpretation of the electron density map. Dual-space algorithms were first introduced with the ‘Shake and Bake’ method, a procedure based on alternating phase refinement (‘shake’, reminiscent of direct methods) in combination with real-space filtering (‘bake’) (DeTitta et al., 1994; Weeks et al., 1994). For this project, heavy use was made of the dual-space methods FOCUS and charge-flipping, both of which are discussed below.

4.1 Patterson method

The Patterson method can be used to obtain interatomic vectors by interpreting a map generated using measured intensities (\( |F_{hk}|^2 \)) as Fourier coefficients directly, in place of the structure factor amplitudes \( F_{hkl} \) (Patterson, 1935). The so-called Patterson function is defined as

\[
P(u, v, w) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}|^2 e^{-2\pi i (hu + kv + lw)},
\]

(4.1)
CHAPTER 4. STRUCTURE DETERMINATION

where \( V \) is the unit cell volume, and \((u, v, w)\) represent the position vectors. The function calculated with this Fourier series is equivalent to

\[
P(u, v, w) = \int_{x=0}^{1} \int_{y=0}^{1} \int_{z=0}^{1} \rho(x, y, z)\rho(x + u, y + v, z + w)dx dy dz, \tag{4.2}
\]

where \((x, y, z)\) are coordinates in the electron density \(\rho\). While the Patterson function contains information about the electron density, it cannot be used to calculate it. \(P\) is called a self-convolution of \(\rho\) and therefore has \(N^2\) peaks where \(N\) is the number of atoms in the cell. A maximum in \(P\) at location \((u, v, w)\) corresponds to the interatomic vector from \((x, y, z)\) to \((x + u, y + v, z + w)\). The peak height in \(P\) is a product of peaks in the electron density \(\rho\), therefore the vector from one heavy atom to another heavy atom is much more pronounced than for light atoms. The Patterson function is therefore frequently used to derive a partial structure or the positions of a few heavy atoms for initial phasing. The rest of the structure follows from direct methods or Fourier recycling. In practice, the Patterson function is quite robust with respect to reflection overlap when it comes to XPD data, and is used to improve the estimation of the reflection intensities in direct methods (Rius, 1993, 2010). The Patterson function has recently gained renewed interest for solving the structures of organic materials (Burla et al., 2007b), and to analyze short-range order in materials via the pair distribution function (Proffen et al., 2003).

4.2 Direct methods

Direct methods are commonly used in chemical crystallography for structure solution. They aim to determine the missing phase information directly from the data. This approach revolves around the generally sensible notion that crystals are made of atoms, implying that not all functions can represent realistic electron density. This means that electron density is not negative or interrupted and the peaks do not lie close together. These restrictions can be formulated in mathematical terms, stating that the electron density \(\rho(x, y, z)\) must be a positive, continuous function with maxima that lie within a certain range of one another (Karle and Hauptman, 1950; Sayre, 1952). The algorithm uses a probabilistic approach to determine the most likely phases. Direct methods have been adapted for use with powder diffraction data, and are available via the programs \textsc{EXPO} (Altomare et al., 2013) and \textsc{XLENS} (Rius, 1999). The maximum entropy method is also based on the idea of atomicity, but instead, phases are determined based on entropy maximization and likelihood ranking (Bricogne, 1984; Bricogne and Gilmore, 1990) and implemented in the program \textsc{MICE} (Gilmore and Bricogne, 1997; Gilmore et al., 1999).

4.3 Direct-space methods

Automated direct-space methods are a relatively new class of approaches to structure solution, that have been enabled by the advances made in computing during the 1990s. The idea behind direct-space methods is simple and effective when some prior chemical information about the system is known. Information
used in manual model building, such as chemical composition, geometry, and
connectivity are used. The methods work by trying to optimize the atomic ar-
rangement of the crystal structure in direct space, and comparing the associated
diffraction profile with the observed one. Expected atoms, molecules or rigid-
body fragments are initially placed randomly in the unit cell and moved around
by modifying their positions and/or orientations. After each rearrangement, the
difference between the experimental and calculated data is evaluated, until the
best agreement (i.e. weighted profile $R_{wp}$ or full profile $\chi^2$) has been reached.
As a result, the overlap problem is completely avoided, because the individual
structure factor amplitudes are not used. The global optimization algorithms
commonly used are Monte Carlo simulations (Harris et al., 1994), simulated
annealing (Andreev et al., 1997; Coelho, 2000; Favre-Nicolin and Černý, 2002;
David et al., 2006) and genetic algorithms (Kariuki et al., 1997; Shankland et al.,
1997a). A more recent approach that combines a scan of possible arrangement of
molecular fragments with fast restrained least-squares minimizations (Vallcorba
et al., 2012) is also worth mentioning. Direct-space methods are widely used for
organic materials, where the molecular structure is known. Direct-space meth-
ods may also be used for structure determination of zeolites, and have been
implemented in the zeolite-specific programs ZEFS, which used simulated an-
nealing (Deem and Newsam, 1989), and later ZEFSA-II, which uses a biased
Monte Carlo approach (Falcioni and Deem, 1999).

4.4 FOCUS

Many zeolites can only be synthesized as polycrystalline materials, and are
therefore unsuitable for routine structure solution with single-crystal XRD tech-
niques. Structure determination is therefore usually limited to XPD data. The
dual-space method implemented in FOCUS (Grosse-Kunstleve, 1996; Grosse-
Kunstleve et al., 1997, 1999) uses a priori crystal chemical information to sup-
plement XPD data to overcome the loss of information due to reflection overlap.
FOCUS combines Fourier recycling with atom assignment and a topology search
specific to zeolite frameworks in a way that can be described as automated model
building.

The connectivity of the atoms in zeolites is well known. The Si node atoms
form a three-dimensional 4-connected network with bridging O atoms and a
Si–O–Si angle of approximately 145°. The distance between the node atoms is
about 3.1 Å. This is all the information required for a typical zeolite framework
search. To begin a trial, a random density map is generated by assigning ran-
dom phases to structure factor amplitudes derived from diffraction intensities,
especially generating a random structure. For centrosymmetric structures, this
means around half of the phases will be correct, which is a good starting point
for structure determination. The electron density is integrated and the highest
peaks are stored in a list. There are two routines for interpreting this list:

1. Atoms types are assigned based on the correlation between peak height
and atom weight (atom recycling).

2. A full topology search is performed based on peak geometry and atoms
are assigned to the largest framework (or fragment) found (framework
recycling). This uses a specialized backtracking algorithm and is by far
Alternating the framework and atom recycling procedures was found to be the most effective strategy. The assigned atoms are then used to generate a new phase set, which can be used to generate a new electron density map. This cycle is repeated until the phases converge (Figure 4.1) or a pre-defined number of cycles has been reached. A completed cycle does not necessarily result in a correct framework. New trials are started as often as needed to generate a sufficient number of possible framework solutions.

The FOCUS method uses a statistical approach, therefore classifying the generated topologies is essential. The topology of each complete framework found is classified by computing the coordination sequence of each of the T-atoms in the asymmetric unit. These sets of numbers act as a fingerprint of the framework (Brunner, 1979). Once FOCUS has finished, the number of occurrences for each topology is counted, with the idea that the most frequently found topology is the most likely to be the correct one. Only the positions of the T-atoms are reported, the bridging O atoms are then added in the expected positions, and the framework geometry can be optimized using distance least-squares (Baerlocher et al., 1976) to give the best possible starting point for
4.5 Charge-flipping

Charge-flipping is a recently developed algorithm for structure solution for single-crystal data (Oszlányi and Sütő, 2005, 2004) and surprisingly effective in some cases, despite the fact that the algorithm itself looks very simple (Figure 4.2). At first, random phases are assigned to the structure factor amplitudes, to generate a starting density map. The signs of all electron density below a certain user-defined or automatically generated threshold $\delta$ are then inverted ("flipped") to produce a perturbed electron density map. A new set of structure factor amplitudes and phases are generated from this map and the latter are used in combination with the measured amplitudes to start a new cycle. This process is repeated until observed and calculated amplitudes converge or a user-defined number of cycles has been reached. As a result of its simplicity, charge-flipping has been implemented in a large number of software suites, such as PLATON (Spek, 2003), CCTBX (Grosse-Kunstleve et al., 2002), TOPAS (Coelho, 2007), GSAS-II (Toby and Von Dreele, 2013), and the dedicated pro-
gram SUPERFLIP (Palatinus and Chapuis, 2007). The latter is the program used in this project.

With some modifications, the charge-flipping routine can also be used with XPD data (Wu et al., 2006; Baerlocher et al., 2007c). The powder charge-flipping (pCF) described by Baerlocher et al. was implemented in SUPERFLIP, and adds a second perturbation every \(N\) cycles, where the histogram of electron density at every pixel is matched against that of a pre-determined map (user supplied or generated by the program) reflecting the expected chemical composition of the sample. The structure factor amplitudes from the subsequent Fourier transform are then used to repartition the amplitudes of overlapping reflections before a new cycle is started. This allows some structures to be solved that could not be solved before, and significantly reduces the time taken to reach convergence.

All calculations are performed in space group \(P1\). After the iterative process is completed, the program looks for compatible symmetry operations in the electron density and ranks the symmetry elements according to the agreement factor of the symmetrized electron density with the calculated one. The space group is assigned based on the symmetry operations with an agreement factor below the threshold value of 25.0. Because calculations are performed in space group \(P1\), this makes SUPERFLIP useful for evaluating the symmetry of a density map, although the space group determination generally tends towards the space group the data were extracted in. The symmetry determination can be used to shift the density map to align the symmetry elements with the unit cell and to average the symmetry equivalent electron density. At the end of each run, the maps are ranked according to their agreement factor \(R_{sf}\), which is defined as

\[
R_{sf} = \frac{\sum \left| |G_{hkl}| - |F_{hkl}| \right|}{\sum |F_{hkl}|},
\]

where \(F_{hkl}\) and \(G_{hkl}\) are the observed and perturbed structure factor amplitudes, respectively.

For problematic data, like powder diffraction data with overlapping reflections, or complicated structures, convergence is not usually reached. In such cases, the algorithm is stopped after a certain number of iterations, and the resulting map may or may not be fully interpretable. In such cases, it may be worth trying to optimize the input parameters (Šišak et al., 2012) or to extract a partial solution from the map and use that as a starting point for a new set of charge-flipping runs (Šišak Jung, 2013). This can be an effective way of guiding the solution in the right direction.
Chapter 5

FOCUS with electron diffraction data

5.1 Introduction

The zeolite-specific structure solution program FOCUS (Chapter 4.4) was originally developed for use with XPD data. Reflection overlap prevents the extraction of reliable intensities from XPD data. By incorporating a priori chemical information to supplement the diffraction data, FOCUS does not require highly accurate intensities in order to be effective. In this sense, XPD data is similar to ED data. Techniques for collecting three-dimensional ED data from small crystallites have evolved at a rapid pace in recent years (Section 3.5). An impressive number of structures (including zeolites) have now been solved on the basis of ED alone by using direct methods (Mugnaioli and Kolb, 2013; Yun et al., 2015). Direct methods make use of the triplet relationship between reflections, and thus require reasonably accurate intensities. However, one of the major drawbacks of ED is that reflection intensities are not accurate, mainly because of dynamical scattering and beam damage of the crystal. Furthermore, collection of a complete data set for crystals with low symmetry is sometimes limited, because of the missing wedge that cannot be accessed because of tilt limitations of the sample holder. These factors affect the effectiveness of direct methods when the structures get too complex.

We reasoned that although the origin of the reduced accuracy for the reflection intensities for ED data (dynamical scattering, beam damage) is different from XPD data (reflection overlap), FOCUS might also be able to overcome the deficiencies of the ED data. Therefore, FOCUS was modified to work with ED data, and tested on several zeolite samples with known framework topologies of differing complexities. For testing purposes, ADT data collected on the known zeolites natrolite (NAT), ZSM-5 (MFI), ITQ-43, and IM-5 (IMF; Mugnaioli and Kolb, 2013; Jiang et al., 2011) were provided by Enrico Mugnaioli and Ute Kolb (Johannes Gutenberg-Universität Mainz, GER). Data on SSZ-45 were collected using the RED method and provided by Dan Xie (Chevron, USA). Crystallographic details for all samples have been summarized in Table 5.1.
Table 5.1: Unit cells of the five test samples

<table>
<thead>
<tr>
<th></th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Vol. (Å$^3$)</th>
<th>T-atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>natrolite</td>
<td>Fdd2</td>
<td>18.293</td>
<td>18.640</td>
<td>6.386</td>
<td>2245</td>
<td>3</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Pnma</td>
<td>20.100</td>
<td>19.924</td>
<td>13.424</td>
<td>5375</td>
<td>12</td>
</tr>
<tr>
<td>ITQ-43</td>
<td>Cmmm</td>
<td>26.411</td>
<td>41.399</td>
<td>12.839</td>
<td>14038</td>
<td>11</td>
</tr>
<tr>
<td>SSZ-45</td>
<td>Fmmm</td>
<td>13.713</td>
<td>22.125</td>
<td>35.192</td>
<td>10677</td>
<td>10</td>
</tr>
</tbody>
</table>

5.2 Experimental details

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 microscopy goniometer (tilt $\alpha$). Using a tomographic holder, it is possible to reach a tilt range of ±60°. 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 on the sample (Kolb et al., 2007). Because of the low illumination, the crystal position was tracked in the microprobe dark-field scanning transmission electron microscopy (STEM) mode. ADT was coupled with precession electron diffraction (Vincent and Midgley, 1994, PED) in order to further reduce the dynamical effects and to improve reflection integration (Mugnaioli et al., 2009). A series of two-dimensional diffraction patterns was recorded, neglecting any crystallographic orientation, and then reconstructed into 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 effects of beam damage on the sample, while all other materials were investigated at room temperature.

Three-dimensional ED data were collected on eight crystals of SSZ-45 (each ca. 100 nm in size) using the RED technique (Zhang et al., 2010). The RED software was installed on a JEOL 2010 microscope operating at 200 kV, and data were collected over a tilt range of ±50° with a tilt step of 0.2° and an exposure time of 2 s. Relatively large tilt steps had to be used for these measurements, because the software to perform the finer tilts by tilting the electron beam had not yet been implemented. The crystal position was tracked in TEM mode. Three-dimensional reconstruction, indexing, and intensity integration were performed using the RED software (Wan et al., 2012c), and the best two data sets were merged for further analysis.

Synchrotron XPD data on SSZ-45 were collected on the MS-Powder beamline at the Swiss Light Source in Villigen, CH (Bergamaschi et al., 2010, wavelength 1.0000 Å, Mythen II detector;).

5.3 Implementation

In order to make FOCUS work well with ED data, analytical scattering factors based on Tables 4.3.2.2 and 4.3.2.3 in the 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 introduced to the input options. Two choices are available, xray is the default and tells the program to use the original analytical
5.4 APPLICATION TO TEST DATA

Table 5.2: General strategy for setting up the FOCUS input file for ED data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Recommended value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_T)</td>
<td>Vol. (\times 20/1000)Å³</td>
</tr>
<tr>
<td>(N_{Fw})</td>
<td>(N_T \times 3)</td>
</tr>
<tr>
<td>MaxRecycledAtoms</td>
<td>(1.2 \times N_T) to (N_{Fw})</td>
</tr>
<tr>
<td>MaxPotentialAtoms</td>
<td>(1.5 \times N_T)</td>
</tr>
<tr>
<td>MaxPeaksFwSearch</td>
<td>(1.5 \times N_{Fw})</td>
</tr>
<tr>
<td>MinNodeDistance</td>
<td>2.6</td>
</tr>
<tr>
<td>MaxNodeDistance</td>
<td>3.8</td>
</tr>
<tr>
<td>CheckTetrahedralGeometry</td>
<td>Normal</td>
</tr>
<tr>
<td>Check3dConnectivity</td>
<td>On</td>
</tr>
<tr>
<td>Grid_xxyz</td>
<td>(3 \times a, 3 \times b, 3 \times c)</td>
</tr>
<tr>
<td>OverlapFactor</td>
<td>0</td>
</tr>
<tr>
<td>SigmaCutOff</td>
<td>3.0</td>
</tr>
<tr>
<td>ReflectionUsage</td>
<td>200</td>
</tr>
<tr>
<td>ScatteringFactorTable</td>
<td>electron</td>
</tr>
</tbody>
</table>

scattering factors for X-rays based on tables derived by Waasmaier and Kirfel (1995), and electron tells the program to use the aforementioned ED scattering factor tables instead. Later, it was also found that the undocumented keyword ScatteringFactor could also be used to introduce custom scattering factors by defining a new atom type. Data were treated with the kinematic approximation, i.e. intensities are considered to be proportional to the square of the structure factor amplitudes.

5.4 Application to test data

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. The most difficult part of the ED tests proved to be tweaking the framework search parameters in order to get a statistically significant solution within a reasonable amount of time. An overview of some of the reasoning used to adjust these parameters, and a general strategy for dealing with ED data is given below, and summarized in Table 5.2.

For the AtomType keyword it was found that setting the bridging O atoms to be included in the atom recycling is generally not worth it. The reasoning behind this is that Si is a much stronger scatterer than O, and for electron radiation the difference is even larger than for X-rays. Because generally only the T-atoms were used in the recycling procedure, MaxRecycledAtoms could be set to the number of T-atoms and MaxPotentialAtoms a bit higher than that, typically at least 1.2 times the number of T-atoms. If the O atoms are also included, the value should be increased to approximately 3.0 times the number of T-atoms (i.e. approximately the same as the number of framework atoms).

I found that the maximum node–node distance (MaxNodeDistance) for the topology search was best increased slightly from the 3.6Å typically used for XPD data to increase the number of frameworks found. MinNodeDistance 2.6 and MaxNodeDistance 3.8 seem to be good values to start with. The MaxNodeDistance can be increased to yield more solutions, but these will generally be low quality with an increased chance of shortcuts in the generated frameworks. For example, FOCUS could make a shortcut and interpret a 5-
Table 5.3: Overview of the input parameters most relevant to the framework search and selectivity of the algorithm for FOCUS structure solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Natrolite</th>
<th>ZSM-5</th>
<th>ITQ-43</th>
<th>IM-5</th>
<th>SSZ-45</th>
</tr>
</thead>
<tbody>
<tr>
<td>MaxPotentialAtoms</td>
<td>120</td>
<td>130</td>
<td>270</td>
<td>1200</td>
<td>300</td>
</tr>
<tr>
<td>MaxRecycledAtoms</td>
<td>40</td>
<td>96</td>
<td>180</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>MaxPeaksFwSearch</td>
<td>1000</td>
<td>500</td>
<td>1080</td>
<td>900</td>
<td>800</td>
</tr>
<tr>
<td>MinNodeDistance</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>MaxNodeDistance</td>
<td>3.6</td>
<td>3.8</td>
<td>3.7</td>
<td>3.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

ring as a 4-ring. This is something that is especially prevalent with poor data or in structures with a large asymmetric unit. On the other hand, the range can be tightened to provide a helpful filter if a large number of different solutions are generated.

The input parameters MaxPeaksFwSearch and MaxPeaksFwFragmentSearch were found to be very difficult to balance. These tell the program the number of peaks to consider for the framework, and framework fragment search. Increasing their values will lead to slower trials, but usually more solutions per trial. On the other hand, lowering the values will lead to significantly faster trials, but potentially good electron density maps might be discarded as a result, leading to fewer solutions per trial. As a general rule of thumb, for MaxPeaksFwSearch, a value of 4.5 to 6 times the number of T-atoms was used and for MaxPeaksFwFragmentSearch a value of 1.5 times the number of T-atoms.

MaxLoopSize was kept at the default of 24 for all structures. Initially, MaxLoopSize was set to 30 for ITQ-43 to account for the large pore size, but it made no difference. CheckTetrahedralGeometry Normal is not worth changing, as this leads to a lot of solutions with very bad geometry. Turning off Check3DimConnectivity is sometimes worthwhile if no solutions are found, because a partial (two-dimensional) solution may reveal something about the structure.

For each data set, the 200 reflections with the largest structure factor amplitudes (sorted by \( m \times F \), where \( m \) is the multiplicity of the reflection) were used for structure solution. For each data set, the resulting resolution was well below the minimum T–O distance of 1.4 Å. Although it seemed sensible to use a larger number of reflections for structures with larger unit cells (IM-5, ITQ-43), this did not result in any noticeable difference in the structure solution process. However, the minimum \( d \)-spacing reached should be below the T–O distance.

A summary of the samples and their structure solutions with FOCUS can be found in Table 5.4 and the corresponding histograms in Figure 5.1. 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 get better statistics and a cleaner result (Table 5.3). Naturally, in all cases the overlap factor was set to 0 and the electron scattering factors for electrons were used. For the natrolite, ZSM-5 and IM-5 data sets, high coverage was achieved by merging data from 2 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.
5.4. APPLICATION TO TEST DATA

Figure 5.1: Histograms showing the distribution of the number of solutions for the 10 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).

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

5.4.1 Natrolite

Natrolite is a simple natural zeolite, whose structure was first deduced by Pauling (1930b). Its framework consists of 3 independent T-atoms (1 Al, 2 Si) with Na\(^+\) and H\(_2\)O 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., 2007a), and all 10 non-H atoms could be located and correctly assigned (Mugnaioli and Kolb, 2013).

Structure solution with FOCUS was equally straightforward and default input parameters were enough to find the correct framework. Optimizing the input parameters lead to an increase in selectivity towards the correct structure. The most frequently found solution represents 60\% of all solutions (Figure 5.1a). 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 atoms in the pores and the distribution of Al and Si over the T-atom sites have to be determined subsequently using difference Fourier maps during the course of the structure refinement with XPD data.
Table 5.4: FOCUS structure solution details for the five zeolites studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Natrolite</th>
<th>ZSM-5</th>
<th>ITQ-43</th>
<th>IM-5</th>
<th>SSZ-45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data collection</td>
<td>ADT</td>
<td>ADT</td>
<td>ADT</td>
<td>ADT</td>
<td>ADT</td>
</tr>
<tr>
<td>Data set</td>
<td>1+2</td>
<td>1</td>
<td>2</td>
<td>1+2</td>
<td>1</td>
</tr>
<tr>
<td>Total refs.</td>
<td>4432</td>
<td>22423</td>
<td>13032</td>
<td>7982</td>
<td>32541</td>
</tr>
<tr>
<td>Unique refs.</td>
<td>743</td>
<td>5825</td>
<td>2735</td>
<td>2461</td>
<td>2314</td>
</tr>
<tr>
<td>Crystal size (nm)</td>
<td>500×500</td>
<td>500×300</td>
<td>-</td>
<td>200×90</td>
<td>250×140</td>
</tr>
<tr>
<td>Refs. used</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>$d_{\text{min}}$ (Å)</td>
<td>1.00</td>
<td>1.14</td>
<td>1.19</td>
<td>1.17</td>
<td>1.19</td>
</tr>
<tr>
<td>Completeness</td>
<td>100%</td>
<td>81%</td>
<td>98%</td>
<td>89%</td>
<td>87%</td>
</tr>
<tr>
<td>$N_{\text{trials}}$</td>
<td>2000</td>
<td>2815</td>
<td>16156</td>
<td>40000</td>
<td>20554</td>
</tr>
<tr>
<td>$N_{\text{solutions}}$</td>
<td>3938</td>
<td>311</td>
<td>1898</td>
<td>2326</td>
<td>2470</td>
</tr>
<tr>
<td>$N_{\text{correct}}$</td>
<td>2340</td>
<td>300</td>
<td>1791</td>
<td>2043</td>
<td>2319</td>
</tr>
<tr>
<td>Percentage</td>
<td>60%</td>
<td>96%</td>
<td>94%</td>
<td>88%</td>
<td>94%</td>
</tr>
<tr>
<td>Total CPU time</td>
<td>6 min</td>
<td>6 hr</td>
<td>4 hr</td>
<td>5.5 hr</td>
<td>5.5 hr</td>
</tr>
<tr>
<td>Rate ($N_{\text{corr}}$/min)</td>
<td>390</td>
<td>0.83</td>
<td>7.5</td>
<td>6.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Rate (s/sol)</td>
<td>0.15</td>
<td>72</td>
<td>8.0</td>
<td>9.7</td>
<td>8.5</td>
</tr>
</tbody>
</table>

1 Data sets labeled (1) and (2) represent the individual unmerged data sets for ITQ-43 and IM-5.
2 Completeness of the full data set up to $d_{\text{min}}$ corresponding to the reflections used.
5.4. APPLICATION TO TEST DATA

5.4.2 ZSM-5

The structure of ZSM-5 was first solved by model building using single-crystal XRD data (Kokotailo et al., 1978). Its solution from ADT data more than 30 years later using direct methods was straightforward (Mugnaioli and Kolb, 2013). All Si and O atoms could be located, despite the fact that the coverage was relatively low (81%) and all h00 reflections were missing.

The framework was easily deduced using FOCUS, once it was recognized that the MaxNodeDistance should be relaxed from the conventional 3.6 to 3.8 Å, and 96% of the frameworks found corresponded to the correct one (Figure 5.1b).

5.4.3 ITQ-43

ITQ-43 is an interesting germanosilicate with a huge cloverleaf-shaped pore (21.9 Å × 19.6 Å) delimited by 28 T-atoms, and a low framework density of 12.8 T/1000 Å³. The structure was first solved using direct methods on ADT data and was then refined with XPD 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 destroys 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[isoindoline-2, 1′-piperidin]-1′-ium hydroxide) per unit cell. These were approximated by including 16 × C15N as non-framework atoms in the FOCUS input file to make the scaling more correct.

2. There are Q3 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 three-connected T-atoms was indicated in the FOCUS input file. In this case, the structure was known, so Q3 T-atoms were included. For a material of unknown structure, this information could be derived from MAS-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, an option that allows the scattering factor for the T-atoms to be calculated as a linear combination of 0.35 Ge and 0.65 Si was used.

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 Q3 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. 94% of the retrieved frameworks were correct (Figure 5.1c). In view of the large number of solutions found, the MaxNodeDistance was reduced to 3.7Å 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.

5.4.4 IM-5

The structure of IM-5 was first solved using a complicated procedure involving the charge-flipping algorithm in combination with XPD and high quality HRTEM data (Baerlocher et al., 2007a). 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 and 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 h00 direction are missing. Over a period of 24 hours, 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 supposedly less accurate. The same input file was used and the framework structure was recovered easily using either data set. The simplicity with which FOCUS was 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 (Figure 5.1d). This example shows that FOCUS is able to solve a very complex structure from ADT data, despite the missing h00 reflections.

5.4.5 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 (Smeets et al., 2014b, see also Section 7.3). A total of 155147 trials were performed with FOCUS over 16 hours of total computing time, yielding 238 framework solutions. The most frequent solution represents 108, or 45%, of the total number found (Figure 5.1f). Subsequent structure refinement confirmed that the solution was correct. The framework structure was later identified as being the same as that reported for ERs-18, which had been solved earlier using FOCUS on XPD data (Zanardi et al., 2011).
5.5. USING INTENSITIES AS F

The RED data set is only 53% complete up to a resolution of 1.05Å. 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 scattering factors were used. 8000 trials were found to be sufficient to produce 351 possible frameworks in just 80 minutes. Of these, the correct solution is the most frequent one, occurring 142 times (40%; Figure 5.1e). 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 3D ED data in combination with FOCUS. The solutions with RED data were produced in only 80 minutes, while those for XPD data took 16 hours.

5.5 Using intensities as F

FOCUS assumes input of kinematic structure factors. If ED data were fully kinematic, the intensities would be directly proportional to the square of the structure factor, i.e. \( I \propto |F|^2 \). In practice, the observed values of \(|F|^2\) lie somewhere between \( F \) and \(|F|^2\), and sometimes this fact is taken into account by using \( F \), rather than \(|F|^2\), as input in structure solution programs. To test the effect of this with FOCUS, the structure solution tests were repeated for the ADT data sets assuming \( \sqrt{F} \) instead of \( F \) as input (Table 5.5. In general it was found that the MaxNodeDistance should be increased to 3.9 or 4.0Å for the more complicated crystal structures, and that ReflectionUsage 200 was no longer sufficient.

Although all structures could still be solved, the time taken to get a significant number of solutions was considerably longer than with \( F \)'s. In terms of speed, natrolite was the least affected, and solutions were generated at a similar rate. This time, however, only 37% corresponded to NAT, versus 60% before. ZSM-5 and ITQ-43 were the most difficult to solve this way, and took nearly 2 weeks to generate only a handful of solutions. For ZSM-5, the top solution corresponded to the MFI framework, and represented 18 out of 50 solutions. The second best solution was also related to MFI, with the difference that a 5-ring had been replaced with a highly strained 4-ring.

The problems with ITQ-43 have already been described in Section 5.4.3. Further tweaking of the input parameters was necessary, primarily increasing the MaxNodeDistance to 3.9Å in order to generate any solutions at all. Although a reasonable number of solutions (525) were then generated, and the top solution was found 67 times, it did not correspond to the correct framework. The correct solution appeared in 5th place and was found 32 times. Most of the higher ranked solutions were not entirely wrong—the characteristic cloverleaf shaped channel could often be discerned. Sometimes, a double or triple 4-ring structure could be located inside the channels. This can be understood by considering that the low-angle, low-index reflections typically contain information about total electron density contained in the zeolite channels. For example, calcination results in increased intensity of the low-angle reflections. However, by assuming \( \sqrt{F} \), these intense low-angle reflections get reduced by a disproportionate amount, emphasizing the electron density occluded in the channels, which for ITQ-43 contributes approximately 25% of all scattering power.
Table 5.5: *FOCUS* structure solution details for the five zeolites assuming $\sqrt{F}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Natrolite</th>
<th>ZSM-5</th>
<th>ITQ-43</th>
<th>IM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Data collection</strong></td>
<td>ADT</td>
<td>ADT</td>
<td>ADT</td>
<td>ADT</td>
</tr>
<tr>
<td><strong>Data set</strong></td>
<td>1</td>
<td>1+2</td>
<td>1+2</td>
<td>1+2</td>
</tr>
<tr>
<td><strong>$N_{\text{trials}}$</strong></td>
<td>2500</td>
<td>57262</td>
<td>216369</td>
<td>673</td>
</tr>
<tr>
<td><strong>$N_{\text{solutions}}$</strong></td>
<td>1221</td>
<td>50</td>
<td>525</td>
<td>271</td>
</tr>
<tr>
<td><strong>$N_{\text{correct}}$</strong></td>
<td>454</td>
<td>18</td>
<td>32</td>
<td>215</td>
</tr>
<tr>
<td><strong>Percentage</strong></td>
<td>37%</td>
<td>35%</td>
<td>6%</td>
<td>79%</td>
</tr>
<tr>
<td><strong>Total CPU time</strong></td>
<td>2 min</td>
<td>13 days</td>
<td>13 days</td>
<td>8.5 days</td>
</tr>
<tr>
<td><strong>Rate ($N_{\text{corr}}$/min)</strong></td>
<td>227</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
</tr>
</tbody>
</table>

1 Data sets labeled (1) and (2) represent the individual unmerged data sets for ITQ-43 and IM-5.

Compared to ZSM-5 and ITQ-43, IM-5 was relatively easy to solve in this way. It was necessary to set `MaxNodeDistance` to 4.0 Å, and all 571 reflections with $F/\sigma > 3$ were used in the structure solution. Furthermore, setting `Check3dimConnectivity Off` seemed to help generate solutions. In total, 271 solutions were found, most of which corresponded to IM-5. The best solution was found 215 times and was identified as IMF. The second best solution was also closely related to IMF, albeit with some 5-rings replaced by 4-rings. It is interesting to note that given the long runtime for IM-5, only 671 trials were performed. This was traced down to the large values set for `MaxPeaksFwSearch` and `MaxPeaksFwFragmentSearch` of 1900 and 600, respectively. By reducing these numbers to 900 and 400, more trials could be performed over a shorter amount of time (3751 over 12 hours) to yield 179 solutions. 130 of these corresponded to IMF with shortcuts, and 46 to the correct IMF.

### 5.6 Conclusion

The program *FOCUS* was modified to work with ED data, and used to solve the structures of four test samples with known framework topology and of differing complexities. While the reflection intensities derived from three-dimensional ED 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 test cases presented here 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 zeolite framework structures from three-dimensional ED data. In fact, *FOCUS* was able to solve the structure of IM-5 convincingly, while direct methods only generated a partial solution.

For SSZ-45, both XPD data and ED data were available. From the comparison of the two types of data, 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. In this case, structure solution from both the XPD and RED data set was possible, but the latter allowed the structure to be solved much faster.

This finding could be corroborated when the structure of SSZ-87 was solved more recently from RED data (Section 7.6). The XPD data were of high quality, but resisted structure solution due to the high degree of reflection overlap (93%). On the other hand, the RED data were only 15% complete, yet contained
enough information for FOCUS to retrieve the correct framework topology in a relatively short amount of time. The reason such low completeness was enough to solve the structure of SSZ-87, is probably because these 15% contain the most significant reflections. Typically, FOCUS picks the strongest 200 reflections for the framework search. If these 15% are mostly the strong ones, and weak ones are not observed, then the difference between having a complete data set and a incomplete data set is marginal.

It is clear that the use of FOCUS with three-dimensional ED data offers a major improvement in both the time and effort required to solve a zeolite framework structure, as long as the sample is ordered, and allows the ED data to be collected in the first place. The work presented in this chapter have now been published in Smeets et al. (2013).
Chapter 6

Combining powder and electron diffraction data

6.1 Introduction

ED and XPD data have similar problems: the intensities are unreliable. ED intensities are dynamical and full coverage cannot always be achieved, but because single crystallites are measured, all diffraction peaks are well resolved. XPD data suffers from an ambiguity in diffraction intensities due to reflection overlap, but the data are complete, diffraction intensities kinematical, and the total intensity accurate. Therefore, the data are highly complementary, and there are now several examples of how this can be exploited so solve the structures of complex materials.

The first reports about electron crystallography being used to aid the solution of zeolite structures appeared approximately 30 years ago. Initially, researchers used HRTEM images and ED data collected along several zone axes to find the unit cell and space group, and then used this information to solve the structures of ZSM-23 (MTT; Rohrman Jr. et al., 1985), Zeolite Beta (*BEA; Higgins et al., 1988; Newsam et al., 1988), and NU-87 (NES; Shannon et al., 1991) via model building. It was with SSZ-48 (SFE) that the first zeolite structure was solved from ED data alone using direct methods (Wagner et al., 1999).

In each of these cases though, XPD data were used to confirm, complete, and refine the structural model.

In an attempt to truly combine the data, phases extracted from HRTEM images were used as a starting point for the solution of the structure of TNU-9 (TUN) with FOCUS (Gramm et al., 2006), and IM-5 (IMF) with pCF (Baerlocher et al., 2007c) from XPD data. Later, Baerlocher et al. (2008) also showed that HRTEM phases can be used to generate a structure envelope (Brenner et al., 1997, 2002) and this was used to facilitate the solution of the structure of SSZ-74 (*SVR) from XPD data. In his Ph.D. thesis, Xie (2010) explored two ways of combining the intensities from PED experiments with XPD data: (1) to estimate the phases of the reflections in a projection, and (2) to identify weak reflections to improve the XPD data (weak reflection elimination; WRE). He showed that both methods significantly improved the structure solution process. The WRE method can be described in four simple steps:
CHAPTER 6. COMBINING DATA

Figure 6.1: Equipartitioned reflection intensities extracted from XPD pattern are repartitioned in order to better approximate the correct reflection intensities.

1. Calculate the average structure factor amplitude of all reflections from ED data.

2. Calculate a threshold value based on a percentage of the average amplitude (a threshold of around 50% was shown to be most effective).

3. Remove all reflections from the XPD data set with amplitude < threshold.

4. Use the reduced $hkl$ list to re-extract intensities from the XPD pattern.

The approach taken is conservative, but effective for combining ED and XPD data. The method was demonstrated to be capable of aiding the solutions of known zeolites TNU-9 and ZSM-5 (Xie et al., 2008). In a similar vein, Sun et al. (2009) used the intensities from SAED data to prepartition the XPD data to solve the structure of the cubic ITQ-37 with charge-flipping. Low resolution reflections ($d > 3.3$ Å) were used to get a better estimation of the 16 overlap groups with $2\theta < 26^\circ$. Although each way of incorporating HRTEM or ED (PED/SAED) unmistakably improved the structure solution process, they all share the limitation that only two-dimensional data could be collected along a few (low-index) zone axes.

With the advent of EDT (Section 3.5), collection of three-dimensional ED data collection became possible. Since these data are more complete than those previously available, the approaches of Xie et al. and Sun et al. were revisited. The idea was that the structure solution process could be improved even further by combining the three-dimensional ED and XPD data sets: the deficiencies of each could be compensated by the other. The goal was to generate a data set more suitable for structure solution than either one alone. Therefore, I developed an algorithm to combine the data via a repartitioning scheme (Figure 6.1), and applied it to several test structures for which both ED and XPD data were available.
6.2 Repartitioning

Because of the dynamical nature of ED data, accurate ED intensities cannot be extracted, but the ratios between intensities of reflections with similar \( d \)-spacings should be more reliable than those obtained from XPD data. A pragmatic approach was taken by using the ratios of the structure factor amplitudes obtained from the ED data to repartition reflections that overlap in the XPD data. In this way, the total diffraction intensity is conserved and comes from a reliable source (XPD), whereas the ratios between intensities (from ED data) are more correct. This would have a few advantages over WRE:

1. No information is lost. Weak reflections are repartitioned rather than eliminated.
2. The procedure should provide more accurately partitioned reflections. In WRE, strong overlapping reflections are still equipartitioned.
3. The procedure does not depend on a structure solution program to handle subsequent repartitioning. Data can be treated as single-crystal XRD data.

Reflection intensities can be extracted using a Le Bail (Le Bail et al., 1988) or Pawley fit (Pawley, 1981), and should include a list of half-widths. For each sequential pair of reflections (labeled 1 and 2), the following expression determines whether they overlap:

\[
2\theta_2 - 2\theta_1 < \frac{\kappa}{2}(FWHM_1 + FWHM_2)
\]

where \( FWHM \) is the full width at half maximum, \( 2\theta \) is the diffraction angle and \( \kappa \) is the overlap factor (typically \( \kappa = 0.3 \)). All reflections satisfying this criterion are put in the same overlap group \( \Gamma_k \). The overlap groups only cover a small \( 2\theta \) range, so the difference in the value of the scattering factor with \( \sin(2\theta)/\lambda \) becomes negligible, and only the difference between the individual atoms with ED and XPD data affects the accuracy of the repartitioning. Although the shapes of the scattering factor curves for ED and XPD do not match precisely, it holds that if a reflection is strong in ED, it should be strong in XPD as well. The reflections in each overlap group are then repartitioned according to the extracted ED structure factor amplitudes:

\[
|F_{\text{new}}^{hkl}|^2 = |F_{\text{ed}}^{hkl}|^2 \sum_{\Gamma_k} m \cdot |F_{\text{xpd}}^{hkl}|^2 \sum_{\Gamma_k} m \cdot |F_{\text{ed}}^{hkl}|^2
\]

where \( m \) is the multiplicity of the reflection and \( F_{\text{xpd}} \) and \( F_{\text{ed}} \) are the structure factor amplitudes obtained from XPD and ED, respectively.

Reflections in the ED data may be missing because of the missing wedge, so the repartitioning algorithm needs to take this into account. Therefore, each overlap group is categorized, and assigned a case type, depending on the size of the group, number of XPD and ED reflections present, and total intensity. The XPD data are always assumed to be complete. If all ED reflections are present (Case I), the overlap groups are categorized as:

- **Case Ia**: Group contains only one reflection (no overlap).
Case Ib: Sum of XPD intensities equals 0.

Case Ic: Sum of ED intensities equals 0.

Case Id: All remaining groups (sum of XPD intensities is larger than 0, sum of ED intensities is larger than 0).

Overlap groups with missing ED reflections (Case II) require special treatment, and are categorized in a second step:

- Case IIa: All ED reflections are missing.
- Case IIb: Sum of XPD intensities is larger than 0, sum of present ED intensities equals 0.
- Case IIc: Only one ED reflection is present.
- Case IIId: All remaining groups (sum of XPD intensities is larger than 0, sum of ED intensities is larger than 0, two or more ED reflections are present).

If the case assignment is ambiguous (e.g. two or more cases fit), then the group is assigned the first case in the order shown above. Table 6.1 shows how the 982 XPD reflections obtained for SSZ-45 are categorized when combined with 419 RED reflections (363 missing). Each group is then repartitioned according to the case it has been assigned. This was done by setting up a few simple rules. In general, the total group intensity from XPD is always trusted, and whenever the ratio between a number of ED intensities can be established, this information is used. In cases where no extra information can be extracted from the ED data, the XPD intensities are taken.

- Case Ia, Ib, Ic, IIa → The XPD intensities are used.
- Case Id → The XPD intensities are repartitioned according to Eq.6.2.
- Case IIb → Reflections with amplitude equal to 0 in ED data are set to 0. Sum of all XPD intensities is equipartitioned over the remaining XPD reflections.
- Case IIc → A histogram of all observed XPD and ED intensities is generated and divided over 10 bins with equal ranges. All reflections in the group are ranked according to the bin they are in. For each ED reflection present in a group, the average XPD intensity of reflections in the bin corresponding to this rank is retrieved, as long as it does not exceed the total group intensity. Remaining XPD reflections in the group are equipartitioned.
- Case IIId → For reflections that are missing in the ED data, the XPD intensities are used. Other XPD intensities are repartitioned using the ED reflections that are present and with Eq.6.2.

As input, the algorithm requires the reflection intensities (or amplitudes) for the XPD and ED data, the FWHM for the XPD reflections, and a value for $\kappa$. The resulting data set can be used as a single-crystal XRD data set.
Table 6.1: Repartitioning scheme for SSZ-45 with 363 missing reflections in the ED data.

<table>
<thead>
<tr>
<th>Case</th>
<th>Nrefs</th>
<th>Ngroups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>195</td>
<td>195</td>
</tr>
<tr>
<td>Ib</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Ic</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Id</td>
<td>72</td>
<td>28</td>
</tr>
<tr>
<td>Subtotal</td>
<td>293</td>
<td>229</td>
</tr>
<tr>
<td>IIa</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>IIb</td>
<td>39</td>
<td>12</td>
</tr>
<tr>
<td>IIc</td>
<td>61</td>
<td>28</td>
</tr>
<tr>
<td>IIId</td>
<td>581</td>
<td>57</td>
</tr>
<tr>
<td>Subtotal</td>
<td>689</td>
<td>101</td>
</tr>
<tr>
<td>Total</td>
<td>982</td>
<td>330</td>
</tr>
</tbody>
</table>

6.3 Application to test data

### 6.3.1 SSZ-45

SSZ-45 proved to be an excellent test case for the development of the algorithm. XPD data were available with a resolution up to 1.18 Å, with 80% of reflections overlapping with an overlap factor of 0.3. The structure of SSZ-45 had already been solved with *FOCUS* using the XPD and RED data alone (Section 5.4.5), so the same input file was used in the tests with the combined data.

Initial attempts at structure solution with *FOCUS* using the combined data set were promising. For 100000 trials, 5590 frameworks were produced, and 3366 (60%) of these were found to correspond to the correct one. With the combined data set, a correct solution was generated every 11 seconds, compared to one per 34 seconds with the RED data, or 11 minutes for the XPD data (Table 6.2). In other words, structure solution using the combined data was substantially better than using either XPD or ED data individually. Several overlap factors were tried to see if this would affect the result, but a value of 0.3 proved to be ideal. This highlights an advantage of working with a program like *FOCUS*, because the statistical approach it takes in classifying frameworks allows the quality of a data set to be evaluated rapidly in a quantitative manner. By using the same seed for the random number generator, each *FOCUS* run can be made to evaluate the same sets of starting phases. The most suitable data set is then the one that generates the highest percentage of correct solutions, and does so at the fastest rate. Therefore, *FOCUS* can be used as a benchmark tool to judge the quality of a data set.

After these initial tests, improvements could be made to the algorithm by tweaking the assignments of the overlap groups, and how each case was treated, to give the scheme given in Section 6.2. At first, remaining XPD reflections in case IIb groups were not equipartitioned, but repartitioned using the extracted XPD intensities. Another change was in the treatment of groups assigned to case IIc. For these, the XPD intensities were initially used directly.

With these improvements, another 100000 trials were performed, but this time 7062 frameworks were produced, 5023 (71%) of which were found to be correct. This means that a correct solution was generated every 8.6 seconds. Furthermore, the number of correct solutions generated jumped from 3366 to 5023. Repeated tests gave similar results.
Table 6.2: Details of the solutions of the structure of SSZ-45 using FOCUS with XPD and RED data, and a combination of both data sets.

<table>
<thead>
<tr>
<th></th>
<th>XPD</th>
<th>RED</th>
<th>Combined*</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflections</td>
<td>982</td>
<td>4326</td>
<td>982</td>
<td>982</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>982</td>
<td>782</td>
<td>982</td>
<td>982</td>
</tr>
<tr>
<td>Overlapping reflections</td>
<td>795</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reflections used</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>(d_{\text{min}}) (Å)</td>
<td>1.18</td>
<td>1.05</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>Completeness</td>
<td>100%</td>
<td>53%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Trials</td>
<td>155147</td>
<td>8000</td>
<td>100000</td>
<td>100000</td>
</tr>
<tr>
<td>Number of solutions</td>
<td>238</td>
<td>351</td>
<td>5590</td>
<td>7061</td>
</tr>
<tr>
<td>Correct solutions</td>
<td>108</td>
<td>142</td>
<td>3966</td>
<td>5023</td>
</tr>
<tr>
<td>Total CPU time (min)</td>
<td>1200</td>
<td>80</td>
<td>600</td>
<td>720</td>
</tr>
<tr>
<td>sec/correct solution</td>
<td>667</td>
<td>34</td>
<td>11</td>
<td>8.6</td>
</tr>
</tbody>
</table>

* Initial algorithm

Figure 6.2: Electron density map obtained for SSZ-45 using charge-flipping with the (a) XPD, (b) RED, and (c) combined data set. The correct framework is overlaid for comparison.

FOCUS relies on \textit{a priori} information to supplement the – usually poor – diffraction data. To show that the approach is generally applicable, the combined data were also used with the charge-flipping routine implemented in \textsc{SUPERFLIP} (Palatinus and Chapuis, 2007), and compared with the best density maps obtained from the XPD and RED data (Figure 6.2). The XPD density map clearly shows some features that resemble the correct structure, but not enough to be able to solve the structure. The RED data proved to be unsuitable for structure solution with \textsc{SUPERFLIP}. However, using the combined data set, all Si and most O atoms could be retrieved, a significant improvement.

6.3.2 IM-5

XPD data collected on calcined IM-5 at SNBL at ESRF in Grenoble, FR (wavelength 0.5 Å) were also available, and 90% of the reflections were found to be overlapping for \(\kappa = 0.3\). Unlike SSZ-45, IM-5 could not be solved with FOCUS from the XPD data alone. Structure solution using ADT data had been shown to be possible (Section 5.4.4).

Initial attempts to solve the structure with FOCUS using the same input file as for the ADT data with the combined data were unsuccessful, and resulted in no solutions. Only by increasing the overlap used for the assignment of the overlap groups, was it possible to increase the number of solutions (Table 6.3). The best result was obtained using \(\kappa = 1.2\), in which case all solutions generated corresponded to the correct one. This combined data improved the rate at
6.3. APPLICATION TO TEST DATA

Table 6.3: Number of solutions \( N_{\text{sols}} \) obtained after 50000 trials with \( \text{FOCUS} \) using a data set combined with different overlap factors for IM-5

<table>
<thead>
<tr>
<th>( \kappa )</th>
<th>( N_{\text{sols}} )</th>
<th>( N_{\text{cor}} )</th>
<th>%</th>
<th>time (min)</th>
<th>rate (s/sol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>3</td>
<td>3</td>
<td>100</td>
<td>607</td>
<td>12159</td>
</tr>
<tr>
<td>0.6</td>
<td>176</td>
<td>176</td>
<td>100</td>
<td>593</td>
<td>292</td>
</tr>
<tr>
<td>0.8</td>
<td>322</td>
<td>321</td>
<td>100</td>
<td>587</td>
<td>110</td>
</tr>
<tr>
<td>1.0</td>
<td>373</td>
<td>372</td>
<td>100</td>
<td>613</td>
<td>99</td>
</tr>
<tr>
<td>1.2</td>
<td>598</td>
<td>597</td>
<td>100</td>
<td>627</td>
<td>63</td>
</tr>
<tr>
<td>1.4</td>
<td>336</td>
<td>334</td>
<td>100</td>
<td>612</td>
<td>110</td>
</tr>
<tr>
<td>1.6</td>
<td>475</td>
<td>468</td>
<td>98</td>
<td>674</td>
<td>86</td>
</tr>
<tr>
<td>1.8</td>
<td>122</td>
<td>122</td>
<td>100</td>
<td>598</td>
<td>295</td>
</tr>
<tr>
<td>2.0</td>
<td>136</td>
<td>136</td>
<td>100</td>
<td>607</td>
<td>268</td>
</tr>
<tr>
<td>2.2</td>
<td>143</td>
<td>143</td>
<td>100</td>
<td>622</td>
<td>261</td>
</tr>
<tr>
<td>2.4</td>
<td>126</td>
<td>122</td>
<td>96</td>
<td>597</td>
<td>294</td>
</tr>
<tr>
<td>2.6</td>
<td>126</td>
<td>122</td>
<td>96</td>
<td>597</td>
<td>294</td>
</tr>
</tbody>
</table>

Figure 6.3: By combining two electron density maps (left), a map that is fully interpretable (right) can be obtained for IM-5. The framework topology is overlaid for comparison. View along [001].

which solutions were generated over the ADT data set by itself by a factor two. Overlap factors other than 1.0, 1.2, and 1.6 resulted in data sets less suitable for structure solution with \( \text{FOCUS} \) than pure ADT data. It is not clear why this is happening.

Structure solution with combined data (\( \kappa = 1.2 \)) was then attempted using charge-flipping with \( \text{SUPERFLIP} \). A problem with the origin definition for IM-5 prevented straightforward structure solution. When one of the maps was used as a reference map to circumvent the origin definition problem, the complete framework could be recovered by combining a handful of electron density maps (Figure 6.3).

6.3.3 ZSM-5

XPD data on as-synthesized ZSM-5 were collected at the MS-Powder beamline on the Swiss Light Source in Villigen, CH (wavelength 1.0000 Å; Mythen II detector; Bergamaschi et al., 2010). Reflection intensities were extracted using the Le Bail method in \( \text{FULLPROF} \).

The XPD data were of very high quality, with sharp peaks and thus a relatively low degree of reflection overlap (49%), so \( \text{FOCUS} \) had no problem finding the MFI framework with the XPD data. Normally, \( \text{FOCUS} \) performs an equipartitioning step on the data. However, by using the diffraction intensities determined using the Le Bail peak fitting routine (no subsequent equipartitioning), \( \text{FOCUS} \) was much more efficient at solving the crystal structure. Sur-
Table 6.4: Details of the solutions of the structure of ZSM-5 using FOCUS with XPD and ADT data, and a combination of both.

<table>
<thead>
<tr>
<th>Data set</th>
<th>ADT(^a)</th>
<th>ADT(^b)</th>
<th>XPD(^c)</th>
<th>XPD(^d)</th>
<th>combined(^a)</th>
<th>combined(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trials</td>
<td>2000</td>
<td>2000</td>
<td>4000</td>
<td>4000</td>
<td>8000</td>
<td>4000</td>
</tr>
<tr>
<td>Number of sol.</td>
<td>322</td>
<td>184</td>
<td>25</td>
<td>1337</td>
<td>8845</td>
<td>4242</td>
</tr>
<tr>
<td>Correct solutions</td>
<td>318</td>
<td>180</td>
<td>21</td>
<td>1314</td>
<td>8798</td>
<td>4218</td>
</tr>
<tr>
<td>Percentage %</td>
<td>99</td>
<td>98</td>
<td>84</td>
<td>98</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>Total CPU time (h)</td>
<td>2.9</td>
<td>3.3</td>
<td>2.5</td>
<td>3.8</td>
<td>9.5</td>
<td>4.1</td>
</tr>
<tr>
<td>sec/correct solution</td>
<td>32.7</td>
<td>120</td>
<td>427</td>
<td>10.5</td>
<td>3.9</td>
<td>3.5</td>
</tr>
</tbody>
</table>

\(^a\) ADT data on calcined ZSM-5 \(^b\) ADT data on as-synthesized ZSM-5
\(^c\) Equipartitioned in FOCUS \(^d\) Not equipartitioned in FOCUS

Surprisingly, these data proved to be more effective for structure solution than the ADT data (Table 6.4). This gives us a feeling for the accuracy of the ADT data in comparison to data obtained with XPD. Somewhere between the degree of overlap of 49% for ZSM-5 and 80% for SSZ-45 (as far as overlap is an indication of quality), the ADT data overtakes the XPD data in terms of effectiveness for structure solution with FOCUS.

The ADT data of both the as-synthesized and calcined forms of ZSM-5 were used to repartition the XPD data of the as-synthesized material with \( \kappa = 0.3 \). In both cases this led to an increased rate of structure solution. Compared with ADT data alone, solutions were generated approximately 8 and 34 times faster for the calcined and as-synthesized repartitioned data, respectively. Compared with the XPD data, FOCUS performed three times better with the combined data. Combining data collected on a calcined material with those from an as-synthesized one proved to have no noticeable negative effect on the data suitability.

### 6.3.4 ITQ-43

XPD data on as-synthesized ITQ-43 collected on a PANalytical X’Pert PRO lab diffractometer were provided by José Luis Jordá (University of Valencia). Data were extracted using the Pawley routine in TOPAS, and contained 90% overlapping reflections.

Using the default overlap factor of 0.3, the structure of ITQ-43 could be solved, but at a much slower rate than with the ADT data directly (Table 6.5). A problem similar to that found for IM-5 was observed: the optimal overlap factor had to be found by trial and error. Just using a slightly larger \( \kappa \) of 0.5 improved the number of solutions generated significantly, but the best value was found to be 1.8. With \( \kappa = 0.3 \), the data are divided into 462 overlap groups, but as \( \kappa \) goes up, the number of overlap groups go down. With \( \kappa = 0.5 \), the data are assigned to 255 overlap groups, and with \( \kappa = 1.8 \) to 51. With a large overlap factor, repartitioning of groups spanning several degrees \( 2\theta \) can occur, but this appears to be favorable over repartitioning with smaller groups.

### 6.4 Conclusion

The conclusions drawn from the results presented here are mixed. On the one hand, the goal of combining XPD and ED data in order to generate a data set
6.4. CONCLUSION

Table 6.5: Details of the solutions of the structure of ITQ-43 using FOCUS with XPD and ADT data, and a combination of both data sets.

<table>
<thead>
<tr>
<th>Data set</th>
<th>ADT</th>
<th>combined</th>
<th>combined</th>
<th>combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>κ</td>
<td>16156</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
</tr>
<tr>
<td>Trials</td>
<td>1898</td>
<td>401</td>
<td>4607</td>
<td>6501</td>
</tr>
<tr>
<td>Number of sol.</td>
<td>1791</td>
<td>3</td>
<td>2737</td>
<td>6233</td>
</tr>
<tr>
<td>Correct solutions</td>
<td>94</td>
<td>1</td>
<td>59</td>
<td>96</td>
</tr>
<tr>
<td>Percentage %</td>
<td>3.9</td>
<td>6.1</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>sec/correct solution</td>
<td>7.9</td>
<td>54.6</td>
<td>5.1</td>
<td>3.6</td>
</tr>
</tbody>
</table>

that is better for structure solution was achieved. For every test structure, the combined data proved to be more effective for structure solution than either XPD or ED data individually. The routine is generally applicable, straightforward to use, and not necessarily restricted to ED. Data obtained with any method that provides well-resolved reflection intensities can be used.

On the other hand, the results obtained for IM-5 and ITQ-43 highlight a major pitfall in the assignment of the reflections to overlap groups. It’s not always obvious which overlap factor should be used, and choosing the wrong one will result in a poorer data set. A suitable value for $\kappa$ may be found by trial and error, but this is only worthwhile if all other options are exhausted. Some improvements were made to the algorithm so that overlap groups can be assigned manually, but this defeats the purpose of having a fully automatic routine that takes the XPD and ED data and returns an improved data set, and there is no guarantee that it will result in better repartitioning.

In summary, my experience in trying to apply the method and use the combined data from several sources is that the demands for data quality are quite high. The XPD data needs to have sharp peaks, so reflections can be assigned to overlap groups reliably. Often, with poor data, reflections at high angle tend to have broad peaks, and are therefore put in large overlap groups. On top of that, the ED data needs to be complete enough, so that there is a reasonable chance that the multiple reflections required to perform the repartitioning are present in a group. Most of the work presented here focused on the use of FOCUS for structure solution of zeolites, in which case, having ED data available is already a huge benefit. For example, RED data collected on SSZ-87 are only 15% complete, and a quick test showed that these data are not suited for the repartitioning algorithm, because for the most part there are not enough RED reflections to determine the ratios between the intensities in a group. Nonetheless, the same RED data could be used directly with FOCUS to solve the structure (Section 7.6). In short, if the data are good enough for repartitioning, they are also good enough for structure solution by themselves. So far, no example has been found that proves the contrary. However, the charge-flipping algorithm, which is sensitive to incomplete data, may benefit more from the combined data.
Chapter 7

Application of hybrid methods of structure solution

7.1 Introduction

Solving the structure of a polycrystalline material is often fraught with difficulties that are inherent to the material. The data may be of unavoidably poor quality, the sample may contain multiple phases, the material may be disordered, reflection overlap may be high, or the structure may simply be complex. In the ideal case, there would be a well-defined road map to solve the structure of a polycrystalline material. However, just having a routine approach to structure solution is not enough, because one data set by itself may not always contain enough information to determine the crystal structure unequivocally. Consideration of multiple data sets at once is often required. In this chapter, I describe my efforts to overcome these problems by using a combination of computational methods, XPD, ED, HRTEM, and/or other data, as well as paying careful attention to the chemistry behind the problem.

7.2 Charge-flipping and simulated annealing

Over the course of my Ph.D. work, most of the focus has been on solution of zeolite structures. However, as part of collaborations with other groups, several other types of inorganic materials were also analyzed (Chen et al., 2013; Amarante et al., 2014; Majano et al., 2014; Smeets et al., 2015b). In hindsight, a noticeable trend is visible in the way the structure elucidations of these materials were approached. Each of the materials contains some inorganic component in the form of a heavy element (Zr, Mo, Zn, or Cu), and an organic component, such as a ligand, or an SDA. The charge-flipping procedure greatly benefits from the presence of heavy elements, but is notoriously ineffective when it comes to weak scatterers (Šišak Jung et al., 2014). On the other hand, the molecular arrangement of the weak scatterers is often known beforehand, and this plays into the strength of the simulated annealing algorithm. The structure of each material was solved by first locating the strong scatterers using charge-flipping, and then completing the structures using simulated annealing.
CHAPTER 7. HYBRID METHODS

Figure 7.1: Electron density map obtained from charge-flipping (green) with the Zn–Zn framework structure overlaid.

Two of these studies, involving the structure of a new zeolitic imidazolate material ZIF-L (Section 7.2.1) and those obtained by degrading HKUST-1 (Section 7.2.2), have been selected for further clarification here. The structures of a molybdenum oxide/pyrazolylpyridine polymeric hybrid material ([Mo₄O₉(2-[3(5)-Pyrazolyl]pyridine)]ₙ; Amarante et al., 2014) and the zirconium phosphate ZrPOF-Epy (Smeets et al., 2015b) were also determined, but these were relatively straightforward, so no further details are given.

7.2.1 ZIF-L

ZIF-L is a layered zeolitic imidazolate framework material with Zn as the metal and methylimidazole (Meim) as the organic linker. This was the first crystal structure I managed to solve from XPD data. This work was performed as part of a collaboration with Qinfen Gu (Australian Synchrotron) and Rizhi Chen (Monash University) to characterize a new ZIF with leaf-like morphology (hence the ‘L’) and excellent CO₂ adsorption properties (Chen et al., 2013). Data on ZIF-L were collected on the Powder diffraction beamline at the Australian Synchrotron (wavelength 0.8237 Å, MYTHEN II detector) and kindly provided to us by Qinfen Gu. The data could be indexed with an orthorhombic unit cell (Cmce; a = 24.0610 Å, b = 16.9673 Å, c = 19.6783 Å) using the indexing routine in TOPAS.

Structure solution was performed using the pCF method in SUPERFLIP. Although the full structure did not emerge, two independent tetrahedral Zn atoms could be located (Figure 7.1). The Zn–Zn distances of around 6.0 Å corresponded well to the intermetallic distance expected for a ZIF. However, charge-flipping did not reveal any electron density between the Zn atoms, so a tentative model was constructed by manually placing the Meim linkers midway between the Zn atoms. Initial Rietveld refinement of this model with the program XRS-82 (Baerlocher, 1982) did not converge. The starting orientations
of the Meim molecules were varied in order to find which ones would result in a better refinement, but with four independent Meim molecules (one of which was terminal), this became a time-consuming and tedious task. Besides that, it did not result in a better refinement. It was at this point that I discovered that TOPAS provided all the tools required to overcome this problem.

Zn-Meim-Zn fragments were constructed as rigid bodies. The Zn atoms were treated as dummy atoms in the rigid body fragments, and their positions were restrained to the positions located in the pCF electron density maps. Consequently, the orientation of the Meim fragments could be optimized by allowing rotation around their respective Zn–Zn axes. This reduced the number of parameters for the orientation of the Meim molecules to four (Figure 7.2). Simulated annealing could then be used to determine the best possible orientation to start structure refinement. During this process, the starting orientations were randomized for a large number of runs in order to eliminate the possibility of

Figure 7.2: (a) The Zn₂(Meim) fragment is introduced into the model in the expected position. (b) Rotation is allowed around the Zn–Zn axis only, so the problem of finding the orientation of the Meim linkers is reduced to finding the optimal rotation angle.

Figure 7.3: Observed (blue), calculated (red) and difference (black) plot for the Rietveld refinement of ZIF-L.
Table 7.1: Crystallographic data for the Rietveld refinement of ZIF-L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZIF-L</th>
<th>(H_2O)<em>{41.1}[[Zn</em>{24}(Meim)_{62.6}]]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>$\text{ZIF-L}$</td>
<td>$\text{(H}<em>2\text{O)}</em>{41.1}[[\text{Zn}<em>{24}(\text{Meim})</em>{62.6}]]$</td>
</tr>
<tr>
<td>Space group</td>
<td>$C_{mce}$</td>
<td>$C_{mce}$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>24.1191(5)</td>
<td>24.1191(5)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>17.0604(3)</td>
<td>17.0604(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>19.7398(4)</td>
<td>19.7398(4)</td>
</tr>
<tr>
<td>$V$ (Å³)</td>
<td>8122.6(3)</td>
<td>8122.6(3)</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>$\rho$ (g/cm³)</td>
<td>1.4043(1)</td>
<td>1.4043(1)</td>
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<td>Reflections</td>
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<td>1274</td>
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<td>Parameters</td>
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<td>75</td>
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<td>$\lambda$ (Å)</td>
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<td>0.8237</td>
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<td>$2\theta$ (°)</td>
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<td>3.0 to 40.0</td>
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<td>0.075</td>
</tr>
<tr>
<td>$R_{\text{exp}}$</td>
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<td>0.049</td>
</tr>
<tr>
<td>GoF</td>
<td>1.53</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Figure 7.4: (a) Two-dimensional layer of ZIF-L showing the linking Meim molecules (numbered 1-3), and (b) the interdigitating interactions between neighboring two-dimensional networks in ZIF-L. The groups formed by monodentate Meim-4 and ‘free’ Meim-5 lie in the ‘cups’ of the opposing layer.

There are two crystallographically independent Zn ions, four bridging Meim ligands, and one ‘free’ Meim molecule (%5) in the asymmetric unit (Figure 7.4). Each Zn atom adopts a regular [ZnN₄] tetrahedral geometry, where Zn1 is coordinated by four μ₂-bridging imidazole units (two ≠1 and two ≠2), while Zn2 is coordinated to four independent ligands, one of which is monodentate (≠4). Six bridging Meim ligands bind two Zn1 ions and four Zn2 ions to form a large hexagon, while four Meim ligands connect two Zn2 ions to produce a smaller parallelogram. These hexagons and parallelograms are interconnected to create two-dimensional layers parallel to the ab-plane, and these are then stacked along the c direction. The two-dimensional network is further stabilized by interdigitating interactions involving the terminal Meim-4 ligand and the ‘free’ Meim-5 ligand.
molecule (Figure 7.4b). ZIF-L has one large zero-dimensional cushion-shaped cavity with dimensions of $9.4 \times 7.0 \times 5.3$ Å, well suited to accommodate CO$_2$ molecules. Further details about the structure, and CO$_2$ adsorption capabilities of ZIF-L can be found in Chen et al. (2013).

7.2.2 Decomposition of HKUST-1

HKUST-1 is a metal-organic framework (MOF) consisting of Cu connected by 1,3,5-benzenetricarboxylate (BTC) linkers, forming a highly efficient and versatile material for reversible CO$_2$ sorption. However, as with most MOFs, HKUST-1 only possesses moderate hydrothermal stability and degrades in the presence of water vapor, limiting its potential for large-scale industrial applications. Gerardo Majano and co-workers (ETH Zurich) devised a way of reconstructing the original material via a solvent-assisted treatment. They were interested in understanding the process, so we collaborated with them to determine the crystal structure of the degraded material. Synchrotron XPD data were collected on the MS-Powder beamline at the Swiss Light Source in Villigen, CH (wavelength 0.7085 Å, MYTHEN II detector; Bergamaschi et al., 2010) on samples degraded by exposing them to water, 0.1M HCl, or steam. The patterns were necessarily of poor quality, and all samples contained multiple phases. Only the structures of the phases present in the HCl treated sample (hereafter $H$) could be determined fully, and these are described in this section. This information then allowed some of the other patterns to be unraveled.

Initial attempts to index the diffraction pattern of $H$ were unsuccessful. However, after examining the diffraction pattern more closely, two clearly distinct peak shapes could be identified, hinting at the presence of two phases. One of the phases ($H_1$) possessed relatively narrow peaks, and could be indexed with a monoclinic cell ($P2_1/n$; $a = 6.841$ Å, $b = 18.851$ Å, $c = 8.565$ Å, $\beta = 92.869^\circ$) using the indexing routine in TOPAS. Intensity extraction was performed using the Pawley peak fitting routine, and due to the presence of strong scatterers (Cu), structure solution was straightforward with the pCF routine in SUPERFLIP. Only two C atoms in the organic linker were missing, but could be added easily based on geometric considerations. The structure of $H_1$ was later found to be identical to that reported by Pech and Pickardt (1988).

Structure solution of the other phase ($H_2$) was less straightforward. The remaining Bragg peaks in the diffraction profile of $H$ could be indexed with a monoclinic cell (extinction symbol $P-2_1$; $a = 13.544$ Å, $b = 18.234$ Å, $c = 3.655$ Å, $\beta = 91.529^\circ$). Although the indexing was not unambiguous, this cell was chosen because the $c$-parameter corresponds well to the interlayer distance found in $H_1$. Due to the broad peaks and second phase, accurate intensity extraction was difficult. As a result the structure could not be solved directly using the pCF algorithm. Only partial solutions were found. At best, the location of the Cu and some of the coordinated O atoms (water) could be identified. Using this information, in combination with the fact that the only possible arrangement for the BTC linkers would be to have them stacked along the $c$-axis, an initial model for the simulated annealing routine could be constructed. Several different space groups and starting positions for the Cu atoms and organic linkers, which were added as rigid body models, were tried. The structure was eventually solved by fixing the positions of the Cu atoms, limiting the degree of freedom of the BTC molecules, so they could be stacked along $c$, and using...
Simultaneous Rietveld refinement of the structures of $\text{H}_1$ and $\text{H}_2$ was performed with TOPAS. The background was removed using the program LINES (Appendix B), restraints on the Cu–O distances were added where necessary, and the BTC molecules were refined as rigid body models. Comprehensive refinement was hindered by the presence of two phases, but refinement converged with an $R_I = 0.120$ for $\text{H}_1$, $R_I = 0.086$ for $\text{H}_2$, and $R_{wp} = 0.171$ ($R_{exp} = 0.014$), indicating a reasonable, if not perfect, fit to the data (Figure 7.5 and Table 7.2).

$\text{H}_2$ is the major phase, and accounts for ca. 85% of the diffraction intensity. The two structures are depicted in figure 7.6. In both, the three-dimensional framework structure is lost and basically differ only in the number of acid groups per BTC molecule that are coordinated to Cu. In $\text{H}_1$, each BTC molecule has two carboxyl groups coordinated to a Cu atom, which leads to a one-dimensional zigzag BTC:Cu polymer chain with a BTC:Cu ratio of 1:1. In $\text{H}_2$, on the other hand, only one carboxyl group per BTC is coordinated to a Cu atom, resulting in a molecule with two BTC and one Cu (BTC:Cu ratio of 2:1). The Cu atom has a square pyramidal coordination geometry in $\text{H}_1$, and a square planar one in $\text{H}_2$. In both structures, the Cu is coordinated to two O atoms of different BTC molecules in a trans arrangement. Sample $\text{H}$ can be considered a model for the partial disruption of the BTC:Cu coordination to form layers, and allows a better understanding of the reconstruction process (Majano et al., 2014).

### 7.2.3 Conclusion

Simulated annealing as an *ab initio* method for structure solution is very effective for organic materials, where the problem is well-defined. However, with more complicated materials, and thus a larger number of parameters, it can
### Table 7.2: Crystallographic data for the Rietveld refinement of sample H.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H1</th>
<th>H2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td>Cu[BTC]O$_2$·O$_4$</td>
<td>Cu[BTC]O$_2$$_2$</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$P2_1/n$</td>
<td>$P2_1$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.8414</td>
<td>13.5441</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>18.8513</td>
<td>18.2338</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>8.5653</td>
<td>3.6546</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>92.869</td>
<td>91.529</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1103.29</td>
<td>902.24</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
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<td>1.8542</td>
</tr>
<tr>
<td>$R_I$</td>
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</tr>
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<td><strong>Reflections</strong></td>
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<td><strong>Parameters</strong></td>
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<td>28</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>0.708597(5)</td>
<td></td>
</tr>
<tr>
<td>$2\theta$ (°)</td>
<td>2.0 to 45.0</td>
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</tr>
<tr>
<td><strong>Observations</strong></td>
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</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.171</td>
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<tr>
<td>$R_{exp}$</td>
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<td></td>
</tr>
<tr>
<td><strong>GoF</strong></td>
<td>11.79</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 7.6**: Crystal structures of H1 along the crystallographic (a) $z$-, (b) $x$-, and (c) $y$-axes, and H2 along the (d) $z$-, (e) $x$-, and (f) $y$-axes. Fading is used to indicate depth.
CHAPTER 7. HYBRID METHODS

Figure 7.7: Schematic drawing of the N-cyclopentyl-DABCO structure directing agent used in the synthesis of SSZ-45.

become time consuming. Structure solution is not always guaranteed, but the results may point in the right direction. With this in mind, its combination with charge-flipping was previously researched extensively in our lab, mainly focusing on the structures of organic materials. By using simulated annealing with known molecular fragments, approximate solutions could be generated and used as a seed for the $pCF$ routine in SUPERFLIP (Šišak Jung, 2013; Šišak Jung et al., 2014). As a structure completion tool, simulated annealing may be used to complete coordination polyhedra (Altomare et al., 2000; Giacovazzo et al., 2002), locate extra-framework species (i.e. Chapter 8), or complete fragments of inorganic materials (this section). In each of these, the search space is reduced by supplying a priori information, and knowing what to look for. When the problem is well-defined, simulated annealing offers a quick and versatile way of determining the location/orientation of the fragment in question from the data directly.

7.3 SSZ-45

SSZ-45 was discovered over a decade ago in a zeolite synthesis screening program that was focused on using diazabicyclooctane (DABCO) derivatives as SDAs (Yuen and Zones, 2000). Earlier experiments had shown that the diquaternary SDA formed by linking two DABCO units with a methylene chain could be used to crystallize the zeolites SSZ-16 (AFX; Zones, 1985; Lobo et al., 1996), SSZ-41 (Zones and Santilli, 1997) or VPI-8 (VET; Yoshikawa et al., 1997), depending on the synthesis parameters used. With the benzyl derivative of the tertiary nitrogen on DABCO, Zones and co-workers discovered the borosilicate SSZ-42 (IFR; Chen et al., 1998). A similar synthesis (ITQ-4) was reported about the same time by the Corma group (Cambor et al., 1997). Continuing this approach, the C5 derivatives, based upon either an iso- or cyclopentyl group (Figure 7.7) were investigated. Using very-high-silica synthesis conditions, the novel phase SSZ-45, with well-formed crystallites (Figure 7.8) was produced (Yuen and Zones, 2000). Samples of SSZ-45 were provided by Stacey Zones at Chevron ETC.

7.3.1 Structure solution

The auto-indexing routine in TOPAS was used to index the XPD data. Although an orthorhombic unit cell ($a = 13.7129 \text{ Å}, b = 35.1924 \text{ Å}, c = 22.1253 \text{ Å}$) was found, some small peaks were not indexed and the space group proved to be
Figure 7.8: Scanning electron micrographs of SSZ-45 showing the platelet morphology of the crystallites.

ambiguous (extinction symbols $F-\cdots$, or $B-\cdots$, or a subgroup). Therefore, intensities were extracted using the Pawley profile-fitting procedure in TOPAS assuming several different space groups. Each of these data sets was then used as input to the $pCF$ algorithm in SUPERFLIP. However, no clear structure emerged. In retrospect, one can see that some features of the maps resemble those of the structure, but they were not sufficiently well defined to allow interpretation. Therefore, the RED technique for collecting three-dimensional single-crystal ED data on tiny crystallites was brought into play in the hope that such data would provide some additional information. All eight RED data sets could be indexed on an $F$-centered orthorhombic unit cell similar to the one found for the XPD pattern. No violations of the $F$-centering condition were observed, so $Fmmm$ was assumed. Reflection intensities were then extracted for each data set using the RED software and the best two of these were merged (53% coverage) for further analysis.

Independently, Dan Xie (Chevron ETC) attempted to solve the structure directly from these data using SUPERFLIP. Although his initial attempts failed, when some non-overlapping reflections from laboratory XPD data were added to the RED data, a layered structure could be discerned. By adding a layer of isolated 4-rings (four tetrahedral SiO$_4$ units, each sharing two O atoms to form a ring) between the layers, a fully connected framework structure could be constructed. The simulated XPD pattern for this model was found to match the experimental one quite well.

At the same time, I applied the zeolite-specific structure solution program FOCUS (Grosse-Kunstleve et al., 1997) to the SSZ-45 synchrotron XPD data. Reflection intensities were extracted assuming the $Fmmm$ symmetry indicated by the RED data, and the best solution proved to be the same as the one derived above.

I was also working on adapting FOCUS to work with ED data (Chapter 5). SSZ-45 proved to be an excellent opportunity to test the modified version of the program (Section 5.4.5). Again, the solution found most frequently was identical to the one found with XPD data. The main difference was that the solutions with RED data were produced in just 80 minutes of CPU time, while those with XPD data required 20 hours. It appears that poor, incomplete single-crystal ED data are better than high-quality XPD data for structure solution with FOCUS. A summary of the two FOCUS runs is given in Table 5.4.
The fact that the same framework structure (Figure 7.10), with 10 Si atoms in the asymmetric unit, was found with three different methods, gave us confidence that it was likely to be correct. Bridging O atoms were added to the model, and then the geometry was optimized using the distance-least-squares program DLS-76 (Baerlocher et al., 1976). The framework structure was later identified as being the same as that reported three years ago for ERS-18 (Zanardi et al., 2011). That structure was solved by Zanardi and co-workers using FOCUS and high-resolution synchrotron XPD data. The framework has now been assigned the code EEI by the Structure Commission of the International Zeolite Association (Baerlocher et al., 2007b).

7.3.2 Structure refinement

Structure refinement of SSZ-45 with the Rietveld method was initiated using the DLS-optimized atomic coordinates with TOPAS. Geometric restraints were applied to all unique bond distances and angles (Table 7.4). To locate the SDA within the pore structure, a model of the organic cation was generated and optimized using the energy minimization routine in Jmol (Hanson, 2010), and then added to the SSZ-45 model as a rigid body. Its approximate position and orientation in the channel system were then found via the simulated-annealing algorithm in TOPAS. In this way, two symmetry-equivalent cations were positioned in each of the long cavities formed by the framework structure. Their locations and orientations were then refined, allowing internal rotation around the C1–N1 bond (Figure 7.7).

In the space group \textit{Fmmm}, two of the 19 O framework atoms lie on a center of symmetry, producing Si–O–Si angles of 180°. By reducing the symmetry to \textit{Fmm2}, the positions of these two O atoms could be refined freely, leading to more favorable Si–O–Si angles and an improved profile fit. The symmetry
reduction also resolved some, but not all, of the disorder of the SDA cations. During the course of the refinement, the SDA seemed to align itself along the mirror plane perpendicular to the short axis, so the rigid body description was changed to a geometrically restrained molecule with C1, N1, C6, and C7 fixed on the mirror plane. This resolved the remaining disorder of the SDA. In the final stages of the refinement, H atoms were added in their geometrically expected positions. The OH\(^{-}\) counter-ions could not be located from the data, but I would expect to find them in the 8-rings along the x-axis. A March-type correction for the anisotropic line broadening (March, 1932) was applied along the [031] direction. The final structure, with 59 non-hydrogen atoms in the asymmetric unit (18 Si, 32 O, 7 C, and 2 N) converged with the agreement values \(R_I = 0.008\) and \(R_{wp} = 0.145\) (\(R_{exp} = 0.038\); Table 7.3). The main differences in the profile fit can be attributed to problems with the description of the peak shape (Figure 7.9).

### 7.3.3 Discussion

The framework structure of SSZ-45 is closely related to those of nonasil (NON; Marler et al., 1986), EU-1 (EUO; Briscoe et al., 1988) and NU-87 (NES; Shannon et al., 1991). This relationship has been described very nicely by Zanardi and co-workers in their description of ERS-18 (Zanardi et al., 2011), so only the SSZ-45 framework structure with its small oval pore opening and large cavity is depicted in Figure 7.10. The pore system consists of one-dimensional 8-ring channels running parallel to the short \(a\)-axis with large side pockets extending along the long \(b\)-axis on both sides of the channel. The framework geometry of SSZ-45 appears to be more regular than that reported for ERS-18. This may be a result of the different synthesis conditions that produced a purer phase in the case of SSZ-45, the effect of using a lower symmetry for the structure refinement, or because the SSZ-45 sample was in its as-synthesized form. The calcination of ERS-18 prior to structure analysis may have caused a reduction in the sample integrity.

The SDAs fit well into the large cavity of SSZ-45 (Figure 7.10b). Unlike the 6-azonia-spiro-[5,5]-undecane (\(C_{10}H_{20}N\)) SDA used in the synthesis of ERS-18, the SSZ-45 SDA has a mirror plane that matches the symmetry of the framework. It is also larger (\(C_{11}H_{21}N_{2}\)) and less symmetric than the ERS-18 SDA. These differences may have allowed the framework structure to form with less strain. This is the second case we are aware of, in which two bulky organic cations have paired up within a zeolite cavity. The other instance is SSZ-52, which also has an elongated cavity with 8-ring openings (Xie et al., 2013). The effective pore opening of the oval 8-ring is only ca. 2.2 Å × 3.9 Å (Figure 7.10d), but the cavity itself is approximately 5.6 Å in diameter and 19.8 Å long. In other words, SSZ-45 has a small pore opening that can discriminate between small molecules, but a large cavity that gives the zeolite a high adsorption capacity.

### 7.3.4 Conclusion

The work on SSZ-45 has now been published in Smeets et al. (2014b), and includes further characterization of the gas adsorption and separation properties. In summary, the high-silica zeolite SSZ-45, synthesized using a DABCO
Figure 7.10: Projections of the structure of SSZ-45 along the (a) $a$-axis, (b) $c$-axis, and (c) $b$-axis showing the framework structure (O atoms omitted for clarity) and the arrangement of the organic SDA cations. One large cavity with its small pore opening has been highlighted in each projection. The top of the cavity in c has been removed to show the diameter of the cavity. (d) Eight-ring pore with the delimiting O atoms and its effective dimensions (O atom radius of 1.35 Å subtracted).
Table 7.3: Crystallographic data for the Rietveld refinement of SSZ-45.

| Composition | \(|(\text{C}_{11}\text{H}_{21}\text{N}_2)\text{s(OH)}_8|\text{Si}_{200}\text{O}_{400}\) |
|-------------|--------------------------------------------------|
| Space group | \(Fmmm\) |
| \(a\) (Å)   | 13.7195(1) |
| \(b\) (Å)   | 35.2249(6) |
| \(c\) (Å)   | 22.1362(1) |
| \(V\) (Å³)  | 10697.5(2) |
| \(Z\)       | 6 |
| \(\rho\) (g/cm³) | 2.09047(4) |
| \(\lambda\) (Å) | 0.99822(1) |
| \(2\theta\) (°) | 3.0 to 55.0 |
| Observations | 13479 |
| Reflections  | 1273 |
| \(R_I\)     | 0.008 |
| \(R_{wp}\)  | 0.145 |
| \(R_{exp}\) | 0.038 |
| \(GoF\)     | 3.82 |
| Parameters   | 214 |
| Restraints   | 277 |

Table 7.4: Selected bond distances and angles for SSZ-45 (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>min.</th>
<th>max.</th>
<th>avg.</th>
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</thead>
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<td>(\text{Si-O})</td>
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<td>1.633</td>
<td>1.602</td>
</tr>
<tr>
<td>(\text{O-Si-O})</td>
<td>103.7</td>
<td>113.9</td>
<td>109.4</td>
</tr>
<tr>
<td>(\text{Si-O-Si})</td>
<td>132.4</td>
<td>179.9</td>
<td>155.0</td>
</tr>
</tbody>
</table>

derivative as the SDA, exhibits excellent thermal stability and unusual adsorption properties that might be put to use in small molecule separation processes. Elucidation of its complex framework structure, with 18 Si atoms in the asymmetric unit, was approached in three different ways, using both XPD and RED data. Of particular note is the evident power of combining even poor RED data with the zeolite-specific structure solution program FOCUS. The framework structure proved to have the same topology as ERS-18 (Zanardi et al., 2011), but in the case of SSZ-45, the geometry of the framework is less strained, and it was possible to locate the SDA within the pores and refine its position. Access to the large 19.6 Å × 5.6 Å cavity is limited by small oval 8-rings, and this makes the zeolite an attractive one for small molecule separations.

7.4 SSZ-61

In this section, I describe the structure solution of high-silica SSZ-61, which was synthesized using a particularly bulky polycyclic SDA (Figure 7.11) with relative dilute conditions using fluoride rather than hydroxide as the mineralizer. With the fluoride route, high reactant concentrations tend to produce multidimensional channel systems, because the Si-F interaction is significant. In more dilute systems, where the structure directing influence of the fluoride is diminished, one-dimensional channel systems and higher framework densities are favored (Zones et al., 2007). It is under the latter conditions that a new material, SSZ-61, was discovered (Zones and Elomari, 2005; Zones et al., 2005).

A significant amount of effort had already gone into the solution of the structure of calcined SSZ-61 by Dan Xie (Chevron ETC), Wei Wan, and Xiaodong
Zou (both Stockholm University) before I became involved. They had come up with a model that made sense given the HRTEM data, but refinement against the XPD data did not converge. Their efforts proved to be instrumental in solving the structure of SSZ-61, and have therefore been summarized in Section 7.4.2. To allow us to try to obtain better quality XPD data, Stacey Zones (Chevron ETC) provided us with fresh samples of as-synthesized and calcined SSZ-61.

### 7.4.1 Experimental details

Synchrotron XPD data were collected on a calcined sample of SSZ-61 using the powder diffractometer on the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, FR (wavelength 0.5012 Å; multiple-analyzer-crystal detector). In a second measurement, data sets were collected on both as-synthesized and calcined samples of SSZ-61 on the MS-Powder beamline at the Swiss Light Source in Villigen, CH (wavelength 1.0000 Å, MYTHEN II detector; Bergamaschi et al., 2010).

HRTEM images of the SSZ-61 sample were taken on a JEOL JEM-2100F transmission electron microscope equipped with a field-emission gun and operated at 200 kV (point resolution 1.9 Å). Because of the needle shape of the crystals, ultra-microtome was used to prepare the TEM samples to obtain projections along the needle ([010]) direction. Through-focus HRTEM image series (each consisting of 20 images) were collected with a focus step of 53.3 Å on a Gatan UltraScan 1000 2k × 2k CCD camera. Defocus values and astigmatism of these image series were determined and compensated for using the software QFocus (Wan et al., 2012a), which is an implementation of the structure projection reconstitution method (Wan et al., 2012b), to obtain structure images with contrast directly interpretable in terms of structure.

RED data were collected from an as-made SSZ-61 crystal on a JEOL JEM-2100LaB₆ microscope operated at 200 kV. A total of 324 ED frames were collected using the RED software (Wan et al., 2013) with a tilt range of −56.92° to 36.51° and a beam tilt step of 0.3°. Data processing was also performed using the RED software.
7.4.2 Early work

Initial attempts to index the pattern collected at ESRF failed, but by using the data in conjunction with electron diffraction data collected along different projections, a C-centered monoclinic unit cell \((a = 25.03 \text{ Å}, b = 5.30 \text{ Å}, c = 19.99 \text{ Å}, \beta = 104.5^\circ)\) could be derived. The short repeat distance along \(b\) indicated that SSZ-61 was likely to have a one-dimensional channel system in that direction, in line with expectations emanating from the synthesis conditions. A further transmission electron microscopy experiment showed that this short axis was aligned with the needle axis of the SSZ-61 crystal. It was also noted that the \(a\)- and \(b\)-parameters were very similar to those of the framework types MTW \((C2/m; a = 25.6 \text{ Å}, b = 5.3 \text{ Å}, c = 12.1 \text{ Å}, \beta = 109.3^\circ)\) and SFN \((C2/m; a = 25.2 \text{ Å}, b = 5.3 \text{ Å}, c = 15.0 \text{ Å}, \beta = 103.9^\circ)\), which are closely related to one another. SFN can be described as a sigma expansion (Shoemaker, 1973) of MTW.

These observations were corroborated by through-focus HRTEM images of SSZ-61 taken along the \([010]\) projection. These images also showed a large elongated pore delimited by 4-, 5-, and 6-rings very clearly (Figure 7.12). Furthermore, intergrowths of a 12-ring structure (possibly MTW-type) could be identified. With this information, it was then possible to construct a framework model for SSZ-61 with the layers common to SFN and MTW connected via pairs of 5-rings to create a dumbbell-shaped 18-ring pore (model A; Figure 7.13). The 5-rings connect down the channel (parallel to the \(b\)-axis) to form triple zigzag chains. Unfortunately, this model contains a significant number of Si atoms that are only two-connected (rather than four-connected), and this is inconsistent with \(^{29}\text{Si}\) MAS-NMR measurements, which revealed the presence of an unusually large percentage of three-connected \((Q^3)\) Si atoms, with a \(Q^3:\text{Q}^4\) ratio of 1:5, but no \(Q^2\) Si atoms.

The early reconstructed HRTEM images showed a faint line of contrast across the ‘waist’ of the channels, which could be due to truncation effects in the imaging, but could also come from the structure. Therefore, model A was modified to include a bridge of two T-atoms across the channels, thereby creating two 12-rings, eliminating the \(Q^2\) Si atoms and forming \(Q^3\) Si atoms (model B; Figure 7.13). The geometry of this model could be optimized with a DLS refinement (Baerlocher et al., 1976), showing it to be intrinsically robust, and the calculated XPD pattern looked promising. However, Rietveld refinement of this model did not converge.

7.4.3 Structure solution

With the hope of obtaining data of higher quality, XPD data were recollected at the SLS synchrotron facility on an as-synthesized sample of SSZ-61. It was at this point that I also became involved in the project. The new data had slightly sharper peaks, and although they were still not of good quality, they were considerably better than those of the calcined material. Testimony to this is the fact that the data could be indexed directly using the auto-indexing procedure in TOPAS, giving a similar cell \((C\text{-centered}; a = 25.2370 \text{ Å}, b = 5.0367 \text{ Å}, c = 19.7500 \text{ Å}, \beta = 106.9^\circ)\).

Unfortunately, Rietveld refinement of model B described above still did not converge. Furthermore, it became apparent that there was not enough space in
Figure 7.12: Images of SSZ-61 reconstructed from a series of through-focus HRTEM images. (a) Lattice averaged image viewed along the channel direction highlighting the connecting rings (yellow) and a possible arrangement (blue) of the 4-, 5-, and 6-rings around the large pore. (b) Images showing an MTW-type intergrowth. Images taken by Wei Wan (Stockholm University).
the 12-ring channels with the terminal O atom protruding into the channel to accommodate the bulky organic SDA (Figure 7.14a), so the model was modified once again. The connection across the channel was removed to allow more space for the SDA, and the problematic Q^2 Si atoms in model A were connected to one another directly in a pairwise fashion along the channel wall (model C; Figure 7.13). In this way, the two-connected Si atoms became three-connected. This adjustment required that the b-axis be doubled, the space group changed to \( P2_1/c \), the number of Si atoms per asymmetric unit increased to 20, and the unit cell axes switched (\( a = 19.8 \, \text{Å}, \, b = 10.1 \, \text{Å}, \, c = 25.2 \, \text{Å}, \, \beta = 106.9^\circ \)).

These arguments can be reinforced by consideration of the shape of the SDA, and the size of the unit cell. The SDA is quite long and bulky, with dimensions of about 7.1 Å × 2.3 Å × 4.2 Å. The only way the SDA can reasonably fit inside the unit cell is with its long axis parallel to the channel direction. In this way, two SDAs can fit side by side in the channel. With the new b-parameter of 10.0 Å, this would leave approximately 2.9 Å between the SDAs along this axis, which is close to the ideal van der Waals distance.

Structure solution using FOCUS with the RED data was also attempted using both the small and large unit cell, with different space groups. With the large unit cell, no solutions could be generated. In case of the small unit cell, it was possible to generate solutions, although none stood out, and the correct solution was never generated. It is worth mentioning that one of the solutions was found to be the same as model B, while another can be described as a double sigma expansion of MTW.

### 7.4.4 Structure refinement

Structure refinement using the Rietveld method in TOPAS was initiated using the DLS coordinates for model C. The background of the diffraction pattern was estimated by eye and subtracted using LINES (Appendix B). It was then adjusted further as necessary during the course of the refinement. Geometric restraints were applied to all unique bond distances and angles, and an approximate scale factor was determined using just the high angle data. A difference electron density map was then generated using all the diffraction data and the idealized framework structure. It was difficult to recognize the bulky SDA in the difference map. There were two faint clouds of electrons, related by the \( 2_1 \) screw axis, in each 18-ring pore, approximately where the SDA cations were expected to be. \(^{13}\)C NMR data confirmed that the SDA had been included intact, so a procedure similar to the one used for SSZ-45 (Section 7.3.2) was followed. That is, a model of the SDA was generated and optimized using the energy minimization routine in Jmol (Hanson, 2010) and added to the structural model as a rigid body. Its approximate position and orientation in the pore system were found by applying the simulated annealing routine in TOPAS. The rigid body was then converted to a flexible model with geometric restraints using bond distances and angles extracted from similar organic molecules found on the CSD (Allen, 2002). The AI_Anti_Bump function in TOPAS was used to keep all atoms of the SDA at least 3.0 Å from framework O atoms to ensure that the SDA retained a chemically sensible position.

Only in the final stages of the refinement, did we notice that no reflections with odd \( k \) (i.e. those requiring the doubled \( b \)-axis) were observed in the three-dimensional RED data, which prompted a re-examination of the structural
Figure 7.13: Structural models for SSZ-61. (a) Model A with Q^2 atoms, (b) model B with two 12-ring channels, and (c) model C with 18-ring dumbbell-shaped channels. In each case, the [010] projection is shown on the left, and the connecting chain down the channel on the right. The triple zigzag chain is shown in green and the different connections are highlighted in orange. Model C proved to be the correct model, and was used for the structure refinement. Bridging O atoms have been omitted for clarity.
A potential source of disorder involving the $Q^3$ Si atoms was found in the way that these Si atoms are linked along the channel in a pairwise fashion. Two pairing arrangements are possible. To model this disorder, four Si and ten O atom positions were split and a second (constrained) position and orientation of the SDA was added to the model. All were assigned occupancies of 0.5. With this model, the profile fit in the 5 to $10^\circ$ 2$\theta$ region improved considerably and refinement converged with $R_F = 0.070$ and $R_{wp} = 0.110$ ($R_{exp} = 0.103$). In the ordered structure, the pairs of $Q^3$ Si atoms in adjacent 18-rings are strictly alternating in an up-down arrangement, but in fact, an up-up or down-down sequence is equally probable. Fortunately, the 18-ring channel is not affected at all by this minor disorder. Crystallographic data are given in Tables 7.5 and 7.6, and the final profile fit is shown in Figure 7.15.
Figure 7.15: Observed (blue), calculated (red) and difference (black) plot for the Rietveld refinement of SSZ-61.

Table 7.5: Crystallographic data for the structure solution and Rietveld refinement of sample SSZ-61.

<table>
<thead>
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<th>Composition</th>
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<tr>
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<tr>
<td>$c$ (Å)</td>
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<tr>
<td>$\beta$ (°)</td>
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<tr>
<td>$V$ (Å³)</td>
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<tr>
<td>$Z$</td>
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<td>$\rho$ (g/cm³)</td>
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<td>$2\theta$ (°)</td>
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<td>Fw. Restraints</td>
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</table>

Table 7.6: Selected bond distances and angles for SSZ-61 (Å, °).

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<td>Si–O–Si</td>
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<td>145</td>
<td>133.9</td>
<td>154.7</td>
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</table>
7.4. SSZ-61

7.4.5 Discussion

The three-dimensional framework structure of SSZ-61 is characterized by large one-dimensional, dumbbell-shaped, 18-ring channels running along the [010] direction (Figure 7.16). Si atoms at the waist of the channel are only three-connected and are bonded to terminal O atoms pointing into the channel. The free distance between these terminal O atoms across the channel is less than 1 Å (assuming an oxygen radius of 1.35 Å). The effective pore openings of the two rings that form the dumbbell (each defined by 11 O atoms) are approximately 5.3 Å × 6.1 Å (Figure 7.16c). Along the [100] direction, the terminal O atoms form what could be viewed as a window between the two halves of the channel, with an effective opening of 6.9 Å × 3.3 Å (Figure 7.16d). The shortest distance between the SDAs in the channel is 3.370 Å (C9A···C16A, C9B···C16B). The framework wraps tightly around the SDA, with minimum distances of 3.074 Å between O27B and C1B, 3.154 Å between O11A and C1A, 3.167 Å between O11B and C13B, and 3.197 Å between O11B and C8B. All other distances between the SDAs and the framework were determined to be over 3.20 Å.

The framework structure is closely related to those of ZSM-12 (MTW; LaPierre et al., 1985) and SSZ-59 (SFN; Burton et al., 2003a). All three have the same layers; they differ only in the connection between these layers. In MTW the layers are connected directly, creating single zigzag chains running down the sides of the 12-ring channel. In SFN the layers are separated by 4-rings, which increases the c-axis by 2.9 Å and creates a 14-ring channel with double zigzag chains. In SSZ-61, the connection is via two 5-rings, extending the axis by 7.7 Å and creating an 18-ring channel with triple zigzag chains. The three chains are linked in an alternating fashion to form a series of 6-rings, and the 6-rings are spanned in turn by an additional Si atom to form two 5-rings, and these Si atoms are linked pairwise to form *mor units on both sides of the chains (Figure 7.13c).

Each half of the 18-ring channel in SSZ-61 contains one SDA cation to give a total of four per unit cell (Figure 7.16). The dumbbell-shaped pore provides room for the bulky part of the SDA, and allows the positively charged N atom to lie near two terminal O atoms. Of the 80 Si atoms per unit cell in SSZ-61, eight are only three-connected, which is less than the thirteen $Q^3$ Si atoms per unit cell expected on the basis of the NMR data. We assume that the additional $Q^3$ Si atoms arise from defects in the material. The fourth bond of these $Q^3$ Si atoms is to a terminal O atom that protrudes into the 18-ring channel. From charge balance considerations, it is likely that four of the eight terminal O atoms are protonated and that the four organic cations compensate for the charge on the other four.

7.4.6 Conclusion

The complete work on SSZ-61 has been published in Smeets et al. (2014a), including details of the synthesis, further description of the disorder, and adsorption experiments. The framework topology has been assigned the code *-SSO by the Structure Commission of the International Zeolite Association. By combining several modern structure analysis techniques with zeolite crystal chemistry, the unusual structure of SSZ-61 could be elucidated. Not only the complex interrupted framework structure with 20 Si atoms in the asymmet-
CHAPTER 7. HYBRID METHODS

Figure 7.16: Framework structure of SSZ-61 showing the 18-ring channels and the location of the SDAs viewed (a) along the channel, and (b) from the side. The terminal O atoms are shown in red and other O atoms have been omitted for clarity. Details of the effective pore openings of (c) the 18-ring and (d) the window across the waist of the 18-ring. All O–O distances shown are in Å and the O radius of 1.35 Å has been subtracted.

SSZ-70 is a molecular sieve that was first prepared as a borosilicate (B-SSZ-70) over 10 years ago at Chevron (Zones and Burton, 2006). By investigating the structure directing effects of 16 imidazolium SDAs, the original synthesis under boron-rich conditions could be modified to produce pure-silica (Si-SSZ-70) and aluminosilicate SSZ-70 (Al-SSZ-70; Archer et al., 2010b). Initial characterization of B-SSZ-70 suggested that its structure may have features similar to
those of MWW-type zeolites SSZ-25 and MCM-22. Because of the commercial importance of MWW-type materials as heterogeneous catalysts, and the fact that it was possible to produce pure-silica and aluminosilicate versions, further investigation into the physicochemical properties and catalytic behavior were performed (Archer et al., 2010a). They concluded that SSZ-70 must be a layered material given the relatively broad XRD peaks and large d-spacing of the first reflection (approximately 26.6 Å). However, to date, all attempts to unravel the structure of SSZ-70 have failed, despite the large amount of data that is now available. The structure of SSZ-70 had been a long standing problem in our group, so naturally, it grabbed my attention. Samples of as-synthesized and calcined B-SSZ-70, Al-SSZ-70, and Si-SSZ-70 were provided by Stacey Zones (Chevron ETC).

7.5.1 Experimental details

Synchrotron XPD data were collected on both an as-synthesized (using fluoride media) and a calcined sample of Si-SSZ-70, each in a rotating 0.3 mm capillary, on the MS-Powder beamline at the Swiss Light Source in Villigen, CH (wavelength 0.708 48 Å, MYTHEN II detector; Bergamaschi et al., 2010). Although diffraction patterns of B-SSZ-70 and Al-SSZ-70 were also collected, there were difficulties initially in obtaining good quality patterns, so the XPD data discussed in this section correspond to those collected on Si-SSZ-70.

7.5.2 Structure solution

Previous work

SSZ-70 crystallizes as hexagonal flakes approximately 50 nm in thickness. The XPD data showed clear signs of disorder, but could still be indexed with an orthorhombic C-centered unit cell (a = 13.876 Å, b = 24.635 Å, c = 53.635 Å; Xie, 2012). Initial attempts to solve the structure of SSZ-70 focused on the as-synthesized version in the orthorhombic setting using Cmmm symmetry, although a hexagonal setting was also considered (a = 13.876 Å, c = 53.635 Å). The structural relationship between SSZ-70 and MWW could be confirmed using HRTEM images, which show a nice fit of the MWW-layers (Figure 7.17b). The images also reveal the irregular stacking of these layers. If the horizontal axis is taken as [100], each layer is shifted by approximately \( \frac{1}{2} \) along this vector with respect to the previous one in a random fashion (Figure 7.17a). The dark layer between the MWW-layers could indicate the presence of additional Si species. Such layers have been observed before in IEZ-Ti-MWW (Ruan, 2008), however, the structure of that material was never determined. Unfortunately, the disorder in SSZ-70 makes structure determination difficult, and although previous work has revealed many details about the material, a structural model remains elusive.

ITQ-1

Nearly all the previous work focused on solving the structure of as-synthesized SSZ-70, which is complicated by two factors: (a) SSZ-70 is disordered, and (b) the interlayer region between the MWW-layers is poorly understood. At the time of writing, no definitive structure of any precursor (including the interlayer
region) to MWW-type materials has been published. On the other hand, materials with MWW-type frameworks are well understood, so a new strategy was devised to take one of these complications out of the equation, and first consider calcined SSZ-70. Surprisingly, the structure of calcined SSZ-70 has not received the same amount of attention as its as-synthesized counterpart. Once the disorder of SSZ-70 is better understood, this information can be extrapolated to the structure of as-synthesized SSZ-70.

ITQ-1P is similar to SSZ-70 in the way that it is a layered precursor to the MWW-type material ITQ-1, which is formed only upon calcination, when the layers condense (Figure 7.18). First, the refinement of the structure of ITQ-1 was published (Camblor et al., 1998a), and in a follow-up study, an attempt was made to determine the species in the interlayer region of the precursor in order to better understand what happens upon calcination, but the results were inconclusive (Njo, 1998).

Published $^{29}$Si MAS-NMR spectra of high-silica ITQ-1P show a very intense and characteristic peak around $-95.0$ ppm. Resonances below $-105$ ppm indi-
cate the presence of $Q^3$ species in the material. However, Camblor et al. showed that upon calcination, this peak disappears completely, and assigned this to the annealing of the sample. Structure refinement against XPD data confirmed that the structure of calcined ITQ-1 is indeed free of defects, and has a three-dimensionally 4-connected framework. In the same study, they claimed that the distribution of $Q^3$ Si defects in ITQ-1P is not random, which was corroborated in the follow-up study by Njo. ITQ-1P is produced using a mixture of two SDAs, hexamethyleneimine (HMI) and $N,N,N$-trimethyl-1-adamantammonium (TMAda). The HMI could be located in the intralayer channels of ITQ-1P, and the TMAda was assigned to residual electron density in pockets of the interlayer region. The $Q^3$ sites were assigned to Si1 (Figure 7.18c), and the best agreement values were obtained with partial occupation (occupancy = 0.5) of the terminal SiOH group ($R_{wp} = 0.277$), or by completely removing it ($R_{wp} = 0.285$). The remaining electron density between the channels was not fully understood, but was tentatively assigned to disordered species of HMI or an additional anionic silicate cluster ($Si_3O_9H_4$), the latter of which was favored on the basis of molecular modeling.

**Structure of calcined SSZ-70**

$^{29}$Si MAS-NMR spectra for SSZ-70 were published as part of a study by Archer et al. (2010a). The spectrum for as-synthesized SSZ-70 looks similar to that of ITQ-1P. The latter has a large resonance peak at $-95.0$ ppm which can be assigned to $Q^3$ and completely disappears after calcination. This peak is also present in as-synthesized SSZ-70, with the key difference that it does not disappear completely upon calcination. Other than that, the similarity between the NMR spectra of the calcined materials is striking.
Table 7.7: Unit cell parameters of the as-synthesized and calcined versions of Si-SSZ-70 and ITQ-1.

<table>
<thead>
<tr>
<th></th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Vol. ($Å^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITQ-1P (as-synth)*</td>
<td>$P6/mmm$</td>
<td>14.2091</td>
<td>27.4877</td>
<td>4806.39</td>
</tr>
<tr>
<td>ITQ-1 (calc)</td>
<td>$P6/mmm$</td>
<td>14.2081</td>
<td>24.9450</td>
<td>4361.00</td>
</tr>
<tr>
<td>SSZ-70 (as-synth)</td>
<td>$P6_3/mmc$</td>
<td>14.2230</td>
<td>53.7860</td>
<td>9422.85</td>
</tr>
<tr>
<td>SSZ-70 (calc)</td>
<td>$P6_3/mmc$</td>
<td>14.2271</td>
<td>49.8061</td>
<td>8730.64</td>
</tr>
</tbody>
</table>

1 Njo, 1998
2 Camblor et al., 1998a

The population of $Q^3$ for as-synthesized SSZ-70 was estimated to be 10.5% based on the intensity of this peak. Considering the MWW-layer in $P6/mmm$ symmetry has 72 Si per cell, this corresponds to approximately 7.3 $Q^3$. Each layer has 4 terminal Si1 ($Q^3$) species. If all of these were removed, this would create four silanol nests giving rise to 12 $Q^3$ ($4 \times 3$ Si2) species per layer (Figure 7.18c). The number found fits in between these two extremes, and is also corroborated by the findings of Njo for ITQ-1P, that Si1 is not necessarily fully occupied. Further assignment of $Q^3$ species is ambiguous. A resonance signal at $-105.2$ ppm could indicate the presence of another 11.5% $Q^3$ species. Twelve terminal Si2 correspond to 18% $Q^3$ species per layer. This falls nicely into the expected range of 10.5 to 22%. However, the part of the NMR spectrum of calcined SSZ-70 below $-105$ ppm is very similar to that of ITQ-1, which was found not to contain any $Q^3$ (confirmed with Rietveld refinement), and zeolites synthesized via the fluoride route are typically defect-free. Therefore, the ambiguous resonance at $-105.2$ ppm is more likely to arise from the presence of $Q^4$ in the MWW-layer.

After calcination, the number of $Q^3$ is reduced to 4.6%, or approximately 3.2 Si per layer. This could indicate that half of the number of silanol nests/terminal SiOH are now used in connecting the MWW-layers, as in ITQ-1. The annealing goes hand-in-hand with a reduction of the $c$-parameter in ITQ-1 by 2.54 Å (Table 7.7). When the organic is removed, the MWW-layers come closer together and connect via an Si1–O1–Si1 bridge. This behavior has been well described in literature for MWW-type materials (Roth and Dorset, 2011). The equivalent contraction of the $c$-parameter in SSZ-70 is approximately 1.99 Å, while the MWW-layer width of 24.903 Å corresponds very well to that found in MWW-type materials (Table 7.7).

With the constraint in mind that half of the terminal Si1 of the MWW-layers atoms need to align with one another, a new model could be proposed (Figure 7.19). In this model, half of the Si1 atoms in one layer align with those of the opposing layer, and the other half point into a cup of the opposing layer. The shift of the coordinates of each hexagonal MWW-layer is described by $x + \frac{1}{3}, y + \frac{2}{3}$ or $x + \frac{2}{3}, y + \frac{1}{3}$ with respect to the neighboring one (Figure 7.20). This model fits perfectly with the disorder observed in the HRTEM images, because there are two possibilities for the layers to arrange themselves, and these can be described as a random ABC stacking sequence. Such disorder is well known, and has been used to describe the structure of hexagonal cobalt (Edwards and Lipson, 1942; Wilson, 1942), for example. Prominent examples of zeolites include the ABC-6 family (e.g. Millward et al., 1985) and the FAU/EMT systems (Treacy et al., 1996).
Figure 7.19: Schematic representation of (a) as-synthesized SSZ-70 and (b) calcined SSZ-70.

Figure 7.20: Schematic representation of the two possible stacking arrangements of the MWW-layers in SSZ-70. The layers can be viewed as a hexagonal grid. Each O atom (O1) acts as a node that can connect to the next layer. Three out of six O atoms of the two neighboring layers are used in making this connection. View along [001].
The program DIFFaX (Treacy et al., 1991) was used to simulate the stacking disorder in calcined SSZ-70. Three identical MWW-layers (A, B, and C) were introduced into the program with a c-parameter (stacking distance) of 24.903 Å and the layer shifts described above. There was no indication in the HRTEM image of AA stacking or of any layer being preferred over the others, so each shift was assumed to have equal probability. In essence, \( A \rightarrow B \) and \( A \rightarrow C \) have equal probabilities \( (P(A \rightarrow B) = P(A \rightarrow C) = 0.5) \), but \( A \rightarrow A \) is forbidden \( (P(A \rightarrow A) = 0) \). The resulting simulated pattern corresponds very well to the observed one, and accurately simulates the observed line broadening (Figure 7.21). The low angle reflections are somewhat overestimated in intensity, probably due to the presence of residual species or sorbed \( \text{H}_2\text{O} \) that are absent in the model. Because Njo found that Si1 was not necessarily fully occupied in ITQ-1P, two additional models were constructed. One with all terminal Si1/O1 included, and one with all terminal Si1/O1 removed, keeping only those required for the connection between the layers. The two simulated diffraction patterns are similar, but the one with the lowest number of Si1/O1 reproduces the observed data a slightly better.

7.5.3 Discussion

Calcined SSZ-70 is highly disordered, and consists of layers similar to those found in MWW. Every layer is shifted by \( (x + \frac{1}{3}, y + \frac{2}{3}) \) or \( (x + \frac{2}{3}, y + \frac{1}{3}) \) with respect to the previous one with a probability of 50% for either shift. The average structure can be described in \( P6_3/mmc \) symmetry with \( a = 14.2271 \) Å and \( c = 49.8061 \) Å as an ABAB stacking of MWW-layers. A model for calcined SSZ-70 with these stacking probabilities results in a diffraction pattern that shows good agreement with the observed data (Figure 7.21). There is a small discrepancy to the left of the broad peak at 4.0°, where the observed data have a shoulder. Although this could come from an MWW-type impurity, other
features related to MWW are not present. Thinking that the shoulder might be linked to a higher probability of $AB \rightarrow A$ than $AB \rightarrow C$, a second simulation was performed varying the probability from true randomness ($P(AB \rightarrow A) = P(AB \rightarrow C) = 0.5$) to true order ($P(AB \rightarrow A) = 1.0, P(AB \rightarrow C) = 0$; essentially ABAB stacking). The shoulder becomes more pronounced when some short-range stacking order of successive layers is introduced into the system (Figure 7.22). The best visual match is given by the pattern calculated with a 60% probability of short-range ordering (i.e. ABA) of the layers (Figure 7.23).

The model for the disorder could then be extrapolated to that of the as-synthesized version, which is likely to have the same stacking disorder. However, a DIFFaX simulation with the same input parameters as for calcined SSZ-70, with the only difference that the layers are spaced 2.0 Å further apart, does not represent the observed diffraction pattern as closely as I had hoped. Comparison with the observed data only shows some similarities (Figure 7.24). The disordered model is missing the SDA, which can be expected to have a significant effect on the diffraction pattern.

A wide variety of layer packing possibilities in the MWW family has been discovered (Roth and Dorset, 2011). However, one with lateral disorder was still missing. Roth and Dorset have classified each type of layer stacking (conventional, layered ordered/disordered, delaminated, swollen/pillared), and they showed how each type can be identified with a few unique features in the low angle region of the XPD patterns. The diffraction pattern of SSZ-70 can be distinguished clearly on the basis of the characteristic broad peak at 4.0° ($d = 10.0$ Å).

### 7.5.4 Conclusion

The structure of calcined SSZ-70 could be solved by considering the information available, and looking at the problem from a different perspective. The work on ITQ-1 proved to be invaluable in understanding the layered nature of SSZ-70,
Figure 7.23: Observed (blue), and calculated (red) pattern generated by DIF-FaX for calcined Si-SSZ-70 with a 60% chance of short-range ordering of the layers.

Figure 7.24: Observed (blue), and calculated (red) pattern generated by DIF-FaX for as-synthesized Si-SSZ-70.
and what happens upon calcination. However, the structure of as-synthesized SSZ-70 remains elusive. Now that a good model for the disorder has been found, perhaps the second complication (the interlayer region) could be tackled in a similar way, by studying an analogous, but ordered precursor to MWW and working the information obtained into the structure of as-synthesized SSZ-70.

7.6 SSZ-87

Zones and Hwang (2011) recently described a new synthesis approach for silica-based zeolites using boric acid and ammonium fluoride to yield an alkali-free synthesis system, in which both boron and fluoride became part of the synthesis product. Two themes that emerged from that study were that products rich in boron could be made, and that the selectivity for the given zeolite product was often different from that of the zeolite synthesized using conventional sodium-borate-based reactions. By combining this new chemistry with a novel SDA (Figure 7.25), the new borosilicate zeolite SSZ-87 was produced (Zones, 2013). The same SDA is also known to produce zeolite ZSM-12 (MTW) in the sodium-borate system.

A useful assessment of a novel zeolite, when the crystal structure has not yet been determined, is the use of the isomerization of n-hexane by the Pd-loaded zeolite as a probe of its shape selectivity. In this test reaction, n-hexane is isomerized to bulkier products like methylpentanes and dimethylbutanes, the latter having the most difficulty in exiting the pores if there are restrictions (Chen et al., 2012). The values obtained for SSZ-87 were found to be very much in line with those typical for 12-ring zeolites. These results were corroborated by Al insertion experiments. Zones et al. (2014) have shown that Al can replace B when B is in a 12-ring or larger, and this substitution worked well for SSZ-87. This created a bit of a puzzle, because the structure solution of SSZ-87 revealed a framework with large cages interconnected by 8- and 10-rings (Smeets et al., 2015c). To better understand what was going on, the structures of calcined, and aluminated SSZ-87 were also analyzed.

In this section, I describe the structure solution of SSZ-87 using a combination of methods, subsequent structure refinement of all three samples, and our efforts to understand the unusual results of the hydroisomerization and Al insertion experiments. Samples were provided by Stacey Zones at Chevron ETC. The published work (Smeets et al., 2015c), includes further details about the synthesis, hydroisomerization, Al insertion, and adsorption experiments, as well as further characterization of the as-synthesized and calcined samples with $^{29}$Si and $^{11}$B solid state MAS-NMR.

7.6.1 Experimental details

Synchrotron X-ray powder diffraction (XPD) data were collected on an as-synthesized sample of SSZ-87 in a 0.3 mm capillary on the MS-Powder beamline at the Swiss Light Source in Villigen, CH (wavelength 1.0000 Å, MYTHEN II detector) in Villigen, CH (Bergamaschi et al., 2010). In later experiments on the same beamline, data were also measured on a calcined sample of SSZ-87 and the same calcined sample subjected to an alumination treatment (wavelength 0.7749 Å). Both samples were allowed to rehydrate in ambient air.
Three-dimensional ED data sets were collected on six different crystals of as-synthesized SSZ-87 using the rotation electron diffraction (RED) technique (Zhang et al., 2010). The RED software was installed on a JEOL 2010 microscope operating at 200 kV, and data were collected over a tilt range of ±50° with a tilt step of 0.2° or 1.0° and an exposure time of 2 s. Relatively large tilt steps had to be used for these measurements (by tilting the sample stage only), because the routines to perform the finer tilts by tilting the electron beam had not yet been implemented. The data used for the structure solution were collected from −44.9° to 53.9° with a tilt step of 1.0° (107 frames). As a result, the RED data were not of optimal quality.

### 7.6.2 As-synthesized SSZ-87

#### Structure solution

The XPD pattern appeared to be of good quality, and could be indexed unambiguously with a monoclinic $C$-centered unit cell (extinction symbol $C1\bar{1}$; $a = 21.21$ Å, $b = 17.84$ Å, $c = 12.30$ Å, $\beta = 124.75°$) using the indexing routine in the program TOPAS. This was followed by intensity extraction using the Pawley profile-fitting routine. Structure determination was attempted in space groups $C2$, $Cm$, and $C2/m$, both with the zeolite-specific structure solution program FOCUS and with the $pCF$ algorithm in SUPERFLIP using optimized input parameters (Šišak et al., 2012), but no interpretable solutions could be identified, presumably because of the high degree (93%) of reflection overlap.

Fortunately, RED data were also available, and even though the data sets were far from ideal, at least reflection overlap would not be an issue. Using the
7.6. SSZ-87

RED software (Wan et al., 2013), each of the six data sets could be indexed with a triclinic cell, but none of these cells were the same, none corresponded to the cell found from the XPD data, and none could be used to index the XPD data. Nonetheless, intensities were extracted for each RED data set and structure solution was attempted using the version of FOCUS modified for ED data (Chapter 5), but no solutions emerged. I was confident that the unit cell found from the XPD data was accurate and that the structure could be solved if the triclinic cells could be transformed into ones that resembled the one obtained from the XPD data. Typically, lattice parameters derived from ED data have an error of up to 1.0%, so the LePage algorithm implemented in the program PLATON (Spek, 2003) was used to search for higher symmetry. After considerable effort and only by using very high tolerances, was it possible to identify an approximately monoclinic \( C \)-centered unit cell (\( a = 21.21 \text{ Å}, \ b = 17.11 \text{ Å}, \ c = 11.96 \text{ Å}, \ \alpha = 90.9^\circ, \ \beta = 125.6^\circ, \ \gamma = 90.3^\circ \)) for one of the six RED data sets.

Although the reflection intensities extracted using this unit cell were only 15% complete (to a \( d \)-spacing of 1.2 Å), structure solution with FOCUS was straightforward. Using the space group \( C2/m \), the two top solutions occurred 218 and 109 times, respectively. A DLS refinement (Baerlocher et al., 1976) showed both to be intrinsically feasible, but a quick refinement using the Rietveld method indicated that the most frequently occurring solution was the correct one. Details of the structure solution are given in Table 7.8.

Structure refinement

Once the correct framework had been identified (Figure 7.26), geometric restraints were applied to all unique bond distances and angles. An approximate scale factor was determined by performing a few cycles of refinement with just the higher angle XPD data, keeping all other parameters fixed. Then a difference electron density map, generated using this scale factor with the whole pattern, revealed an electron cloud in the zeolite pores with the approximate shape of the SDA (Figure 8.2). As for SSZ-45 (Section 7.3.2) and SSZ-61 (Section 7.4.4), an initial model for the SDA was created and optimized using the energy minimization routine in Jmol (Hanson, 2010). The molecule was added to the structural model as a rigid body, and its location and orientation were optimized using the simulated annealing routine in TOPAS. In this process, the SDA settled on a position with four-fold disorder (\( 2/m \)) in the center of the cage. After a few cycles of refinement, it aligned itself along the two-fold axis, so it was placed on the axis, thereby reducing the disorder by a factor of two, and the rigid body description was replaced with a geometrically restrained model. H atoms were added in their geometrically expected positions for the final stages of refinement.

It was not clear from the synthesis procedure which configuration the SDA would adopt, so a quick analysis of a single crystal of the pure material was performed to remove this ambiguity. It was found to cocrystallize with water in space group \( P2_1/n \), with 4 SDA molecules per unit cell (\( a = 9.5974(6) \text{ Å}, \ b = 16.103(2) \text{ Å}, \ c = 14.9912(17) \text{ Å}, \ \beta = 89.746(8)^\circ \)). Although the crystal was small, the data were good enough to determine the configuration of the SDA. It has two-fold symmetry with the terminal isopropyl groups in a cis configuration.

By introducing an anisotropic peak broadening model (Stephens, 1999), the
Figure 7.26: Framework structure of as-synthesized SSZ-87. (a) The ABC-type stacking of the building block given in red, (b) the large $[10^28^46^85^84^8]$ cavity showing the refined position of the SDA and the location of the two T-sites containing B (red: T7, cyan: T8), and (c) the cavity showing the Hirshfeld surface of the SDA (Spackman and Jayatilaka, 2009). Bridging O atoms in parts a and b have been omitted for clarity.
profile fit could be improved significantly. All atomic positions were refined with isotropic displacement parameters and using scattering factors for neutral atoms. The final difference electron density map was essentially featureless. Details of the refinement are given in Table 7.9, and the profile fit is shown in Figure 7.27.

Up to this point, all T-atoms in the SSZ-87 framework structure had been treated as Si atoms. In order to find the B atoms, the T atom positions were redefined as mixed Si/B positions with a total occupancy of 1. Only the positions T7 and T8 refined with a significant amount of B (0.19 and 0.31, respectively, Figure 7.26). All the others refined close to 1 Si and 0 B, so they were reset to 100% Si, and the geometric restraints for T7 and T8 were adjusted to reflect the shorter B–O distance (using a weighted linear combination of 1.48 Å for B–O and 1.61 Å for Si–O). In the final cycles of refinement, the occupancies of these two positions refined to 0.849 Si (0.151 B) and 0.646 Si (0.354 B), respectively.

### 7.6.3 Calcined SSZ-87

The quality of the data of the calcined material proved to be worse than that of the as-synthesized material, showing significant Lorentzian line broadening and less detail at higher 2θ angles. Refinement was initiated in C2/m using the atomic coordinates from as-synthesized SSZ-87, without the SDA. This immediately revealed a few unindexed peaks, which could be indexed by lowering the symmetry to P2/m. However, this reduction in symmetry did not improve the fit and no intensity was calculated for these reflections, so the refinement was continued in C2/m in order to keep the number of parameters as low as possible. The background was subtracted using program LINES (Appendix B), and adjusted during the course of the refinement. A significant amount of electron density was observed inside the channel system. This was assigned to
disordered water and boric acid (B(OH)$_3$; Supplementary information of Smeets et al., 2015c). The electron density was described by placing several O atoms in the channel system and allowing them to move freely during the course of the refinement. A significant improvement in the fit was achieved by accounting for the anisotropic line broadening (Stephens, 1999). The occupancies of all Si sites were refined, but only that for T8 decreased significantly (to 0.623). All others, including T7, remained close to 1.0, and were afterwards fixed at that value. The final structure converged with the agreement values $R_I = 0.038$, $R_{wp} = 0.109$ ($R_{exp} = 0.028$), and a GoF of 3.9. Crystallographic details are given in Table 7.9. The main differences in the profile fit are in the first two peaks (Figure 7.28), both of which have a significant Lorentzian contribution that could not be fit well with a pseudo-Voigt peak shape function. Another large difference at around 15° is caused by a peak shape significantly narrower than could be described fully with the anisotropic line broadening function.

The framework structure closely resembles that of the as-synthesized material. About 10% Q$^3$ Si sites were expected from $^{29}$Si MAS-NMR, as well as some B from $^{11}$B NMR. Unfortunately, it’s not possible to distinguish between partial vacancies or partial B populations from XPD, but it can be said whether Si is the predominant species at a T-site, and this appears to be the case for all T-sites, except for T8.

Effectively, a Si occupancy of 0.623 would lead to about 21% Q$^3$ sites, a lot more than the 10% expected from NMR. The latter would correspond to a Si occupancy of about 0.81. Considering that all other sites are predominantly Si, this site probably contains all the remaining B in the system. Therefore, the distribution of Si, B and vacancy can be estimated to be around 0.5:0.3:0.2. This observation is in accordance with (1) the XPD data of the calcined material (0.62 Si has about the same electron count as 0.5 Si + 0.3 B), (2) $^{11}$B NMR, (3) $^{29}$Si NMR, and (4) the XPD data of the as-synthesized material, which showed high B occupancy on T8.
7.6.4 Aluminated SSZ-87

The quality of the data after alumination appeared to be significantly improved over that collected on the calcined material. Rietveld refinement was started using the previously refined coordinates. There were no indications of a change of symmetry. The background was subtracted using \textit{LINES}, and adjusted during the course of the refinement. In the difference Fourier map, some electron density could be found inside the cages. Although the electron density was not localized enough to be assigned, 5 water molecules were added to the model as \(\text{O}^{2-}\) and refined freely. At no point did the water molecules come closer than 3.5 Å to the framework, but their occupancies were set to 0.5 to avoid impossibly short interatomic distances between symmetrically equivalent water molecules. In the final model, the closest distance between two water molecules is 2.8 Å. The number of electrons in Al and Si is too close for them to be distinguished on the basis of XPD alone. Sometimes Al sites can be determined by comparing T–O distances, because a typical Al–O distance is about 0.13 Å longer than a Si–O one. However, in the case of SSZ-87, the amount of Al is not large enough to make a difference to the average T–O distance. The occupancies of all T-sites were refined anyway, but did not deviate more than 0.05 from 1.0, so they are all assumed to be fully occupied. Peak broadening was once again modeled with an anisotropic model (Stephens, 1999). The final model converged with the agreement values \(R_I = 0.041, R_{wp} = 0.095 (R_{\exp} = 0.015)\), and a \(\text{GoF}\) of 6.5. Crystallographic details are given in Table 7.9. The alumination of SSZ-87 was performed on the same calcined material that contained B atoms and partial vacancies. During the Rietveld refinement all T-sites were modeled as fully occupied Si, indicating that all B were replaced and all vacancies filled after the alumination treatment. The same conclusion follows from elemental analysis (Supplementary information of Smeets \textit{et al.}, 2015c), giving a Si/Al ratio of 40, Si/B of 203, and Al/B of 5, indicating that a small amount of B remained in the framework. The Si/Al ratio is higher than the Si/B ratio of 15 in the calcined material, so some of the B/vacancies must be replaced by Si. In similar experiments, full B to Al conversion can be achieved by using higher Al\(^{3+}\) concentration in acidic conditions (Zones \textit{et al.}, 2014). Surprisingly, the Si/Al ratio corresponds very well with the estimated Si/vacancy distribution found for the calcined material (Si/vacancy ratio of 37.5).

7.6.5 Discussion

The framework structure of SSZ-87 can be viewed as an ordered ABC-type stacking of an \textit{rte} composite building unit surrounded by four \([45^56^4]\) cages to create the framework shown in Figure 7.26a with large \([102^86^85^44^8]\) cavities in between the units (Figure 7.26b). The cavity can be described as a prolate spheroid with free dimensions of 15.34 Å \(\times\) 7.41 Å \(\times\) 7.15 Å and an effective volume of ca. 290 Å\(^3\). The long axis of the cavity is aligned with the [101] direction, and the next cavity is shifted along this vector by half a cavity length in a staircase-like arrangement. Each cavity is connected to the two neighboring ones via shared 10-rings to form straight 10-ring channels running parallel to the \(z\)-axis (Figure 7.30). The effective pore opening for this 10-ring channel is 4.99 Å \(\times\) 5.54 Å. Each cavity is further connected to four more cavities along the [010] direction via shared 8-rings to form a three-dimensional channel system.
The SDA fits the large cavity very well. This is well illustrated by the Hirshfeld surface (Spackman and Jayatilaka, 2009) (Figure 7.26c). The color scheme used on this surface indicates the contact distances to the framework. Where the contacts are about equal to the sum of the van der Waals radii, the surface is colored white, short contacts are highlighted in red, and long ones in blue. The shortest C···O distance is 3.28 Å, between C5 and O13, and is seen as a red spot on the Hirshfeld surface. All other distances are over 3.6 Å. In the refined structure, the cation is disordered over two positions that are related by a mirror plane. That is, it can adopt either position (isopropyl groups pointing up or down) in any given unit cell. The two N atoms carrying the positive charge are located near the ends of the SDA, and these positions are near the location of the T-sites containing B (Figure 7.26b). Furthermore, the total population of B atoms refined to 4.04 per unit cell, which correlates well with the number required to balance the charge of the two doubly charged cations per unit cell.

While the structure analysis of SSZ-87 was in progress, the synthesis and structure of the borosilicate zeolite ITQ-52 (IFW) was reported (Simancas et al., 2014). They were investigating the use of a new family of amino-phosphonium cations as SDAs. Under certain conditions, the 1,4-butanediyl bis[tris(dimethylamino)]phosphonium dication led to the formation of ITQ-52. The framework structure of ITQ-52 was determined using FOCUS on synchrotron XPD data collected on a calcined sample, and is identical to that of SSZ-87. Because the ITQ-52 structure was determined from data collected on a calcined sample, the location of the SDA was not reported, but a comparison of the ITQ-52 and SSZ-87 SDAs shows that the distance between the charged atoms in the two dications is quite similar. The positions of the B atoms in the framework structure of ITQ-52 were not determined, but the B content is comparable to that of SSZ-87, so we expect that the B atoms occupy similar positions in ITQ-52.
Figure 7.30: Projection of the structure of SSZ-87 along [010] showing the arrangement of the large cavities and the SDA. The 10-rings of one channel along the [001] direction have been highlighted in red, and the 8-rings along [010] for one cavity in green. The top layer has been removed to show the cavities more clearly. Bridging O atoms have been omitted for clarity.

Table 7.9: Crystallographic data for the structure solution and Rietveld refinement of sample SSZ-87.

<table>
<thead>
<tr>
<th>Composition</th>
<th>As-synthesized</th>
<th>Calcined</th>
<th>Aluminated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([C\textsubscript{22}H\textsubscript{42}N\textsubscript{2}]\textsubscript{2}[Si\textsubscript{64}O\textsubscript{128}])</td>
<td>([H\textsubscript{2}O])\textsubscript{2}[Si\textsubscript{61}O\textsubscript{128}]</td>
<td>([H\textsubscript{2}O])\textsubscript{2}[Si\textsubscript{64}O\textsubscript{128}]</td>
</tr>
<tr>
<td>Space group</td>
<td>C\textsubscript{2}/m</td>
<td>C\textsubscript{2}/m</td>
<td>C\textsubscript{2}/m</td>
</tr>
<tr>
<td>a (Å)</td>
<td>21.1727(5)</td>
<td>21.2287(9)</td>
<td>21.5314(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.8092(5)</td>
<td>17.8117(7)</td>
<td>18.0366(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.2869(2)</td>
<td>12.3055(4)</td>
<td>12.3918(3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>124.7932(14)</td>
<td>124.759(2)</td>
<td>124.8725(17)</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
<td>3804.69(17)</td>
<td>3822.7(3)</td>
<td>3948.2(2)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>ρ (g/cm\textsuperscript{3})</td>
<td>1.9381(7)</td>
<td>1.841(2)</td>
<td>1.75188(9)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.99990(1)</td>
<td>0.77465(1)</td>
<td>0.77492(1)</td>
</tr>
<tr>
<td>2θ (°)</td>
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<td>2.0 to 38.0</td>
<td>2.5 to 50.3</td>
</tr>
<tr>
<td>Observations</td>
<td>15135</td>
<td>9490</td>
<td>13270</td>
</tr>
<tr>
<td>Reflections</td>
<td>2123</td>
<td>1297</td>
<td>2910</td>
</tr>
<tr>
<td>R\textsubscript{1}</td>
<td>0.037</td>
<td>0.038</td>
<td>0.041</td>
</tr>
<tr>
<td>R\textsubscript{wp}</td>
<td>0.103</td>
<td>0.109</td>
<td>0.095</td>
</tr>
<tr>
<td>R\textsubscript{exp}</td>
<td>0.010</td>
<td>0.028</td>
<td>0.015</td>
</tr>
<tr>
<td>GoF</td>
<td>10.0</td>
<td>3.9</td>
<td>6.5</td>
</tr>
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<td>Parameters</td>
<td>190</td>
<td>116</td>
<td>112</td>
</tr>
<tr>
<td>Restraints</td>
<td>210</td>
<td>107</td>
<td>107</td>
</tr>
</tbody>
</table>
Internal flexibility of SSZ-87

Recent Al insertion experiments showed that Al can replace B when B is in a 12-ring or larger (Zones et al., 2014), but in the case of SSZ-87, although the largest openings are 10-rings, nearly all B atoms are replaced by Al atoms. Surprisingly, hydroisomerization experiments also show characteristics that are much more in line with those found for 12-ring zeolites (Smeets et al., 2015c). This prompted the analyses of the structure of SSZ-87 after calcination, and after Al insertion. In both cases, the structure was found to be very similar to that of the as-synthesized material, and no significant differences in pore diameter could be discerned.

From the NMR data, it is clear that only about half of the B was removed from the SSZ-87 framework upon calcination. By taking the information from the NMR experiments into account in the XPD structure refinement, T8 was found to have a Si:B:vacancy ratio of approximately 0.5:0.3:0.2. This is in line with the B assignment in the structure analysis of the as-synthesized SSZ-87 material. The presence of vacancies might explain why the hydroisomerization and Al insertion results are more indicative of a large pore than an intermediate pore opening.

Structure refinement shows that all T-sites are fully occupied after the Al insertion. Although the distribution of Al in the framework could not be determined, we expect the Al to occupy primarily the T8 and perhaps the T7 sites. In view of the fact that the Si:Al ratio of 40 is higher than the initial Si:B ratio of 15, we suspect that Si is also acting as a ‘healing agent’ during the Al insertion (Jones et al., 2001; Chen and Zones, 2010). The B content of the aluminated material is lower than that of the calcined material, so it appears that Al or Si replace B, whether it was removed from the framework in a previous step or not.

Because the effective pore opening of the 10-ring in SSZ-87 lies within the range of the five other 10-ring zeolites that were examined for comparison in the n-hexane hydroisomerization experiments (ZSM-5, SSZ-32, SSZ-75, TNU-9, and SSZ-25), we thought there must be some kind of intrinsic structural flexibility that allows a large 2,2-dimethylbutane molecule to wriggle its way through the SSZ-87 pores. The unique feature of SSZ-87 is that it consists of large cages delimited by a 14-ring in the middle, interconnected by single 10-ring windows. It may be that, because the 10-rings are single, the O atoms can be displaced more easily, and because the cages are large, a bulky organic molecule can orient itself more freely to wend its way through the restriction. This flexibility is then further enhanced by the presence of defects in the 10-ring. Although both ZSM-5 (MFI) and TNU-9 (TUN) have three-dimensional channel systems with pore openings slightly larger than those of SSZ-87, their 10-ring openings are reinforced by a second 10-ring connected directly to the first, and this significantly reduces the flexibility of the opening. Even if vacancies are present, the reinforcing 10-ring limits their effect on the effective pore opening. SSZ-75 (STI) and SSZ-32 (MTT) both have straight channels with pore openings smaller than those of SSZ-87, and no large pockets or cages. SSZ-25 (MWW) does have large side pockets between the layers, but the pores to access them are elliptical and much smaller than those of SSZ-87.
Table 7.10: Selected bond distances and angles for SSZ-87 (Å,°).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Restraint</th>
<th>min.</th>
<th>max.</th>
<th>avg.</th>
</tr>
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<tbody>
<tr>
<td>As-synthesized</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si–O</td>
<td>1.61</td>
<td>1.562</td>
<td>1.614</td>
<td>1.592</td>
</tr>
<tr>
<td>(Si/B)–O</td>
<td>1.57, 1.59</td>
<td>1.546</td>
<td>1.591</td>
<td>1.568</td>
</tr>
<tr>
<td>O–Si–O</td>
<td>109.5</td>
<td>104.9</td>
<td>112.3</td>
<td>109.4</td>
</tr>
<tr>
<td>O–(Si/B)–O</td>
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<td>107.3</td>
<td>112.0</td>
<td>109.5</td>
</tr>
<tr>
<td>Si–O–Si</td>
<td>145</td>
<td>142.2</td>
<td>165.8</td>
<td>156.6</td>
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<tr>
<td>Si–O–Si/B</td>
<td>145</td>
<td>139.8</td>
<td>148.1</td>
<td>144.3</td>
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<tr>
<td>(Si/B)–O–(Si/B)</td>
<td>145</td>
<td>144.2</td>
<td>147.2</td>
<td>145.7</td>
</tr>
<tr>
<td>Calcined</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si–O</td>
<td>1.61</td>
<td>1.554</td>
<td>1.621</td>
<td>1.591</td>
</tr>
<tr>
<td>O–Si–O</td>
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<td>106.5</td>
<td>111.7</td>
<td>109.5</td>
</tr>
<tr>
<td>Si–O–Si</td>
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<td>136.4</td>
<td>174.8</td>
<td>152.9</td>
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<tr>
<td>Aluminated</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si–O</td>
<td>1.61</td>
<td>1.576</td>
<td>1.637</td>
<td>1.603</td>
</tr>
<tr>
<td>O–Si–O</td>
<td>109.5</td>
<td>107.7</td>
<td>111.3</td>
<td>109.5</td>
</tr>
<tr>
<td>Si–O–Si</td>
<td>145</td>
<td>138.8</td>
<td>170.0</td>
<td>153.3</td>
</tr>
</tbody>
</table>

7.6.6 Conclusion

The structure of SSZ-87 has been solved from a combination of high quality powder diffraction and poor quality rotation electron diffraction data. What makes the structure solution interesting is that the XPD data provided the unit cell and space group symmetry, and was essential for the initial interpretation of the RED data. Typically, the scenario is reversed, and RED data are used to provide the unit cell and space group information that is often ambiguous for XPD data with a high degree of reflection overlap. Although the RED data were only 15% complete, I was amazed to see that FOCUS was able to solve the framework structure in a relatively straightforward manner, and this nicely highlights the power of combining FOCUS with ED data. These results can be rationalized by the fact that by default, FOCUS takes the 200 most intense reflections. In a poor quality measurement, the weak reflections are the ones that are eliminated first. If only strong reflections are observed, these are the ones that FOCUS would use, and even with a missing wedge that spans 180°, the observed reflections are at least somewhat representative. This is the second example in which low quality RED data proved to be better suited for structure solution using FOCUS than high quality XPD data, the other one being SSZ-45. The framework topology of SSZ-87 was found to be the same as that of ITQ-52, but for SSZ-87 it was possible to locate the SDA within the cage, as well as the positions of the B atoms in the framework. The location of the B atoms could be confirmed by a further structure analysis of a calcined sample. In view of the results of hydroisomerization and Al insertion experiments, the pore system of SSZ-87 appears to be somewhat more flexible in its calcined form than other high-silica zeolites with 10-ring channel systems. This flexibility might be a result of the fact that the 10-rings in SSZ-87 are single ones that connect very large cages coupled with the presence of vacancies in some of these 10-rings. The result is a zeolite with characteristics that are intermediate between those of 10- and 12-ring pore zeolites.
Table 7.11: Summary of the structure solutions described in this chapter.

<table>
<thead>
<tr>
<th>Material</th>
<th>XPD</th>
<th>ED</th>
<th>HRTEM</th>
<th>NMR</th>
<th>FOCUS</th>
<th>MB</th>
<th>CF</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-L</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>[Mo$_4$O$_9$(pzpy)]$_n$</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>C</td>
</tr>
<tr>
<td>H1</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>H2</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>ZrPOF-Epy</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>C</td>
</tr>
<tr>
<td>SSZ-45</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>C</td>
</tr>
<tr>
<td>SSZ-61</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>C</td>
</tr>
<tr>
<td>SSZ-70</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>C</td>
</tr>
<tr>
<td>SSZ-87</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>ISC</td>
<td>S</td>
<td>S</td>
<td>C</td>
</tr>
</tbody>
</table>

I: indexing; S: structure solution; C: structure completion; MB: Model building; CF: charge-flipping; SA: simulated annealing

7.7 Conclusion

The three main stumbling blocks when trying to characterize a new polycrystalline material are finding the unit cell and space group (indexing), structure solution, and structure completion. Each of these can be overcome in different ways, and the best avenue to overcome them is not always the most obvious. With the aim of bringing some order to the work described in this chapter, the structure solutions of the materials have been summarized in Table 7.11.

It appears that XPD data by itself is often enough to find the unit cell of a pure and ordered material, and to complete the structure. Simulated annealing was found to be useful for the latter in all cases. For structure solution, a division can be made between inorganic materials with heavy scatters, all of whose structures could be solved using charge-flipping (sometimes in combination with simulated annealing), and zeolites, for which more creative solutions were required.

The structure of SSZ-45 could probably have been solved on the basis of the XPD data alone. In fact, the structure of calcined ERS-18 was solved using FOCUS with synchrotron XPD data (Zanardi et al., 2011). Similarly, the structure of calcined ITQ-52 was solved by using the XPD data (Simancas et al., 2014), which is slightly unsettling, although the authors did not specify the details of the structure solution process. On the other hand, initial efforts to solve the structure of SSZ-45 focused on the wrong space group, and having the RED data available narrowed down the number of possibilities to just one space group. Furthermore, once difficulties with the data were overcome, the structure solutions of both SSZ-45 and SSZ-87 from ED data were fast and unambiguous.

Model building remains a decisively powerful tool in the belt of the zeolite structural scientist. HRTEM images gave the first hint that SSZ-61 is related to MTW and SFE, and SSZ-70 to MWW, but only by carefully considering the chemistry of the whole system, could their structures be elucidated. This begs the question, what if these materials were not closely related to materials with a known framework? How would they have been solved?

The process of structure solution has been described as a maze in the introduction of Structure Determination from Powder Diffraction Data (David et al., 2002, p. 4). The maze implies that there is a choice to make at every intersection, but also that there is one optimal path to navigate the maze. Sometimes, XPD data by itself does not contain all the information to solve the structure,
and data from other sources should be considered. In these cases, the maze becomes more like a puzzle. The puzzle pieces are chunks of data and methods available. Missing pieces may be filled in by different means, and sometimes, multiple pieces contain the same information. It is up to the scientist to pick the right pieces and put them together in order to reveal the structure.
Chapter 8

Structure completion

8.1 Introduction

A long standing problem in zeolite structural science is that of finding the organic structure-directing agent (SDA) inside the channel system of the zeolite. The tangible connection between the SDA used and the framework formed is of great value to attempt to understand the synthesis process. The first studies in which the SDA could be located surfaced in the late sixties–early seventies, when TMA was located in the cages of two synthetic zeolites using XPD: in sodalite (SOD; cubic; Baerlocher and Meier, 1969) and in Na-P1 (GIS; tetragonal; Baerlocher and Meier, 1970, 1972). The real breakthrough was the location of the TPA molecule in the channel system of ZSM-5 using single-crystal data (Price et al., 1981, 1982), which served as an important model system for studying guest-host relationships in molecular sieves, because it provided detailed coordinates against which theoretical molecular modeling techniques could be validated. Since then, there has been a clear interest in the location of the SDA inside the zeolite framework, as evidenced by the continued efforts to use and improve computational models to predict the host-guest interaction (Burton et al., 2006b) and to direct the synthesis (Pulido et al., 2015).

In a review that appeared twenty years ago, Baerlocher and McCusker (1994) wrote, “It is now taken for granted that the cations of an as-synthesized or of an ion-exchanged zeolite or zeolite-like material can be located with no problem using powder data.” This is not yet the case for organic SDAs. Locating the SDA experimentally is complicated by limitations of the data, such as peak overlap or low resolution, and also by the fact that the symmetry of the SDA is often lower than the symmetry of the framework. For these reasons, the location of the SDA can therefore not be determined on a routine basis, and is often dismissed as just ‘disordered’. To illustrate the scope of the problem, I cataloged the last 100 zeolites published in the zeolite structure database (until July 2015; Baerlocher et al., 2007b) by how the location of the SDA was determined (Figure 8.1). Here, we see that in only about 28% of the cases, was the SDA located from the data directly, using either single-crystal or XPD data. In 15% of the cases, the SDA was not located from the data, but instead estimated using molecular dynamics modeling to find the most optimal location. In other cases, diffraction data on the as-made zeolite were available, but the researchers chose not to determine
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Figure 8.1: Pie chart showing the distribution of methods used to locate the SDA in the last 100 zeolites (until July 2015) published in the IZA database of zeolite structures (Baerlocher et al., 2007b). In only 28% of the structures reported, is the SDA located from the data directly, either via single-crystal methods or Rietveld refinement.

In most cases (36%), however, the problem of locating the SDA was avoided by performing the structure analysis using data collected on a calcined sample. I should note here that not all researchers may be interested in knowing the location of the SDA. However, calcination typically affects sample integrity, which affects the peak shapes (e.g., larger FWHM) and reduces the resolution of the data, so it would be better if the structure refinement were performed including the SDA, to show that the SDA is indeed part of the synthesis, and that all electron density can be explained in a chemically sensible way. Therefore, the motivation for this study was to show that the location of an organic SDA can be determined in a systematic manner.

The location of the SDA is generally determined by careful analysis of the difference maps (e.g., Camblor et al., 1998b; Jordá et al., 2003; Zanardi et al., 2004). By assigning atoms to the density one-by-one, it is possible to determine the location of the SDA. This procedure is typically reserved for cases where single-crystal, or high quality XPD data are available. Others have taken a more pragmatic approach, and used molecular modeling to find an initial location for the SDA, and used this as a starting point for the refinement (Yang et al., 2004; Baerlocher et al., 2008; Xie et al., 2013).

Figure 8.2 shows a comparison of the difference maps of three zeolites with different quality XPD data. The quality of the data is often directly correlated with the quality of the difference map. Not surprisingly, in the case of ZSM-5 with excellent data, the shape of the TPA can be recognized effortlessly,
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Figure 8.2: Comparison of the difference electron density difference maps for (a) ZSM-5 (van Koningsveld et al., 1987), (b) SSZ-87 (Smeets et al., 2014a), and (c) SSZ-61 (Smeets et al., 2015c) in the order of decreasing data quality.

and it was even possible to locate the fluoride ion from the difference map directly. However, despite the quality of the data, individual atoms could not be discerned. SSZ-87 provides a more typical example of what can be expected from a difference map. With some imagination, the general shape of the SDA can be discerned, but the exact location cannot. This example also highlights a common obstacle in locating the SDA from a difference map: the symmetry of the framework is often higher than the symmetry of the SDA, and having an SDA on a site of two-, three-, or four-fold symmetry is not unlikely. SSZ-61 presents the worst case scenario I have come across; initially, the electron density in the channel did not correspond to anything at all. This is because of low data quality (broad peaks, and low resolution), as well as the presence of structural disorder. However, the SDA was confirmed to be intact using elemental analysis. The excellent fit of the SDA within the framework, and the drastic improvement in the profile fit after its inclusion indicate that the location was determined correctly (Section 7.4).

Despite the limitations of the data, or the higher framework symmetry, the location of the SDA can generally be determined from the data directly, provided its composition is known beforehand. Here, I describe an approach using the simulated annealing algorithm in TOPAS that I have found to be effective for locating SDAs in zeolite structures (see also Sections 7.3.2, 7.4.4, and 7.6.2). This approach is simple, and has now been applied in several cases in our group.
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Figure 8.3: Schematic representation of the SDAs used in the syntheses of (a) SSZ-53: \( N,N,N \)-trimethyl-1-(1-phenylcyclopentyl)methanaminium, (b) SSZ-55: 1-(1-(3-fluorophenyl)cyclopentyl)-\( N,N,N \)-trimethylenethanaminium, (c) SSZ-56: 1,1-diethyl-2-methyldecahydroquinolinium, (d) SSZ-58: 1-butyl-1-cyclooctylpyrrolidinium, (e) SSZ-59: 1-methyl-1-(1-phenylcyclopentyl)methyl)piperidinium, and (f) SSZ-60: 1-ethyl-1-(2,4,4-trimethylcyclopentyl)pyrrolidinium.

(Smeets et al., 2014b,a, 2015c,a; Dejoie et al., 2014). Other researchers have used variations of this procedure to locate guest species in porous materials (Porcher et al., 2008; Fyfe et al., 2008; Meilikhov et al., 2010). I was interested to see if it could be applied in a systematic manner, and how the results compare with those obtained from molecular modeling.

For this purpose, samples of the borosilicates SSZ-53 (SFH; Burton et al., 2003a), SSZ-55 (ATS; Wu et al., 2002; Burton et al., 2006a), SSZ-56 (SFS; Elomari et al., 2009), SSZ-58 (SFG; Burton et al., 2003b), SSZ-59 (SFN; Burton et al., 2003a), and SSZ-60 (SSY; Burton and Elomari, 2004), synthesized by Saleh Elomari using the SDAs shown in Figure 8.3, were provided by Stacey Zones (both Chevron ETC). In each case, the structure had been solved originally from powder diffraction data and molecular modeling had been used to simulate the docking of the SDA in the channels of the material.

8.2 Experimental details

Synchrotron XPD data on as-synthesized samples of SSZ-53, SSZ-55, SSZ-56, SSZ-58, SSZ-59, and SSZ-60 in a 0.3 mm capillary were collected at a wavelength of 0.7749 Å with a Mythen II detector on the MS-Powder beamline at the Swiss Light Source in Villigen, CH.
8.3 General strategy

Once the framework structure of a zeolite has been solved, an optimization of the framework geometry should be performed. The simplest way to do this is to use the distance-least-squares algorithm in the program DLS-76, or to set up the distance and angle restraints and perform a penalties_only refinement in TOPAS.

At this point, the background of the diffraction pattern should be removed. Manual background removal is preferred, because of the added control it gives over the sometimes erratic and unreliable nature of fitting a polynomial. To help with this, the program LINES (Appendix B) was developed. Most of the information about the electron density in the channel system is in the low angle data. A reliable estimate for the scale factor can be determined by performing a few cycles of refinement with all parameters fixed using only the high angle data. If the profile fit at the higher $2\theta$ angles is not good, the background should probably be adjusted. Sometimes it is also helpful to refine a global temperature factor for each element, as these can also have a significant impact on the high angle data.

Calculating a difference map with the scale factor obtained with the high-angle data and using the complete $2\theta$ range should show the residual electron density. If an SDA and/or other extra-framework species are present, their approximate locations should be revealed (e.g. Figure 8.4). Difference maps can be visualized using the programs VESTA (Momma and Izumi, 2011) or Chimera (Pettersen et al., 2004).

There are several ways to introduce the SDA molecule into the framework structure. If the structure of the SDA has been determined before, online databases such as the Cambridge structural database (CSD; Allen, 2002) could be consulted to get a starting model. If this is not the case, an approximate model for the molecule can be generated from scratch, and optimized using molecular modeling. This works best for rigid molecules. Chemical editors, such as JSME (Bienfait and Ertl, 2013) or MarvinSketch, allow chemical drawings to be exported to the SMILES syntax (Weininger, 1988). A SMILES string is a convenient way of describing the connectivity of a molecule as a short string that can be read by many different programs. The program Jmol (Hanson, 2010) can be used to load the SMILES string (load $\$SMILES), optimize the geometry of the model using a force field minimization (minimize), and to export the molecule in .xyz format (write molecule.xyz). Alternatively, the program Avogadro (Hanwell et al., 2012) can be used for this purpose. It also allows the user to construct the molecule in three dimensions directly.

It is useful to know that for a rigid body in TOPAS, the first atom in the list is taken as the center of the molecule. The second atom defines the $z$-axis, and the third atom the $xz$-plane. The $x$-axis is in the same direction as the $a$ lattice vector, and $y$ is in the $ab$-plane. By choosing the first three atoms carefully, the placement of the molecule can sometimes be directed by aligning it with a symmetry element. The multi-platform program OpenBabel (O’Boyle et al., 2011) can then be used to convert the .xyz file into a Fenske-Hall z-matrix. Unfortunately, the TOPAS z-matrix syntax is slightly different from the Fenske-Hall one, so a small script to perform the conversion was written.

Once the molecule has been added to the TOPAS input file as a rigid body, the keyword Auto_T(10) tells TOPAS to run the simulated annealing routine
Figure 8.4: Difference maps of SSZ-53 (along $x$), SSZ-55 (along $z$), SSZ-56 (along $z$), SSZ-58 (along $y$), SSZ-59 (along $x$), and SSZ-60 (along $z$) after initial scaling showing the positive differences only. For SSZ-53, SSZ-55, SSZ-59, and SSZ-60, three unit cells are stacked along the channel direction are shown. The surface of the electron clouds is shown in yellow. Where the electron density is cut (i.e. at the cell edges), the color gradient (green to red) corresponds to the electron density. Images were generated using VESTA.
8.4. APPLICATION TO TEST DATA

<table>
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<th>β (°)</th>
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and continue_after_convergence ensures TOPAS repeats the simulated annealing routine until interrupted. All parameters, except the six parameters describing the location and orientation of the SDA, should remain fixed during the global optimization. The occupancy of the SDA can usually be estimated from the location of the electron density cloud in the difference map, but sometimes allowing the global optimization to find a good value is helpful. Sometimes it is worthwhile allowing the scale factor to refine as well, especially if it is difficult to determine otherwise. The peak shape, unit cell, and instrument parameters should be determined beforehand with a Pawley fit and kept fixed during the global optimization, because they will cause it to slow down significantly. In some cases, the AI_Anti_Bump macro can be helpful to push the SDA in the right direction. In general, the simulated annealing procedure should take no longer than 5 minutes to determine a reliable starting position. H atoms are modeled by scaling the occupancy of the parent atom accordingly to account for the additional electron density.

8.4 Application to test data

For each of the samples (Table 8.1), the procedure described above was applied. The structure refinements were initiated using the published framework coordinates, and the initial difference maps after scaling are shown in Figure 8.4. Crystallographic details (including Rietveld refinements) of each material can be found in Table 8.3, and a summary of the framework distances and angles in Table 8.2 at the end of this chapter. The samples can be divided into two groups: those with one-dimensional channel systems (SSZ-53, SSZ-55, SSZ-59, and SSZ-60) and those with two-dimensional channel systems (SSZ-56 and SSZ-58). Starting density maps for each material is shown in Figure 8.4.

To visualize the results, Hirshfeld surface plots (Spackman and Jayatilaka, 2009) were generated using the program CrystalExplorer (Wolff et al., 2012). The color scheme used on these surfaces indicate the contact distances between the SDAs and the framework. Where the contacts are about equal to the sum of the van der Waals radii, the surface is colored white, short contacts are highlighted in red, and long ones in blue. Such plots allow the packing of the SDAs within the pore system of a zeolite to be visualized in a very convenient and intuitive manner.

8.4.1 SSZ-53

The difference map for SSZ-53 (Figure 8.4) revealed a continuous electron density that zigzags along the x-axis. After simulated annealing, the SDA found
its place in a heavily disordered position at the center of the channel on a position with two-fold symmetry (rotation axis along $b$). The occupancy of the SDA refined to 0.33. On a site with two-fold symmetry, this gives 0.66 SDA molecules per channel per unit cell. This indicates that there are approximately two SDAs every three unit cells, and this corresponds with what Burton et al. found in their analyses using molecular modeling. The ends of each SDA are overlapped with its equivalents in the neighboring unit cells, because the length of the molecule is larger than the repeat distance of the unit cell along the channel direction. This complicates finding a reasonable location for the SDA, because combined with a low occupancy of the SDA, any arrangement that approximately fits the electron density cloud will result in a good fit. Therefore, a supercell was constructed stacking three unit cells of SSZ-53 (omitting the SDA) along the $x$-direction. Initially, this operation was performed in $P1$, but the ADDSYM routine in PLATON indicated the framework symmetry of the supercell to be $P2_1/c$, with 144 framework atoms in the asymmetric unit. A

Figure 8.5: Observed (blue), calculated (red) and difference (black) plot for the Rietveld refinement of as-synthesized SSZ-53.

Figure 8.6: View along (a) $c$ and (b) $a$ showing the location of the SDA and its Hirshfeld surface in the one-dimensional channel of as-synthesized SSZ-53.
difference map generated with the expanded cell revealed an electron density map very similar to that found originally. The simulated annealing routine was repeated, this time with two independent molecules. With the reduction in symmetry, the SDAs are no longer disordered, and organize themselves along an apparent $2_1$ screw axis along $x$ in an arrangement that is very similar to the results of molecular modeling. Therefore, the rigid-body model was changed to a restrained one, and both the framework and SDA were refined in the expanded cell. This resulted in a good fit of the pattern ($R_{wp} = 0.118$).

Then, the cell expansion was reversed, taking the positions of the SDAs and placing them on the equivalent positions in the conventional cell. Necessarily, this resulted in disordered, overlapping SDAs with occupancies that refined to approximately $\frac{1}{6}$, so they were fixed at this value. Although the SDAs severely overlapped, their coordinates did not deviate much from their original values, meaning that the orientations found with the supercell are representative. The occupancies of the Si atoms were refined, and only those of Si3 and Si8 refined to values significantly lower than 1.0, so these were redefined as mixed Si/B positions. Their occupancies refined to 0.85 Si (0.15 B) and 0.89 Si (0.11 B), respectively, to give a total B content of 2.4 per 64 T-atoms in the unit cell (Si:B 25.7:1). The anti-bump function was applied between O and C in the final stages of the refinement to maintain reasonable intermolecular distances of over 3.0 Å. Stephens’ model was used to correct the anisotropic line broadening (Stephens, 1999). The final refinement resulted in an excellent fit to the data (Figure 8.5) with agreement values $R_I = 0.036$ and $R_{wp} = 0.088$ ($R_{exp} = 0.019$). For SSZ-53, the shortest intermolecular distances between the SDA and the framework O atoms are 3.023(6) Å, 3.061(5) Å, 3.080(7) Å, and 3.085(5) Å. All other distances are over 3.1 Å.

### 8.4.2 SSZ-55

The refinement of SSZ-55 was started in space group $C222_1$, corresponding to the findings of Burton et al. (2006a). After simulated annealing, the SDA took its place in the center of the channel and its occupancy refined to 0.15. Although this is only approximately equal to $\frac{1}{6}$, on a position of four-fold symmetry, it is close enough to assume approximately two SDAs per three unit cells (as in SSZ-53), and corresponds well to the original structure analysis (Burton et al., 2006a). The channel system runs along $z$, so a supercell was constructed by stacking three unit cells along the same axis. However, it was difficult to find a space group that would allow the inclusion of independent non-overlapping SDAs. Several possibilities ($C222_1$, $C2$, $C21/c$, $Cc$, $P2/c$) were tried, but only with $Cc$ could the optimal arrangement of the SDAs be achieved. Simulated annealing with one independent SDA molecule, led to a position reminiscent of that found in SSZ-53, giving me confidence that it was reasonable. Initially, the occupancy was set to 1.0. As the refinement progressed, the rigid-body model was exchanged for a restrained one, the framework parameters were refined, and the anisotropic line broadening was accounted for (Stephens’ model), but several positive differences remained on the low-angle reflections. To better model these reflection intensities, the occupancy of the SDA was refined and it converged at 0.78.

Once the refinement had converged to give a good fit, the coordinates of the SDA were transformed to the conventional unit cell in space group $C222_1$. The
Figure 8.7: Observed (blue), calculated (red) and difference (black) plot for the Rietveld refinement of as-synthesized SSZ-55.

Figure 8.8: View along $a$ showing the location of the SDA and its Hirshfeld surface in the one-dimensional channel of as-synthesized SSZ-55.

occupancy of the SDA refined to 0.130 or approximately 1.04 SDAs per unit cell. This is different from the structure reported by Burton et al. (2006a), who found $\frac{4}{7}$ SDA molecules per unit cell from elemental analysis. This number corresponds to a full loading of the channels of SSZ-55. Further refinement showed that B atoms preferentially occupy the T1 position (0.86 Si, 0.14 B), giving rise to a total B content of 1.12 per 24 T-atoms in the unit cell (Si:B 20.4:1). The final refinement resulted in a good fit to the data (Figure 8.7) with agreement values $R_I = 0.078$ and $R_{wp} = 0.150$ ($R_{exp} = 0.010$). The major differences are in the peak shapes, which are difficult to model, and there are some broad humps in the pattern that may correspond to residual/amorphous material or diffuse scattering because of disorder. The shortest intermolecular distances between
8.4. APPLICATION TO TEST DATA

Figure 8.9: Observed (blue), calculated (red) and difference (black) plot for the Rietveld refinement of as-synthesized SSZ-56.

Figure 8.10: View along (a) b and (b) c showing the Hirshfeld surface of the SDA and its location at the intersection of the pores of as-synthesized SSZ-56.

the SDA and the framework O atoms are 2.926(3) Å, 2.974(3) Å, 2.975(4) Å, 2.979(4) Å, and 2.995(3) Å. All others distances are over 3.0 Å.

8.4.3 SSZ-56

The refinement was started using the space group $P2_1/m$. Unlike the previous two samples, SSZ-56 has a two- rather than a one-dimensional channel system and the SDA is fairly rigid. This simplifies the procedure. The SDA was located easily using simulated annealing at the intersection between the two channels on a site with two-fold symmetry. The occupancy refined to the maximum expected value of 0.50, so it was fixed at that value. There appeared to be a large void between the SDAs in the channels running along the z-direction. The dimensions of the empty space there are similar to those of the SDA. To
verify whether a second SDA would fit in this space, the simulated annealing algorithm was repeated using two independent SDAs. However, such a model did not converge, and it turned out that an SDA in that location would result in unacceptably short intermolecular contacts.

Anisotropic line broadening was accounted for using Stephens’ model, and this improved the fit significantly. After a few cycles of refinement, the rigid body model for the SDA was dropped in favor of restraints. The T-atoms were redefined as mixed Si/B sites, with a total occupancy of 1.0. Only the B occupancies of T5 (0.092 B, 0.908 Si) and T8 (0.127 B, 0.873 Si) refined to values larger than 0.0. The others were afterwards considered to be pure Si. The total B content was refined to 0.88 per 56 T-atoms in the unit cell (Si:B 62.6:1). The refinement resulted in an excellent fit to the data (Figure 8.9) with agreement values $R_I = 0.053$ and $R_{wp} = 0.103$ ($R_{exp} = 0.014$). For SSZ-56, all short intermolecular distances between the SDA and the framework O atoms are well above 3.4 Å.

8.4.4 SSZ-58

The electron density in the difference map for SSZ-58 (Figure 8.4) shows the location of the SDA in the center of the channel intersection on a position with four-fold multiplicity. As with SSZ-56, a starting position for the SDA could be retrieved easily with the simulated annealing routine. The occupancy of the SDA refined to the expected value of 0.25 and was fixed at that value. In a subsequent difference map, there appeared to be some residual electron density in the channel along $y$, between the SDAs. There was not enough space for another (partially occupied) SDA, so a disordered water molecule with an occupancy of 0.25 was assigned to this position. This made a small, but noticeable improvement to the profile fit. Anisotropic line broadening was described using Stephens’ model. To further improve the fit, the rigid-body model for the SDA was converted to a restrained model, but this appeared to distort the cyclo-octyl group of the SDA somewhat. A quick search of the CSD revealed several 8-rings distorted in the same way, so the refined model was retained. All T-atoms were redefined as mixed Si/B sites with a total occupancy of 1.0. The B occupancy was only significant at sites T2 (0.083 B, 0.917 Si), T7 (0.094 B, 0.906 Si), and T8 (0.058 B, 0.942 Si), giving a total of 1.88 B atoms per 74 T-atoms in the unit cell (Si:B 38.4:1). The final refinement converged with the agreement values $R_I = 0.066$ and $R_{wp} = 0.115$ ($R_{exp} = 0.011$), and a good fit to the data (Figure 8.11). The shortest intermolecular distance between the SDA and the framework O atoms is 3.039(6) Å. All other distances are over 3.1 Å.

8.4.5 SSZ-59

Structure refinement of SSZ-59 was initiated using space group $P\bar{1}$. Simulated annealing was used to find an initial location for the SDA, and it settled on a position with two-fold disorder in the center of the channel. The occupancy of the SDA refined to 0.35 or approximately $\frac{3}{2}$ per channel per unit cell. As for SSZ-53 and SSZ-55, the unit cell was tripled along the channel direction to allow two non-overlapping SDAs to be accommodated. A difference map taken with the expanded unit cell (retaining space group $P1$) looked much nicer than that with
the conventional unit cell. After simulated annealing, the SDAs are arranged in
alternating fashion so that either the piperidinium or benzyl ring of neighboring
molecules are facing one another. Initially, some of the distances between atoms
of the SDA and of the framework and between those of neighboring SDAs were
on the short side (down to 2.6 Å). By carefully increasing the degree of antibump
from 2.6 to 3.1 Å between the C atoms of neighboring SDAs and between the
C and O atoms, these distances could be improved. At this point, framework
restraints were applied and the rigid-body model of the SDA was converted to a
restrained one. While the refinement converged, significant positive differences
were observed for the three strong low-angle reflections. Only by refining the
occupancy of the SDA could these differences be removed. It appears that the
situation in SSZ-59 is similar to that in SSZ-55, as the occupancy refined to
approximately 0.80. Structure refinement of the expanded structure resulted in
a good fit to the data (Rwp = 0.135).

The coordinates of the SDA found in the supercell were transferred to the
conventional unit cell. Stephens’ model was used to correct for the anisotropic

Figure 8.11: Observed (blue), calculated (red) and difference (black) plot for
the Rietveld refinement of as-synthesized SSZ-58.

Figure 8.12: View along (a) c and (b) b showing the Hirshfeld surface of the
SDA and its location at the intersection of the pores of as-synthesized SSZ-58.
Figure 8.13: Observed (blue), calculated (red) and difference (black) plot for the Rietveld refinement of as-synthesized SSZ-59.

Figure 8.14: View along (a) \(c\) and (b) \(a\) showing the location of the SDA and its Hirshfeld surface in the one-dimensional channel of as-synthesized SSZ-59.

Line broadening. For SSZ-59, B is preferentially located on T6 (0.87 Si, 0.13 B) and T7 (0.94 Si, 0.06 B) to give a total of 0.38 B per 16 T-atoms in the unit cell (Si:B 41.1:1). The occupancy of the SDA refined to 0.27 (1.08 SDAs per unit cell), which is approximately in line with the results obtained from the chemical analysis (Burton et al., 2003a). After the refinement converged, a good fit to the data was obtained (Figure 8.13) with agreement values \(R_I = 0.036\) and \(R_{wp} = 0.088\) (\(R_{exp} = 0.019\)). The shortest intermolecular distances between the SDA and the framework O atoms are 3.062(4) Å, 3.076(3) Å, 3.077(2) Å, and 3.079(3) Å. All other distances are over 3.1 Å.

This interpretation deviates from that reported by Burton et al. (2003a), who found (on the basis of molecular modeling simulations and geometric considerations) that the unit cell should be quadrupled to allow for the optimal arrangement of the SDA. There was no evidence from the XPD data alone that indicated a quadrupling of the unit cell was necessary to accommodate the optimal arrangement of the SDAs. Instead, a doubling of the unit cell along the channel direction was attempted (\(P1\)), which is in line with the number of SDAs per channel per conventional unit cell (\(\frac{1}{2}\)) found by Burton et al. In this way, it was possible to find a reasonable position for the SDA in the center of the channel, but its occupancy refined to approximately 0.65, which is more than would
be possible on a position with two-fold multiplicity. Therefore, even though this situation also results in a good fit to the data, the denser packing of the SDA enabled by tripling the unit cell is more likely.

8.4.6 SSZ-60

The data collected on SSZ-60 (Figure 8.15) are noticeably worse than those obtained for the other materials, but also than those reported in Burton and Elomari (2004). The peaks are broader, the noise level is higher, and the signal dies out at a lower 2θ angle. Although the difference map clearly reveals residual electron density inside the one-dimensional channel system (Figure 8.4), it proved to be very difficult to find a satisfactory position with the simulated annealing algorithm. Several attempts were made, including doubling the unit cell along the channel direction, but nothing resulted in both a good fit to the data and an acceptable arrangement of the SDA. Therefore, in view of the poor quality of the data and the fact that the one-dimensional channel system complicates the process of finding the organic, further study of SSZ-60 was abandoned.

8.5 Comparison with molecular modeling results

In this section, the locations of the SDAs obtained from the XPD data are compared with those obtained with molecular modeling. The atomic coordinates of the energy-optimized locations of the SDAs were not available, so the images showing the orientation of the SDA in the original publications have been reproduced here. Unfortunately, the SDAs in the figures of SSZ-53 and SSZ-59 do not match those used to synthesize the materials presented in this chapter, but for the sake of comparison, I have assumed that their locations in the pores will be at least similar.

For SSZ-56 (Figure 8.16), there is a good agreement in the locations of the SDA as determined with both methods. Although the SDA in the refined structure is necessarily disordered, one of the possibilities shows a very good
match to the locations obtained with molecular modeling.

The SDA in SSZ-58 (Figure 8.17) is also disordered in the refined structure, and has arranged itself along the 10-ring running in the \(x\)-direction. A disordered water molecule fills the space between the SDAs in the 10-ring running parallel to \(z\). This is in stark contrast to the location of the SDA determined with molecular modeling, which is oriented along the \(z\)-axis. Figure 8.17 shows that the octyl ring of the SDA is in approximately the same position as the water molecule found with the XPD data. The water molecule may have some structure-directing role here. It would be interesting to see how the end result would be affected if the water molecule were to be included in the simulations.

SSZ-53, SSZ-55, and SSZ-59 have one-dimensional channel systems, and were grouped together in Figure 8.18. From the Rietveld refinement, I found that the SDAs in these systems have similar arrangements, and follow the corrugations of the one-dimensional channels with the pentyl ring pointing towards the channel wall. For all three, a pair of two SDA molecules in a channel spans three unit cells along the channel direction. This interpretation is similar to those obtained from the simulations of SSZ-53 and SSZ-55. For these two, molecular modeling agrees with the Rietveld refinement on the approximate location of the SDA. For SSZ-59, molecular modeling shows a different arrangement of the SDA. Although the chemical composition of the SDA for SSZ-59 is similar to those used to synthesize SSZ-53 and SSZ-55, it is oriented across the channel. Curiously, the SDA in the published image spans three unit cells. This is in contrast with the rest of the text of Burton et al. (2003a), which states that four unit cells were used.

### 8.6 Conclusion

Assuming that the quality of the XPD data is not a problem, when the SDA is in a cage (SSZ-45, SSZ-87) or at a channel intersection (SSZ-56, SSZ-58, ZSM-5), it is trapped and its location well-defined. This facilitates the global optimization, and makes locating a starting position more straightforward. For these cases, the results presented in this chapter, as well as Chapters 7.3 and 7.6, show that routine analysis of the location of the SDA with XPD data is indeed possible. Independent measurements, such as \(^{13}\text{C}\) NMR and CHN elemental analysis, are necessary to confirm that the SDA is intact and included in the framework. However, zeolites with one-dimensional channel systems and a short \((\sim 5.0^\circ)\) lattice parameter along the channel direction (SSZ-53, SSZ-55, SSZ-59, SSZ-60) proved to be tricky. In their analysis of SSZ-55, Burton et al. (2006a) write: “Given this situation there are only a limited number of possibilities: (i) The measured cell is only a subcell, and the real cell is doubled or tripled in the \(c\)-direction to take account of ordering of the SDA; (ii) The SDA is ordered but is incommensurate with the framework; (iii) The cell is correct, which means that the SDA can show no register between one zeolite channel and the next.” and conclude that (iii) is the most likely option. It is for these samples that I am least confident in the position of the SDA. One of the main assumptions going into these structure refinements is that the framework pores are fully loaded with the SDA (i.e. full occupancy of the SDA is preferred). If it is not possible to assume full occupancy of the SDA, how does one distinguish between the situation of having the SDA molecules more spread out and a denser packing...
8.6. CONCLUSION

Figure 8.16: Comparison of SDA location obtained in (a, b) this study with those from (c, d) molecular modeling for SSZ-56, showing a view along the (a, c) 10-ring and (b, d) 12-ring. (c) and (d) reprinted from Elomari et al. (2009) with permission of Elsevier.

Figure 8.17: Comparison of the SDA location obtained in (b, c, e, f) this study with those from (a, d) molecular modeling for SSZ-58. The SDA was found to be disordered in this study, so two representative orientations are shown. (a) and (d) reprinted (adapted) with permission from Burton et al. (2003b). Copyright (2015) American Chemical Society.
Figure 8.18: Comparison of the SDA locations obtained in (a, c, e) this study with those from (b, d, f) molecular modeling for (a, b) SSZ-53, (c, d) SSZ-55, and (e, f) SSZ-59, showing a view perpendicular to the one-dimensional channel. (e) reprinted (adapted) with permission from Burton et al. (2003a). Copyright (2015) American Chemical Society. (d) and (f) reprinted from Burton et al. (2006a) with permission of John Wiley and Sons.

with lower occupancy (i.e. SSZ-55 and SSZ-59)? Surprisingly, by expanding the unit cell to allow full ordering of the SDA, a credible location of the SDA and a reasonable fit to the data could be obtained.

The Hirshfeld surfaces show that the SDAs generally fit tightly within the channels of the zeolites, with minimum distances of approximately 2.9 to 3.1 Å between the SDA and the O atoms of the framework. This is consistent with what was found for SSZ-45, SSZ-61 and Ge-BEC (Smeets et al., 2015a). In SSZ-87, the minimum distance (> 3.2 Å) was a bit larger. SSZ-58 provides an example where the framework fits rather loosely around the SDA, with a minimum distance of approximately 3.4 Å, indicating that a tight fit of the framework is not required for framework formation.

In some cases (SSZ-53, SSZ-55, SSZ-56), the results from molecular modeling compare well with those obtained from the XPD data. Others (SSZ-58, SSZ-59) show clear differences. In the case of SSZ-58, a reason could be that the model used for the simulation was incomplete. Although for SSZ-60 it was not possible to locate the SDA from the data, the difference map shows corrugations of the electron density similar to that observed for SSZ-53, SSZ-55, and SSZ-59. For each of these, the presence of disorder may leave the location of the SDA
### Table 8.2: Framework bond angles and distances

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<tr>
<td></td>
<td>O–T–O</td>
<td>107.047</td>
<td>111.646</td>
</tr>
<tr>
<td></td>
<td>T–O</td>
<td>1.565</td>
<td>1.620</td>
</tr>
<tr>
<td>SSZ-58</td>
<td>T–O–T</td>
<td>144.740</td>
<td>171.599</td>
</tr>
<tr>
<td></td>
<td>O–T–O</td>
<td>106.847</td>
<td>112.668</td>
</tr>
<tr>
<td></td>
<td>T–O</td>
<td>1.547</td>
<td>1.610</td>
</tr>
<tr>
<td>SSZ-59</td>
<td>T–O–T</td>
<td>133.473</td>
<td>163.659</td>
</tr>
<tr>
<td></td>
<td>O–T–O</td>
<td>108.024</td>
<td>111.330</td>
</tr>
<tr>
<td></td>
<td>T–O</td>
<td>1.596</td>
<td>1.616</td>
</tr>
</tbody>
</table>


open to some interpretation, but the electron density in a difference map shows very clearly where and where not to expect it. This begs the question whether information from a difference map can be incorporated into the molecular modeling procedure to act as an extra restraint and to direct the search for a good location.
Table 8.3: Crystallographic details for the structure refinement of the five zeolite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSZ-53</th>
<th>SSZ-55</th>
<th>SSZ-56</th>
<th>SSZ-58</th>
<th>SSZ-59</th>
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<tr>
<td>Space Group</td>
<td>$C2/c$</td>
<td>$C222_1$</td>
<td>$P2_1/m$</td>
<td>$Pmmn$</td>
<td>$P1$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.99798(3)</td>
<td>12.92118(7)</td>
<td>13.93867(16)</td>
<td>25.1484(2)</td>
<td>5.00329(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>33.7801(3)</td>
<td>21.2154(3)</td>
<td>19.91219(17)</td>
<td>12.51857(13)</td>
<td>12.68314(14)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>21.0997(2)</td>
<td>5.09122(4)</td>
<td>12.32845(11)</td>
<td>12.86784(13)</td>
<td>14.71080(18)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90.7745(9)</td>
<td>106.6953(4)</td>
<td>103.2906(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td></td>
<td></td>
<td></td>
<td>90.8510(19)</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td></td>
<td></td>
<td></td>
<td>100.6346(8)</td>
<td></td>
</tr>
<tr>
<td>$V$ (Å³)</td>
<td>3561.99(5)</td>
<td>1395.64(2)</td>
<td>3277.51(6)</td>
<td>4051.07(7)</td>
<td>891.300(15)</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>$\rho$ (g/cm³)</td>
<td>2.0783(5)</td>
<td>2.0135(9)</td>
<td>1.9358(4)</td>
<td>2.0434(6)</td>
<td>2.0663(6)</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>0.77492(1)</td>
<td>0.77492(1)</td>
<td>0.77492(1)</td>
<td>0.77492(1)</td>
<td>0.77492(1)</td>
</tr>
<tr>
<td>$2\theta$ (°)</td>
<td>2 to 50</td>
<td>2 to 50</td>
<td>2.1 to 50</td>
<td>2.5 to 45</td>
<td>2 to 50</td>
</tr>
<tr>
<td>$R_T$</td>
<td>0.036</td>
<td>0.078</td>
<td>0.053</td>
<td>0.066</td>
<td>0.043</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.088</td>
<td>0.150</td>
<td>0.103</td>
<td>0.115</td>
<td>0.090</td>
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<tr>
<td>$R_{exp}$</td>
<td>0.019</td>
<td>0.010</td>
<td>0.014</td>
<td>0.011</td>
<td>0.014</td>
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<td>GoF</td>
<td>4.71</td>
<td>15.21</td>
<td>7.41</td>
<td>10.31</td>
<td>6.46</td>
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<td>13333</td>
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<td>13310</td>
<td>11805</td>
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<td>97</td>
<td>38</td>
<td>171</td>
<td>146</td>
<td>96</td>
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</table>
Chapter 9

Indexing of broad energy bandpass diffraction data

9.1 Introduction

Thanks to the enormous advances made in structure solution from XPD data (David and Shankland, 2008), the structures of materials whose crystals do not grow large enough for conventional single-crystal analysis can now be determined. Although XPD offers a quick and flexible way of collecting data, reflection overlap becomes a limiting factor for solving complex structures. Indexing can be problematic, the space group is often ambiguous, and structure solution can be difficult.

For those materials that resist solution, data from a single crystal is sometimes required. The development of three-dimensional ED data collection techniques (Kolb et al., 2007; Zhang et al., 2010) has made it possible to collect relatively complete diffraction data on tiny crystallites. A notable number of new crystal structures have now been determined using ED data (Yun et al., 2015). However, several problems remain intractable to these methods. Dynamical scattering cannot be completely avoided, and this affects the accuracy of the diffraction intensities. This may be an obstacle for structure solution, and prevents the structures from being fully refined, although efforts to develop software that take the dynamical scattering theory into account are underway (Palatinus et al., 2015). Furthermore, materials requiring a controlled atmosphere cannot be measured yet, and the electron beam is focused and very intense, so beam sensitive materials disintegrate before a complete data set can be collected.

Another option for collecting data on micro-crystalline materials is to use the Laue diffraction technique. The acquisition time is short, and because a broad polychromatic beam is used, data collection on a few stationary crystals is enough to obtain a complete data set (Cornaby et al., 2010). However, because of the difficulties in the data analysis and the fact that higher order reflections overlap in energy, Laue diffraction as a tool for structure solution and refinement of organic/inorganic crystal structures has not yet found widespread use (Dejoie et al., 2013b).

With the development of X-ray free-electron laser (XFEL) sources, which create ultra-fast X-ray pulses of unprecedented brilliance, a new option for the
CHAPTER 9. INDEXING

structural characterization of other micro-crystalline materials has been realized. By exposing a small crystallite to a single monochromatic femtosecond pulse, a diffraction pattern can be obtained. Although the crystal is destroyed in the process, it is possible to obtain a data set that can be used for structure solution by collecting data sequentially on a large number of randomly oriented crystals (Chapman et al., 2011; Boutet et al., 2012). Most effort in the realm of structure analysis using XFELs has focused on monochromatic beams and macromolecular systems (Barends et al., 2014).

Opportunities for studying micro-crystalline materials will open up when the XFEL currently being constructed in Switzerland (SwissFEL) comes online in 2017 (Patterson et al., 2013). This potential was recognized by Dejoie et al. (2013a), who proposed that the use of the 4%-energy-bandpass, which is unique to SwissFEL, could be exploited for the structural analysis of organic and inorganic materials. These materials are more difficult to analyze with a monochromatic XFEL source, because the diffraction patterns are much sparser than those of macromolecular systems. This complicates indexing and intensity reconstruction. Using a 4%-energy-bandpass beam, more reflections can be recorded per shot, and their measured intensities are also more reliable.

In a follow-up paper (Dejoie et al., 2015), where the expected SwissFEL beam was mimicked at a synchrotron source, we could show that it will be possible to record a diffraction pattern of up to 10 randomly oriented crystals in a single snapshot, to index the resulting reflections, and to extract their intensities reliably. In typical XFEL fashion, the crystals can be expected to be destroyed with each XFEL pulse, but by combining several snapshots, a complete data set can be reconstructed, and crystal structures of materials that are difficult to analyze otherwise will become accessible. Existing methods are ill-suited for indexing such data, so as part of this collaboration, I developed methods to index single-shot patterns of randomly oriented crystals collected with a 4%-energy-bandpass beam. Two different approaches were developed, one that tries to find the orientation matrix by assigning indices to two low angle reflections (Section 9.5, referred to as mono1), and another via a brute-force approach (Section 9.7, referred to as mono2). The implementation of the program is described in Appendix D.

9.2 Broad bandpass beam

There are a few advantages to using a broad bandpass beam for structure analysis. For single-crystal diffraction with a monochromatic beam, only reflections that exactly satisfy Bragg’s law (Eq. 3.1) are in diffracting condition. With a polychromatic beam, the equation can be modified slightly to allow for a range of wavelengths:

$$\lambda_{\text{min}} < 2d \sin \theta < \lambda_{\text{max}}.$$  \hspace{1cm} (9.1)

In general, this means that more reflections will be in diffracting condition, and thus more reflections will be observed. In Figure 9.1, $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$ correspond to the centers of the delimiting Ewald spheres with radii of $1/\lambda_{\text{min}}$ and $1/\lambda_{\text{max}}$, respectively. All the reflections in the shaded region between these circles are in diffracting condition, indicating that eight reflections will be recorded when a broad bandpass beam is used, compared to five in Figure 3.1. A beneficial side-effect of using a polychromatic beam is that reflections in diffracting condition
are also measured completely, as long as they are not near the edge of the Ewald spheres for $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$. With a 4% bandwidth, the effective bandwidth for fully measured reflections is around 3.3% (Dejoie et al., 2013a). Reflections collected in this range are fully recorded, whereas with a monochromatic beam reflections are only measured partially. For conventional single-crystal diffraction, this problem is solved by rotating the crystal in the X-ray or electron beam in small steps, and thereby rotating the reflections through the Ewald sphere. In this way, the diffraction profile can be reconstructed for each reflection (Figure 9.2). For serial snapshot crystallography with a monochromatic beam, where all reflections are partially measured, this problem requires a separate processing step in order to estimate accurate reflection intensities (White et al., 2013). That said, when equivalent reflections are merged simply by taking them from a large number of snapshots, the resulting data set is sufficiently accurate to allow for structure solution and refinement (Boutet et al., 2012).

An experimental setup with a broad bandpass beam thus allows more reflections to be collected than with a monochromatic beam, and has the added benefit that all reflection profiles are measured completely in a single shot. While the 4% bandwidth is wide enough to allow full reflections to be measured, it is also narrow enough to prevent reflections from overlapping in energy, setting it apart from Laue diffraction, where this is a significant limitation.

Figure 9.1: Exaggerated Ewald construction for a single-crystal exposed to a broad bandpass beam. All reflections in the shaded red region are in diffraction condition.
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9.3 Experimental details

As SwissFEL will only become operational in 2017, we were looking for a way to simulate the SwissFEL beam experimentally to collect data that would look like those that will be collected at SwissFEL. Such data were collected by Catherine Dejoie (ETH Zurich) with the help of Philip Pattison on BM01A (Swiss-Norwegian Beamlines, SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (FR) over the course of two experimental sessions. In order to mimic the 4% bandwidth, a conventional single-crystal experiment was performed by rotating the crystal around the $\phi$-axis in $1^\circ$ steps and scanning the monochromator over a 4.6% energy range (average wavelength 0.7150 Å, Pilatus detector) at each step to give 360 patterns. The energy of the bending-magnet synchrotron beam is several orders of magnitude lower than expected for SwissFEL, so relatively large crystals of about 15,000 $\mu$m$^3$ were used. For comparison with the 4% bandwidth data, a conventional monochromatic data set was also collected for each sample.

In this way, data were collected on a sample of the zeolite ZSM-5 (Olson et al., 1981), a hydrated cesium cyanoplatinate (hereafter cesium platinate; Johnson et al., 1977), and the mineral sanidine (Taylor, 1933; Ackermann et al., 2004) to provide a good combination of materials with different unit cells typical for small-molecule and inorganic structures, covering three different crystal systems (Table 9.1). Data on a single crystal of ZSM-5 were collected on two different occasions, and are referred to as ZSM-5 I and ZSM-5 II. To test the capabilities of the algorithms to deal with multiple crystals, two diffraction experiments with 3 and 15 crystals of ZSM-5 dispersed on a MiTeGen MicroMesh grid (Figure 9.3) were also performed.
9.4. THE INDEXING PROBLEM

<table>
<thead>
<tr>
<th></th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>Vol. (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>$Pnma$</td>
<td>20.002</td>
<td>19.899</td>
<td>13.383</td>
<td>5326</td>
<td></td>
</tr>
<tr>
<td>Cs$_2$[Pt(CN)$_4$]·H$_2$O</td>
<td>$P6_5$</td>
<td>9.791</td>
<td>19.510</td>
<td></td>
<td>1619</td>
<td></td>
</tr>
<tr>
<td>Sandine</td>
<td>$C2/m$</td>
<td>8.583</td>
<td>13.008</td>
<td>7.194</td>
<td>721</td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.3: Light microscopy image 15 crystals of ZSM-5 deposited on a 400 µm grid (grid size 20 µm × 20 µm). Image provided by Catherine Dejoie.

9.4 The indexing problem

Our problems with indexing these data were four-fold:

1. An accurate orientation had to be retrieved from a single frame.

2. The data were collected using a 4% energy bandpass, so the wavelength associated with each diffraction spot is indeterminate within that range.

3. Organic/inorganic materials typically have small unit cells, so the number of observations per frame is limited.

4. The orientations of multiple crystals should be determined from a single frame.
No methods for dealing with such data were available. The bandwidth is too broad to be considered monochromatic, yet too narrow to be considered as Laue diffraction data. Two approaches for indexing these data were investigated. One approached the problem from a polychromatic point of view using a modification of an algorithm developed at the Advanced Light Source for indexing Laue micro-diffraction data (program XMAS; Tamura, 2014). Catherine Dejoie used a modified version of this algorithm to index the data, and a summary of her work is included below (Section 9.4.1). The other approaches the problem from a more conventional monochromatic point of view, assuming an average wavelength. It is normally possible to obtain unit cell parameters from an XPD pattern, so this information was used as \textit{a priori} knowledge to index the 4\% bandpass data.

### 9.4.1 Indexing using a Laue approach

Finding orientations of crystals with known cell parameters and crystal structures from a single frame is common practice in the Laue micro-diffraction community (Chung and Ice, 1999; Tamura, 2014). In the modified algorithm implemented in XMAS, the structure is no longer required. The indexing process is started with a user-defined number of the most intense observed reflections and reciprocal lattice vectors calculated up to a user-defined $d_{\text{min}}$. The values are chosen depending on the sample, data quality, and number of crystals measured. The reciprocal lattice vectors corresponding to the observed reflections are normalized to give $q_{\text{norm}}$. Because the angles between the reflections are independent of the wavelength, a pattern-matching algorithm (Van Wamelen \textit{et al.}, 2004) is applied to match the observed angles to those calculated from the cell parameters. First, a pair of $q_{\text{norm}}$ vectors defining an angle is selected (starting from the strongest reflections), and the reflections in the immediate vicinities of these two are identified. The ‘distance criteria’ defining the local environment of the selected pair of vectors has to be chosen carefully to keep the computation time low, without decreasing the indexing success rate. This ‘first neighborhood’ is then compared with the calculated vector pair environments to find a local match. These matches are then ranked according to their GoF, at which point the global match with all observed vectors is examined. The algorithm stops when the first sufficiently good global match (number of indexed peaks) is found. The orientation matrix is then refined, a check for reflections not indexed in the first step is performed, and then the orientation matrix is refined again. If the parameters are properly defined, this nearest-neighbors approach was found to be considerably more efficient and faster than the conventional approach used in most Laue indexing algorithms.

A rudimentary approach to deal with multiple crystals is used. Whenever a first match is identified, the indexed peaks are removed from the original list of measured reflections, and the indexing process is continued with the remaining set.

### 9.4.2 Indexing using existing routines

The 4\% bandpass data are also quite close to being monochromatic, and can be interpreted as such by assuming an average wavelength for each reflection. I examined several well-known methods for determining the crystal orientation, and unit cell parameters from conventional monochromatic data, some of which
9.4. THE INDEXING PROBLEM

are also being used through the CrystFEL or cctbx.xfel programs to index single frames collected on macromolecular materials in XFEL experiments (White et al., 2012; Hattne et al., 2014).

These indexing methods typically work on the reciprocal lattice points, and analyze them for periodicity in order to determine the basis vectors and find the metric and orientation of the unit cell. In XDS (Kabsch, 1988, 1993, 2010), the difference vectors between each reflection and its nearest neighbors are determined and ranked in a histogram. The resulting clusters allow a unique basis to be determined. In DIRAX (Duisenberg, 1992), the normal to three randomly picked reciprocal lattice points are taken, and all remaining points are then projected onto this normal. The problem is then reduced to finding the elementary periods in one-dimensional rows. From the direct vectors obtained in this way, a primitive cell can be reconstructed. Later methods implemented in MOSFLM (Steller et al., 1997; Leslie, 2006), DENZO (Otwinowski and Minor, 1997, 2012), and LABELIT (Sauter et al., 2004) follow similar reasoning, but use a brute-force approach to probe all possible lattice vectors. Row periodicity is then examined using a fast Fourier transform (FFT).

The algorithms described by Duisenberg, Steller et al., and Kabsch were implemented and tested on simulated data of 100 ZSM-5 crystals with different random orientations. These orientations were taken from experimental Laue micro-diffraction data and then used to generate data with the appropriate 4% bandwidth (Dejoie et al., 2013a). On average, 190 reflections per frame were available. The first problem to tackle was where to place the reflections in reciprocal space. Since the wavelength for each reflection is indeterminate, the exact position of a reflection in reciprocal space is not known. Or rather, it is known, but only within a certain degree of error, so it was assumed that using an average wavelength $\lambda_{\text{avg}}$ would be a good approximation.

The Duisenberg routine was applied first with some success, but two problems quickly surfaced. Initially, the idea was to apply the method for ab initio indexing of the data. However, it quickly turned out that, because all reflections lie on a sphere, a single frame simply does not contain enough reflections to obtain three independent base vectors. The IndexFit and LevelFit criteria used by Duisenberg did not prove to be as robust for use with non-monochromatic data. At best, a fit of 30 to 40% of all peaks could be achieved. However, by using the unit cell parameters as a priori information, it was at least possible to identify the correct basis vectors based on their magnitudes. All base vectors generated were checked against a precalculated list of indices and their corresponding $d$-spacings with a 2% tolerance to take the bandwidth into account. The goal was to identify two valid base vectors, and then to compute the corresponding orientation matrix. For ZSM-5, the $a$- and $b$-parameters are very similar, so it is difficult to distinguish them based on the length of the vector alone. However, as long as one vector can be identified, the second one can be assigned an index only if the angles between these base vectors match (at least approximately) the expected angle for these indices. This in turn led to the identification of the second problem. Now that some vectors could be identified, it became clear that not all diffraction patterns contained enough information to unequivocally determine the two independent base vectors required. Only in rare cases could the $h00$, $0k0$, and $00l$ vectors be determined. Sometimes, two were found, but in most cases, none or only one vector was found.

The more sophisticated Steller algorithm did not give any better results,
because the same limitations as for the Duisenberg routine were encountered. The Kabsch algorithm was quickly abandoned as well, because with the 4\% bandpass data, it yielded streaks, rather than clusters as an effect of averaging the wavelength. Given that these problems already arose even with perfect simulated data, with no errors in the reflection positions or any spurious reflections, it became clear that existing methods were ill-suited for indexing single snapshots of organic/inorganic materials taken with broad bandpass radiation. Furthermore, there was no guarantee that these methods would scale well with multiple crystals.

9.5 Orientation matrix search (mono1)

Several key points were taken away from the initial tests described above:

- If the unit cell parameters are known, reciprocal lattice points can be assigned an index within a degree of error equal to $\text{bandwidth}/2$.

- Generating a good solution for the orientation matrix is difficult. However, verifying whether one is correct is a much more straightforward problem, as only a good solution will index the majority of reflections. In computer science this is a typical example of a problem with NP complexity.

- The single-crystal algorithms that were examined all rely on having reciprocal lattice points in straight lines. Assuming $\lambda_{\text{avg}}$ causes reciprocal lattice points to lie on curves, and renders these approaches unsuitable.

- Even if one of the single-crystal approaches would work, there is no guarantee that they would be useful when dealing with frames containing reflections from 5-10 crystals.

It was clear that a completely new approach to deal with these data should be developed. The indexing procedure was split into two parts. The first part entails a search for suitable candidate orientation matrices (current section), and the second the evaluation of each candidate orientation matrix (Section 9.6). To perform the orientation matrix search, the cell parameters were assumed to be known. Therefore, each observed reflection can be assigned a set of pre-calculated indices (those with similar $d$-spacings). A semi-exhaustive search for the orientation matrix can then be performed by trying all combinations of non-collinear spots and their corresponding indices, with the idea that the correct orientation matrix would eventually surface. The angle between the reflections is unaffected by the wavelength, so only pairs of reflections where the angle between the observed reciprocal lattice points approximately matches that of their tentative indices are kept. For each pair, the orientation of the crystal can then be determined. It was later found that this approach resembles the one used nearly 50 years ago (Busing and Levy, 1967; Sparks, 1976), when it was necessary to know the unit cell parameters a priori, as well as the indices of two non-collinear reflections. The indices were often assigned manually, sometimes by trial and error, but once they were assigned, the crystal orientation matrix could be calculated directly from the corresponding reciprocal lattice vectors. The algorithm described in this section is referred to as mono1.
9.5. ORIENTATION MATRIX SEARCH (MONO1)

9.5.1 Mathematical background

If crystals are randomly dispersed on a grid, it is necessary to know the orientation of each crystal with respect to the diffractometer axes before the data can be used. In general, the geometry of the experimental setup is known, so the problem becomes one of finding the relation between the reciprocal lattice points and the Miller indices, which describe the planes in crystal lattices. This relation is defined as:

\[
x = A \cdot h.
\]

(9.2)

where \(A\) is the crystal orientation matrix, \(h\) is the three element vector of integers with the indices of a given observed reflection, and \(x\) gives the coordinates of the reciprocal lattice vector with a length equal to \(d^*\). Then the inverse,

\[
h = x \cdot A^{-1}
\]

(9.3)

relates any point in reciprocal space to its corresponding reciprocal lattice vector. If there is some degree of error in \(x\) (i.e. due to assuming \(\lambda_{\text{avg}}\)), \(h\) will not have perfect integer values. This does not pose a problem if the values are close enough to integer values, because they can be rounded to the next nearest integer, even with a 4% bandwidth (Section 9.6). The orientation matrix can be broken down into two parts:

\[
A = U \cdot O.
\]

(9.4)

where \(U\) is a \(3 \times 3\) unitary matrix describing the orientation of the crystal axes (also called rotation matrix), and \(O\) is the crystal orthogonalization matrix, which describes the conversion between crystal and orthogonal (Cartesian) coordinate systems. \(O\) is defined as:

\[
O = \begin{bmatrix}
  a & b \cos(\gamma) & c \cos(\beta) \\
  0 & b \sin(\gamma) & \frac{c \cos(\alpha) - c \cos(\beta) \cos(\gamma)}{V} \\
  0 & 0 & \frac{a \sin(\gamma)}{V}
\end{bmatrix}.
\]

(9.5)

where \(a, b, c, \alpha, \beta, \gamma\) are the cell parameters, and \(V\) is the unit cell volume (Eq. 9.6). The convention used is with \(x \parallel a, z \parallel c^*, \text{ and } z \parallel y'x\) (Dunitz, 1979).

\[
V = a b c (1 + 2 \cos(\alpha) \cos(\beta) \cos(\gamma) - \cos(\alpha)^2 - \cos(\beta)^2 - \cos(\gamma)^2)^{\frac{1}{2}}.
\]

(9.6)

In order to find the correct orientation matrix \(U\), two reflections need to have their indices assigned correctly. If some point \(x_1\) is assigned index \(h_1\), and another point \(x_2\) is assigned index \(h_2\), \(U\) can be calculated as follows. First of all, the expected position for the reciprocal lattice point \(p\) can be calculated:

\[
p_1 = O^{-1} \cdot h_1,
\]

(9.7)

\[
p_2 = O^{-1} \cdot h_2,
\]

(9.8)

where \(O^{-1}\) is the inverse orthogonalization matrix. Once the coordinates of where the reflections should be are known, the rotation matrices to rotate \(x_1\) to \(p_1\), and \(x_2\) to \(p_2\) can be calculated, for example using the function described by Möller and Hughes (1999), which is here referred to as Rotation. The first rotation matrix \(R_1\) is found by:

\[
R_1 = \text{Rotation}(x_1 \rightarrow p_1),
\]

(9.9)
where \( R_1 \) is the rotation around the normal to the plane defined by \( x \) and \( p \), so that
\[
\begin{align*}
    x'_1 &= R_1 \cdot x_1, \\
    x'_2 &= R_1 \cdot x_2.
\end{align*}
\] (9.10) (9.11)
The second rotation matrix is then defined by:
\[
R_2 = Rotation(x'_2 \rightarrow p_2),
\] (9.12)
making sure that the rotation is one around \( x'_1 \). This prevents \( x'_1 \) from being affected by this rotation. This is done by projecting \( x'_2 \) and \( p_2 \) onto the plane to which \( x'_1 \) is the normal, and then using the angle between \( x'_2 \) and \( p_2 \) to construct the rotation matrix (thus rotating around \( x'_1 \)). The full rotation matrix of the crystal is then given by the combination of the two:
\[
U = R_1 \cdot R_2.
\] (9.13)

### 9.5.2 Assignment of indices

In order to keep computation times low, the search is usually performed using a selection of all observed reflections. The density of reflections in terms of \( d \)-spacing is lower at low 2\( \theta \) angles, and therefore corresponds to a lower number of potential indices. On the other hand, low angle reflections are more easily affected by small errors in the orientation matrix, and have a higher chance of being partially measured. This means that the center of these reflections is more likely to fall outside the delimiting Ewald spheres, and this affects the indexing algorithm. High angle reflections are less prone to these problems, but the number of potential indices for these is much higher, and the computation time for the mono1 increases exponentially with the number of indices to process per reflection. Therefore, the best approach is to take the middle ground, and focus on mid angle reflections. Low angle reflections normally only have a small number of indices (\( \leq 5 \)) that can be assigned so they are easily included without a significant hit on computation time. From the unit cell parameters, a list of unique \( hkl \) indices and their corresponding lattice spacings \( d_{\text{calc}} \) are generated. For the selected observed reflections, \( d_{\text{obs}} \) can be calculated via Bragg’s law (Eq. 3.1), assuming \( \lambda_{\text{avg}} \), with an error equivalent to \( \text{bandwidth}/2 \). Then, for each observed reflection, a list of indices is generated with a \( d_{\text{calc}} \) corresponding to
\[
\begin{align*}
    d_{\text{min}} < d_{\text{calc}} < d_{\text{max}},
\end{align*}
\] (9.14)
where
\[
\begin{align*}
    d_{\text{min}} &= d_{\text{obs}} \times (1 - \text{bandwidth}/2), \\
    d_{\text{max}} &= d_{\text{obs}} \times (1 + \text{bandwidth}/2).
\end{align*}
\] (9.15) (9.16)
Since only two indices need to be correctly assigned in order to generate a valid orientation matrix, all combinations of observed reflections and their list of potential indices should be tried. However, the procedure described in Section 9.5.1 is slow (especially the angle calculations and rotations), so several thresholds can be adjusted to tweak the performance of the algorithm. The
resolution limit, maximum number of reflections to use, and maximum number of indices to assign can be adjusted. Furthermore, for each reflection pair and their corresponding candidate indices, a few checks are performed to minimize the number of orientation matrices to be processed. Reflection pairs for which any of the following is true are eliminated:

- The reciprocal lattice vectors are collinear (2° tolerance).
- The distance between \( x_1 \) and \( x_2 \) does not match the distance between \( p_1 \) and \( p_2 \) (assuming an error margin of ±0.04). This is faster than the angle check in the next point, and acts as a rough indicator of whether the indices and reflections match.
- The angle between \( x_1 \) and \( x_2 \) does not match the distance between \( p_1 \) and \( p_2 \) (assuming a ±0.5° error).

This eliminates a large number of possibilities. All remaining reflection pairs with their assigned reflections are used to calculate valid orientation matrices as described in Section 9.5.1, and are stored as candidate solutions. In a second stage (Section 9.6), all of these are evaluated against the data. Application of the algorithm is discussed in Section 9.8.

### 9.6 Verification of orientation matrices

The second part of the algorithm involves the evaluation of all solutions for the orientation of the crystal. This is necessary, because the approach described above yields a large number of candidate orientations, and only a small number of these will allow a large number of the observed reflections to be indexed.

First, each candidate orientation matrix is used to transform the reciprocal lattice vectors of the measured reflections into their corresponding indices (Eq. 9.3), normally yielding non-integer values. A reflection can be considered indexed if all three indices \( hkl \) are close to integer values, so for each reflection, the algorithm computes the distance between the observed and calculated indices. Each reflection with a distance smaller than \( \text{IndexFit} \) (typically 0.15 works well) is considered to fit the lattice. Thus, \( n_{\text{indexed}} \) is the number of indexed reflections in the pattern for a given orientation matrix, and \( \text{score} \) gives the residual sum of the squared differences of the distances between the observed and calculated indices for the fitted reflections (lower \( \text{score} \) is better).

To keep computation times low, each orientation matrix with \( n_{\text{indexed}} \) below a certain threshold value \( n_{\text{min}} \) is discarded. For each remaining solution, the rotation matrix is optimized against \( \text{score}/n_{\text{indexed}}^2 \) using a least-squares routine (SLSQP routine in SciPy). This refinement step greatly improves the number of indexed peaks, despite the fact that the average (monochromatic wavelength) is still being used. In fact, subsequent refinements of the rotation matrix in a later stage after the wavelength has been assigned, had no noticeable effect on the accuracy of the rotation matrix at all, so the rotation matrix determined after the first refinement is actually the final one.

At this point, the wavelength \( \lambda_i \) is assigned to each reflection \( i \) that fits the orientation matrix. Several ways of doing this were evaluated. The most straightforward was to assume that reflections do not overlap in energy, so just
rounding $h_i$ to the nearest integer will give appropriate indices. Then, $\lambda_i$ can be calculated directly via Bragg’s law. While this allowed for correct index assignment in most cases, the system did not allow any flexibility for cases in which the assignment was wrong. As this happened occasionally, a more sophisticated approach was implemented. Starting with a value for $\lambda_i/\lambda_{avg}$ of 1 for each reflection, using boundary restraints for $\lambda_i$ from $\lambda_{min}$ to $\lambda_{max}$, and applying a penalty to prevent two reflections converging on the same $hkl$ index (similar to using ‘anti-bump’ in a Rietveld refinement), a least-squares routine was applied to optimize the value of $\lambda_i$, but it was found to be unreliable and slow.

In the final implementation, the wavelength for each reflection is recovered by minimizing the distance between the indices of a reflection and its nearest integer equivalent. The range between the minimum $\lambda_{avg}/\lambda_{min}$ and maximum $\lambda_{avg}/\lambda_{max}$ is subdivided into 100 linearly spaced points, and each value multiplied as a scalar value with the reciprocal lattice vector. This is equivalent to changing the wavelength via Bragg’s law. At each value, the differences between each of the indices and the closest integer values are calculated. The value with the lowest sum of the differences determines the wavelength of the reflection. Rounding $h_i$ (calculated with the new $\lambda_i$) is now more likely to correspond to the correct index.

The score and $n_{indexed}$ values for each optimized orientation matrix are calculated again, taking into account the wavelength for each reflection. Again, orientation matrices with $n_{indexed}$ below a second threshold value $n_{min2}$ (typically higher than $n_{min1}$) can be discarded. If no solutions remain at this point (i.e. no optimized solutions pass the $n_{min1}$ criteria), the routine gives up on indexing the current frame and moves on to the next one. Orientation matrices follow the crystal symmetry, so equivalent solutions can be merged according to the Laue symmetry of the space group. This is done by grouping equivalent solutions, and picking the one with the lowest score. If the space group is provided, a check for systematic absences is then performed, and any reflections that are found to be systematically absent are flagged as unindexed, and are no longer considered for the current orientation matrix. Finally, the algorithm checks whether all reflections are assigned uniquely, and re-assigns reflections to a new index where possible. It does so by evaluating the distance of each reflection index to its integer values, keeping the ones that fit best. For the other reflections, the wavelengths are re-assigned, masking the wavelengths corresponding to the indices assigned currently. With only one crystal in the beam, this often means that these reflections then fall outside the IndexFit criteria, and are consequently marked as unindexed.

All remaining independent solutions are then ranked by ascending value of $\text{score}/n_{indexed}^2$. With one crystal in the beam, simply the highest ranked orientation matrix is taken.

### 9.6.1 Multi-crystal indexing

When indexing a frame containing diffraction patterns from multiple crystals, several orientation matrices should be taken into account at the same time. Up to this point, orientation matrices were judged solely by their ability to index as many reflections as possible. When dealing with multiple crystals, there is no single good solution. Instead, the best global solution is found through
9.6. VERIFICATION OF ORIENTATION MATRICES

a combination of several good orientation matrices, each corresponding to a separate crystal. Although some reflections may be indexed accidentally by more than one orientation matrix at once, in general the largest fraction of a set of reflections belongs to just one crystal. Therefore, the goal is to identify the smallest subset of orientation matrices that indexes the largest number of reflections. This problem can be described as a weighted set cover problem (Viswanathan, 2008; Young, 2008), a classic problem in computer science. Given a set \( U \) of \( n \) elements, a collection \( S_1, S_2, \ldots, S_m \) of subsets of \( U \), with weights \( w_i \), find a collection \( C \) of these sets \( S_i \) whose union is equal to \( U \) so that \( \sum_{i \in C} w_i \) is minimized. For multi-crystal indexing, the weight \( w = \frac{\text{score}}{n_{\text{indexed}}} \) was found to be suitable. A slightly modified greedy algorithm that assigns the orientation that indexes the most reflections first was applied. The remaining reflections are then assigned to the orientation that indexes the most of them, as long as it indexes at least \( n_{\text{min}} \) reflections. This process is repeated until the number of expected crystals is satisfied (if known) or until no more orientations fulfill the \( n_{\text{min}} \) criterion.

All remaining reflections are labeled as \textit{unindexed}. Once the best set of orientation matrices that indexes the maximum number of peaks has been determined, the peaks are assigned accordingly. In the first instance, this is done by assigning each peak to its best fitting \textit{hkl} index. When only one crystal is expected, this is all that it does. With multiple crystals, the possibility that two or more spots originating from different crystals are in close proximity also increases. This results in an ambiguity when assigning indices to spots. A check for such collisions is performed for each orientation matrix independently. If, for an orientation matrix, the same index is assigned more than once, only the spot that fits the index best (smallest difference to its integer position) is kept. All other spots are marked as \textit{alien} and are no longer considered for that orientation matrix. This frees up these spots to be reassigned to other orientation matrices. The procedure is repeated until no more collisions occur.

9.6.2 Missed symmetry

The data on ZSM-5 were used to develop the algorithm and for testing purposes. Some additions to the routine had to be made to deal specifically with this material. One of the challenges with ZSM-5 is that the \( a \)- and \( b \)-axes differ by only 0.5%, while the assumed error in the \( d \)-spacings was 2.3%. As a result, in the initial implementations of the routine, although nearly all frames could be indexed, only 60% of those were indexed correctly. The remaining 40% were not entirely wrong, but merely had the \( a \)- and \( b \)-axes swapped in the orientation matrix.

It became clear that whenever both solutions were generated, the correct one tended to have a more favorable \textit{score}, indicating that the correct solution could be determined on a geometrical basis alone. For some reason, the correct approximate orientation matrices were not always generated. This might be a side-effect of assuming \( \lambda_{\text{avg}} \), which affects the direction of the reciprocal lattice vectors, or a result of the order in which vectors are picked initially. Although the correct solution may not be found during the initial orientation matrix search, it can be generated by applying a simple transformation. An option was added to specify a transformation matrix \( T \) to be applied to every orientation matrix generated, before they are merged. In this way, the number of correctly
indexed frames could be increased to over 98%. For ZSM-5, the transformation matrix to swap the $a$- and $b$-axes, while maintaining the right-handedness, is given by:

$$
T = \begin{bmatrix}
0 & -1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & -1
\end{bmatrix}.
$$

(9.17)

9.7 Brute-force approach (mono2)

The brute-force approach (referred to as mono2) came together during the final stages of the development. At this point, the whole mono1 routine had already been developed (9.5) and was found to work very well for ZSM-5, and the goal of being able to index multiple crystals from a single snapshot reliably was achieved. That said, the results for the smaller unit cell materials, sanidine and cesium platinate, were not yet satisfactory, as initially only 25% and 42% of all frames could be indexed, respectively. Indexing results from the Laue routine showed that the majority of these frames could in fact be indexed, indicating that there was room for improvement. Furthermore, mono1 scales poorly with the number of crystals and number of reflections per frame.

In order to overcome these problems, a brute-force routine, that generates roughly equally distributed rotation matrices that cover all possibilities, was implemented. The idea is the same as before, in that only a good solution will index a large number of spots. However, in this case, there is a finite number of solutions to examine, depending only on how finely distributed the crystal orientations are. The orientations generated by mono2 are therefore fully independent of the data.

This routine was inspired by the work of Steller et al. (1997), who sampled all possible directions in reciprocal space and used Fourier analysis to identify a good set of basis vectors. The algorithm presented here is based on the one described in that paper. The rotation matrices are generated in two steps. First, polar coordinates $\psi$, $\phi$ are used to define the primary vector $v_1$. Since XRD patterns are centrosymmetric, regardless of whether the crystal structure itself is centrosymmetric, only half of all crystal orientations need to be sampled. This is done by using:

$$
0 < \psi \leq \pi/2,
$$

(9.18)

$$
0 < \phi \leq 2\pi.
$$

(9.19)

For $\psi$, Steller et al. suggest angular increments of 0.03 rad ($1.7^\circ$). For each value of $\psi$, the increment in $\phi$ is taken to be the closest integral value to $(2\pi\sin \psi)/0.03$. The first rotation matrix $R_1$ is then defined as a rotation from $[1 0 0]$ to $v_1$:

$$
R_1 = Rotation([1 0 0] \rightarrow v_1).
$$

(9.20)

This can be imagined as a crystal with a face pointing in the [1 0 0] direction. By rotating the crystal so the face points in any direction, only a subset of all orientations is probed. To test all possible orientations, at each position the crystal should be rotated around the normal to the face. This is done by defining a second rotation of $\theta$ around $v_1$:

$$
R_2 = RotationMatrix(v_1, \theta)
$$

(9.21)
in the range $0 < \theta \leq 2\pi$. For $\theta$, angular increments of 0.03 rad were also found to be suitable. Eq. 9.13 is then used to generate the full rotation matrix. With increments of 0.03 rad, this approach produces about $1.4 \times 10^6$ rotation matrices, a roughly equally distributed sampling of all possible crystal orientations. On a desktop computer these can be generated in about 1.4 s using a scripting language like Python2.7, or ca. 10 $\mu$s per orientation matrix. Each orientation is then treated as a candidate solution in Section 9.6.

### 9.7.1 Establishing the threshold value for $n_{\text{min1}}$

One of the main difficulties with indexing is to define meaningful values for the thresholds $n_{\text{min1}}$ and $n_{\text{min2}}$, especially when dealing with a large number of frames with a fluctuating number of crystals, incident flux, and scattering power of the crystals. Each of these affects the number of reflections observed and may therefore influence the number of ‘accidentally’ indexed reflections.

In order to estimate appropriate values, the brute-force algorithm can be exploited to run with large angle increments ($17^\circ$, 0.3 rad) to probe a representative distribution of approximately 1500 orientations. The assumption is that most, if not all, will be incorrect. The mean and standard deviation ($\sigma$) of all corresponding values of $n_{\text{indexed}}$ are calculated. In this way, the approximate number of reflections that can be indexed with incorrect orientations can be estimated for a particular frame (i.e. to get an idea of its ‘noise’ level). A formula for $n_{\text{min1}}$ that works well was found empirically to be $\text{mean} + 3\sigma$. By applying this formula (probe subroutine), the indexing algorithm can adjust to arbitrary variations in the data automatically, and a meaningful $n_{\text{min1}}$ value can be found for each frame pragmatically and reliably. This improves the effectiveness and usability of the routine considerably. The value for $n_{\text{min1}}$ suggested is fairly conservative, but can also be scaled by a user-determined factor. A value for $n_{\text{min2}}$ can be set in a similar way, but is usually less important than that of $n_{\text{min1}}$.

### 9.8 Application to test data

The two algorithms ($\text{mono1}$ and $\text{mono2}$) were evaluated using data collected on the three test samples (Table 9.1. Indexing results are reported in Table 9.2), and are compared with those obtained using the Laue approach ($\text{laue}$).

#### 9.8.1 ZSM-5

First, a typical run for ZSM-5 I is described for both algorithms for a frame with 58 reflections. With $\text{mono1}$, using the 10 reflections with the lowest $2\theta$ angles, 45048 combinations of reflection and index pairs were generated. Most of these could be dismissed immediately, because the expected angles between the indices did not match those between the observed reciprocal space vectors. 1943 (4.3%) remained, and generated valid orientation matrices. After a least-squares refinement of the rotation part of each matrix against all observed spots, and assigning the indices and wavelengths for each of these, only 44 possible solutions were left with $n_{\text{indexed}} > 25$. Duplicate, or symmetry equivalent solutions were merged assuming $Pnma$ symmetry, and this led to two unique possibilities, with
the only difference between them being that the $a$- and $b$-axes were switched. Of these, the first solution had $n_{\text{indexed}} = 55$ and $\text{score} = 0.1517$, while the second had $n_{\text{indexed}} = 52$ and $\text{score} = 0.2671$. The first one, with the lowest $\text{score}$ was picked as the correct solution.

The $\text{mono2}$ routine is a bit simpler. For ZSM-5, crystal symmetry can be used to lower the number of orientations to process. $Pnma$ corresponds to Laue group $mmm$, so the number of crystal orientations to process is reduced by a factor of four to 357052. Each of these is then treated the same way as for $\text{mono1}$. Only 2 solutions with $n_{\text{indexed}} > 25$ were found, differing only in the assignment of the $a$- and $b$-axes. Once again, the rotation matrix was optimized by least-squares refinement, and the indices and wavelengths of all reflections were assigned. Of these, the first solution had $n_{\text{indexed}} = 58$ and $\text{score} = 0.1520$, while the second had $n_{\text{indexed}} = 55$ and $\text{score} = 0.2132$. The first solution with the lower $\text{score}$ was taken as the correct solution.

Not surprisingly, for this particular frame, both routines show nearly identical results, but perhaps it is interesting to note that although $\text{mono2}$ only generates two solutions (as opposed to the 44 with $\text{mono1}$), it indexed 3 more spots than did $\text{mono1}$.

When the $\text{mono1}$ approach is applied to all 360 frames of ZSM-5 $\text{I}$, with on average 44 reflections per frame, 353 frames can be indexed. Since the data collection was performed as a single rotation, solutions could be compared and grouped by simply looking at the base vectors of the orientation matrix. In this way, it could be seen that the correct orientation matrix had been determined in 343 cases. The remaining 10 solutions are false positives, due to swapping of the $a$- and $b$-axes. For 7 frames, no solution could be found. It should be noted that a careful tweaking of the input parameters for these frames could solve this problem. For ZSM-5 $\text{II}$, with only around 26 reflections per frame, 308 solutions were found. 304 of these corresponded to the correct orientations, and 4 solutions had the $a$- and $b$-axes swapped. For the remaining 37 frames, no solution could be found.

With $\text{mono2}$, the number of solutions found is comparable with that of $\text{mono1}$. For ZSM-5 $\text{I}$, 334 solutions were found, 321 of which were correct, and for ZSM-5 $\text{II}$, the numbers are 328 and 321. The only source of error was again the assignment of the $a$- and $b$-axes. For both samples, these solutions are generated in 12 s per frame, which is one order of magnitude slower than $\text{mono1}$.

It is worth mentioning that for ZSM-5, all frames can be analyzed in under 3 min total using $\text{mono1}$, which corresponds to under 0.5 s per frame. This is significantly faster than the $\text{mono2}$ approach (12 s per frame), and the $\text{laue}$ approach (1 to 10 min per frame). The reason for the fast performance of $\text{mono1}$ is the relatively small spot sizes of the reflections. As such, their positions on the detector are well determined, so the angle tolerance can be set very tightly. As a result, a large number of incorrect orientation matrices can be discarded at a very early stage in the routine.

### 9.8.2 Sanidine & cesium platinate

The other two samples, cesium platinate, and sanidine, have significantly smaller unit cells than does ZSM-5, and this means they have significantly lower numbers of 15 and 11 reflections per frame, respectively. Nonetheless, they proved to be...
good samples for testing the routines because of their monoclinic and hexagonal symmetries.

For \textit{mono1}, the lower number of reflections proved to be a limiting factor. The problem was exacerbated by the fact that in both cases the size of the spots was larger than for ZSM-5, making it more difficult to determine their exact positions. \textit{mono1} is very sensitive to small errors in the peak position, because it relies on the angles between these spots to be somewhat accurate in order to generate an orientation matrix. During the orientation matrix search, candidate solutions are judged solely by the number of reflections they index ($n_{\text{indexed}}$). With fewer spots to index, only after a least-squares refinement is $n_{\text{indexed}}$ a good indicator of a good or bad solution. However, performing least-squares refinements on tens of thousands of potential solutions slows the algorithm down significantly. As a result, the indexing for each frame takes approximately 4 to 5 s, \textit{i.e.} ten times longer than for ZSM-5. With the larger number of observed reflections for ZSM-5, this is less of a problem, because there is a higher chance that at least \textit{some} reflections fit an orientation matrix initially, making it easier to differentiate good orientations based on $n_{\text{indexed}}$.

Initially, the resolution limit for sanidine and cesium platinate was set to 2.0 Å. By releasing this limit and allowing all spots to be included in the angle matching step, but increasing the threshold value for $n_{\text{min1}}$ to prevent too many solutions to be refined, the results and computing times greatly improved. For cesium platinate, 266 frames were reported as indexed, and 291 for sanidine. However, any frames with less than 10 reflections indexed were found to be unreliable, and were discarded. The remaining solutions were mostly correct. In the case of cesium platinate, 203 of the 205 solutions were correct, and for sanidine all 105 solutions correctly indexed the reflections. The main point is that the good solutions can be differentiated based on the number of reflections indexed, and the number of false positives in that case is low.

Using the \textit{laue} approach, however, the majority of the frames could be indexed, indicating that the problem is with the algorithm, and not with the data. This initially prompted the development of the \textit{mono2} approach, and it proved to be particularly well suited for these data. Initially, 349 and 353 frames were indexed by setting the value for $n_{\text{min1}}$ manually, but by using the probing algorithm to determine the values, it was possible to index all frames correctly. The $6/m$ Laue symmetry could be exploited to reduce the number of orientations to consider by a factor of four, making it only about 2.5 times slower than \textit{mono1}, but significantly more efficient.

### 9.8.3 Multiple crystals

For the tests with the \textit{mono1} routine on data collected with 3 crystals of ZSM-5 on the grid, the same parameters were used as for one crystal and specifying that 3 crystals were present. In total, 964 orientations were found in 360 frames. 826 of these proved to be correct. Only a single frame did not yield any crystal orientations at all. 124 of the 138 incorrect solutions were due to the misassignment of the $a$- and $b$-axes, despite the fact that the routine described in Section 9.6.2 was applied.

The main problem with trying to index a data set with 15 crystals proved to be finding the right input parameters for the \textit{mono1} routine. Allowing too many reflections caused the search times to increase, but too few limited the
Table 9.2: Results of the indexing tests with the 4% bandwidth data

<table>
<thead>
<tr>
<th>Method</th>
<th>No. generated orientations</th>
<th>No. correct orientations</th>
<th>Time per frame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanidine - ca. 11 refs/frame</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mono1</td>
<td>105</td>
<td>105</td>
<td>5 s</td>
</tr>
<tr>
<td>mono2</td>
<td>349</td>
<td>345</td>
<td>40 s</td>
</tr>
<tr>
<td>mono2 + probe</td>
<td>360</td>
<td>360</td>
<td>40 s</td>
</tr>
<tr>
<td>laue</td>
<td>332</td>
<td>285</td>
<td>1 min</td>
</tr>
<tr>
<td>Cs₂[Pt(CN)₄] - ca. 15 refs/frame</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mono1</td>
<td>205</td>
<td>203</td>
<td>4 s</td>
</tr>
<tr>
<td>mono2</td>
<td>353</td>
<td>353</td>
<td>12 s</td>
</tr>
<tr>
<td>mono2 + probe</td>
<td>361</td>
<td>361</td>
<td>12 s</td>
</tr>
<tr>
<td>laue</td>
<td>360</td>
<td>357</td>
<td>1 min</td>
</tr>
<tr>
<td>ZSM-5 I - ca. 44 refs/frame</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mono1</td>
<td>353</td>
<td>343</td>
<td>0.5 s</td>
</tr>
<tr>
<td>mono2</td>
<td>334</td>
<td>322</td>
<td>12 s</td>
</tr>
<tr>
<td>mono2 + probe</td>
<td>360</td>
<td>352</td>
<td>12 s</td>
</tr>
<tr>
<td>mono2 + mono1 + probe</td>
<td>360</td>
<td>353</td>
<td>20 s</td>
</tr>
<tr>
<td>laue</td>
<td>357</td>
<td>320</td>
<td>5 min</td>
</tr>
<tr>
<td>ZSM-5 II - ca. 26 refs/frame</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mono1</td>
<td>308</td>
<td>304</td>
<td>0.3 s</td>
</tr>
<tr>
<td>mono2</td>
<td>328</td>
<td>322</td>
<td>12 s</td>
</tr>
<tr>
<td>mono2 + probe</td>
<td>359</td>
<td>352</td>
<td>12 s</td>
</tr>
<tr>
<td>mono2 + mono1 + probe</td>
<td>359</td>
<td>355</td>
<td>20 s</td>
</tr>
<tr>
<td>laue</td>
<td>357</td>
<td>320</td>
<td>5 min</td>
</tr>
<tr>
<td>ZSM-5, 3 crystals - ca. 63 refs/frame (21/crystal)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mono1</td>
<td>964</td>
<td>826</td>
<td>22 s</td>
</tr>
<tr>
<td>mono2</td>
<td>943</td>
<td>852</td>
<td>33 s</td>
</tr>
<tr>
<td>mono2 + probe</td>
<td>1004</td>
<td>902</td>
<td>12 s</td>
</tr>
<tr>
<td>mono2 + mono1 + probe</td>
<td>1010</td>
<td>913</td>
<td>35 s</td>
</tr>
<tr>
<td>laue</td>
<td>835</td>
<td>791</td>
<td>20 min</td>
</tr>
<tr>
<td>ZSM-5, 15 crystals - ca. 482 refs/frame (32/crystal)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mono1</td>
<td>2192</td>
<td>1936</td>
<td>55 s</td>
</tr>
<tr>
<td>mono2</td>
<td>2923</td>
<td>2702</td>
<td>30 s</td>
</tr>
<tr>
<td>mono2 + probe</td>
<td>3027</td>
<td>2854</td>
<td>30 s</td>
</tr>
<tr>
<td>mono2 + mono1 + probe</td>
<td>3119</td>
<td>2961</td>
<td>60 s</td>
</tr>
<tr>
<td>laue</td>
<td>-</td>
<td>-</td>
<td>&gt; 3 h</td>
</tr>
</tbody>
</table>

possibility of finding orientation matrices. Taking all reflections with \( d > 2.2 \, \text{Å} \) proved to be a good compromise. Secondly, a good guess for \( n_{\text{min1}} \) is required in order to prevent the routine from processing too many bad solutions. In 5.5 h, all 360 frames could be processed, yielding 2192 orientation matrices from 12 independent crystals. As with the previous experiments, all incorrect solutions can be attributed to a swapping of the \( a \)- and \( b \)-axes.

A major improvement in the indexing of multiple crystals was achieved by implementing the brute-force algorithm \( \text{mono2} \). One of the issues with \( \text{mono1} \) is that it is difficult to optimize the input parameters, and many repeat tests were required to get to the numbers presented in Table 9.2. Surprisingly, for both data sets (3 and 15 crystals), the numbers obtained after the first run were immediately better than those achieved with \( \text{mono1} \), in a time that is comparable to that required for \( \text{mono1} \). Because \( \text{mono2} \) processes a fixed number of orientation matrices, the time per frame is essentially unaffected by the increased number of crystals, whereas the \( \text{mono1} \) approach scales poorly. The
only difficulty with the mono2 approach proved to be setting the values for \( n_{\min 1} \) and \( n_{\min 2} \), but by using the probe subroutine to determine them, this problem could be solved and the number of crystal orientations determined improved.

Because mono1 and mono2 both generate orientation matrices, I was curious to see if allowing the evaluation of solutions from both algorithms simultaneously would improve the indexing results. This was tested for the multi-crystal samples, and indeed, resulted in a slight improvement of 6 and 92 more orientations being determined for the 3-, and 15-crystal experiment. With 3 crystals on the grid, this means that on average 2.8 crystal orientations per frame could be recovered. With 15 crystals, 8.5 crystal orientations per frame could be retrieved for 12 independent crystals. Although 15 crystals can be seen on the grid (Figure 9.3), 3 of them do not diffract strongly enough to be indexed (insufficient number of reflections).

Because the data were collected by rotating the grid around a single axis, the contributions from each crystal could be determined by tracking the positions of the 100, 010 and 001 reflections (Table 9.3). For the data set from 3 crystals, it can be seen that the orientations of all 3 crystals can be determined approximately equally well. Crystal 1 has the highest number of correctly assigned orientations, with only 2 of 355 solutions having the axes swapped. For crystals 2 and 3 this number is significantly higher than for crystal 1. Inspection of the orientation matrices for crystal 2 and crystal 3 reveals a particularly unlucky arrangement, because their \( b \)-axes are almost parallel with an angle of less than 3° between them. ZSM-5 forms as flat distorted prisms (e.g. Yan et al., 1995), so if several crystals are deposited on a surface, the preferential orientation would be with the \( b \)-axis normal to the surface. This affects score, because the closest peak within IndexFit of an integer position is taken into account, regardless of which crystal it belongs to.

For the data set collected on 15 crystals, approximately 9 crystals have the same orientation of the \( b \)-axis, 3 have apparently random orientations, and 3 crystal orientations could not be determined. Preferred orientation does not significantly hinder the orientation matrix search, but it would be beneficial if it could be avoided. It appears that neither routine has any problems dealing with a data set from 15 independent crystals, however, as the number of crystals in the beam increases, so does the reflection density (Figure 9.4). This needs to be taken into account, so based on the results described here, I feel that with the current experimental setup, the optimal number lies somewhere between 5 and 10 crystals per grid.

### 9.8.4 Monochromatic data

The algorithms were also tested on monochromatic data collected on single crystals of ZSM-5, sanidine and cesium platinate (Table 9.4). This was done by setting the program to run with a bandwidth of 0%. For ZSM-5, between 10 and 20 spots per frame could be found (average 12), for Sanidine between 5 and 15 (average 9), and for cesium platinate between 10 and 25 (average 15).

To allow for some deviation in the observed position, an error of up to 1% in the \( d \)-spacing was allowed during the index matching for mono1. For ZSM-5 nearly all frames could be indexed with this algorithm, but it proved to be a bit more difficult than before to assign the \( a \) and \( b \)-axis correctly. For cesium
Figure 9.4: Typical frame showing 664 observed reflections from 15 crystals. The ones originating from one of those crystals are indicated with green circles.
Table 9.3: More detailed results of the indexing of the ZSM-5 samples with multiple crystals obtained by combining *mono1* and *mono2*

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>generated orientations</th>
<th>correct orientations</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 crystals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>355</td>
<td>355</td>
</tr>
<tr>
<td>2</td>
<td>344</td>
<td>294</td>
</tr>
<tr>
<td>3</td>
<td>311</td>
<td>266</td>
</tr>
<tr>
<td>total</td>
<td>1010</td>
<td>913</td>
</tr>
<tr>
<td>15 crystals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>339</td>
<td>291</td>
</tr>
<tr>
<td>2</td>
<td>318</td>
<td>304</td>
</tr>
<tr>
<td>3</td>
<td>317</td>
<td>310</td>
</tr>
<tr>
<td>4</td>
<td>312</td>
<td>226</td>
</tr>
<tr>
<td>5</td>
<td>302</td>
<td>290</td>
</tr>
<tr>
<td>6</td>
<td>301</td>
<td>272</td>
</tr>
<tr>
<td>7</td>
<td>289</td>
<td>284</td>
</tr>
<tr>
<td>8</td>
<td>285</td>
<td>264</td>
</tr>
<tr>
<td>9</td>
<td>255</td>
<td>255</td>
</tr>
<tr>
<td>10</td>
<td>204</td>
<td>204(^1)</td>
</tr>
<tr>
<td>11</td>
<td>194</td>
<td>179</td>
</tr>
<tr>
<td>12</td>
<td>83</td>
<td>82</td>
</tr>
<tr>
<td>total</td>
<td>3119</td>
<td>2961</td>
</tr>
</tbody>
</table>

\(^1\)The orientations of these crystals are very similar, so it was not possible to determine the number of incorrect solutions.

Table 9.4: Results of the indexing tests using the indexing algorithms on 200 frames of monochromatic data

<table>
<thead>
<tr>
<th>Material</th>
<th>Algorithm</th>
<th>No. generated orientations</th>
<th>No. correct orientations</th>
<th>Time per frame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanidine</td>
<td><em>mono1</em></td>
<td>19</td>
<td>19</td>
<td>1 s</td>
</tr>
<tr>
<td></td>
<td><em>mono2</em></td>
<td>147</td>
<td>142</td>
<td>40 s</td>
</tr>
<tr>
<td>Cs(_2)[Pt(CN)(_4)]·H(_2)O</td>
<td><em>mono1</em></td>
<td>191</td>
<td>165</td>
<td>1 s</td>
</tr>
<tr>
<td></td>
<td><em>mono2</em></td>
<td>195</td>
<td>190</td>
<td>12 s</td>
</tr>
<tr>
<td>ZSM-5</td>
<td><em>mono1</em></td>
<td>199</td>
<td>158</td>
<td>1 s</td>
</tr>
<tr>
<td></td>
<td><em>mono2</em></td>
<td>194</td>
<td>144</td>
<td>12 s</td>
</tr>
</tbody>
</table>

platinate, a large number of frames could be indexed correctly. For sanidine, the algorithm was not as successful, as only 19 frames could be indexed. This is probably due to the small number of available spots per frame. However, all of the assigned orientation matrices proved to be correct. Because the reflection positions are much more reliable for monochromatic data than for a 4% bandwidth data, the algorithm proved to be very fast, taking about 1 s per frame for each material.

The *mono2* approach could also be used to index the data. For cesium platinate and ZSM-5, similar numbers as for *mono1* were obtained, but they were generated at a much slower rate. Only for sanidine, did *mono2* prove to be much more effective, as 147 of the 200 frames could be indexed. 142 of these were found to be correct.

### 9.9 Discussion

The *mono2* approach was developed at a very late stage, but the results presented here show that it works significantly better than the *mono1* approach. It also has the advantage that the implementation of the brute-force algorithm
is less complex, easy to understand, and requires approximately 50 lines of code. For comparison, \textit{mono1} requires approximately 300 lines of code, is much more complicated, and took several iterations to develop, test, and optimize. The \textit{mono2} algorithm is easier to use, and there are fewer input parameters to tweak. It is slower than \textit{mono1} for individual crystals, but it is significantly more effective for sanidine and cesium platinate. Both \textit{mono1} and \textit{mono2} perform significantly better than the existing \textit{laue} method in terms of number of crystals indexed, accuracy, speed and completeness, especially with multiple crystals in the beam. Because no information about the experimental setup is assumed, and the algorithm requires only a list of reciprocal lattice vectors, it can be used with any type of data. The results show that monochromatic data can be indexed just as well as those obtained with a broad bandpass beam. Therefore, I believe that any data collected with either monochromatic, polychromatic (at least up to a 4.6% bandwidth) beam can be indexed using this approach. The \textit{laue} method would probably work better when larger bandwidths are used.

Splitting the indexing routine in two parts, the generation, and subsequent evaluation of the orientation matrices, has the advantage that orientation matrices generated from different sources (\textit{i.e. mono1} and \textit{mono2}) can be evaluated simultaneously. This can led to an increased number of crystal orientations found (Table 9.2). Building on that will allow multi-crystal experiments on multi-phasic materials to be handled, by applying the \textit{mono1} or \textit{mono2} algorithm with different unit cell parameters. The solutions obtained for the different unit cells can then be evaluated simultaneously in the set optimization procedure, and the algorithm can decide which phase to assign the reflections to. An early implementation shows that this is possible, but it has not been
fully tested.

There are two main sources of error in the indexing routine. The first is that data can be incorrectly assigned an orientation matrix (i.e. false positives) by the indexing routine. Sometimes this is unavoidable, like for cesium platinate, because of an indexing ambiguity related to the space group $P6_5$. The protein community have developed methods to overcome this ambiguity in a post-indexing step by looking at the reflection intensities (White et al., 2013; Liu and Spence, 2014). Another source of false positives can come from lattice vectors being very similar, as for ZSM-5. Up to 10% of all crystal orientations may be incorrectly assigned. The second source of error applies only to the multi-crystal data sets. With an increased number of reflections, the chance that reflections of one crystal accidentally fit the lattice of another crystal also increases. It is unclear how these errors affect the merged data set, and further investigation is required. As long as the structure can be solved though, the incorrectly assigned reflections can be rejected as outliers (Dejoie et al., 2015).

Figure 9.5 shows that the completeness of the data in each frame of the 15-crystal data set lies between 4 and 8%. For each crystal, the completeness is between 0.5 and 2.0%, up to a resolution of approximately 0.9 Å, depending on the $d$-spacing of the reflection set (the completeness is calculated up to the lowest $d$-spacing observed). A resolution of approximately 1.3 Å is sufficient for structure solution. With this limit, each frame is between 8 and 14% complete, with each crystal contributing roughly 1.0 to 4.0%. To put this in perspective, the structure of SSZ-87 could be solved from a data set with a similar resolution ($d_{\text{min}} = 1.21$ Å) that was only 15% complete (Section 7.6).

Because a broad bandpass beam was used, specific problems inherent to Laue diffraction have to be checked. One of them is the possible presence of harmonics (e.g. the reflections 100, 200, and 300 will have identical diffraction angles for wavelengths $\lambda$, $\lambda/2$, and $\lambda/3$, respectively). The formula

$$\frac{1}{\Delta d^*} = 2\sin \theta \cdot \left( \frac{1}{\lambda_{\text{min}}} - \frac{1}{\lambda_{\text{max}}} \right)$$  \hspace{1cm} (9.22)


gives the relationship between the minimum distance between two reciprocal lattice points $\Delta d^*$, the diffraction angle $\theta$, and the wavelengths of the two delimiting Ewald spheres $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$. The maximum diffraction angle $\theta$ that can be used to suppress all harmonics can then be calculated for any given unit cell and wavelength range. For ZSM-5, the minimum distance between two reciprocal lattice points is given by $|a^*|$, where $a = 20.0022$ Å (Table 9.1). This gives a maximum 2$\theta$ angle of 46.2° for $\lambda_{\text{avg}} = 0.7153$ Å ($d = 0.9116$ Å). With the current setup, 93% of all reflections fall below this threshold, and only the $h00$ and $0k0$ reflection classes are affected at the higher angles. When SwissFEL comes online, the minimum wavelength will be close to 1.000 Å, so the probability of recording harmonic reflections will be reduced even further.

### 9.10 Conclusion

The fact that single snapshot diffraction patterns from materials with small unit cells can indeed be indexed opens up new horizons for the structure analysis of polycrystalline materials. It means that high-quality single-crystal XRD data can be obtained from tiny crystals in a very short period of time, and this has
implications for all areas of materials science, particularly for beam-sensitive materials. Furthermore, because several crystals can be measured simultaneously, agglomerates do not pose a problem and a useful data set that is roughly 10% complete can be obtained from a single snapshot. This allows possibilities in the area of time-resolved and *in situ* experiments. The unique 4%-energy-bandpass mode that is planned at the SwissFEL facility is ideal for these kind of experiments, because more reflections can be measured in a single shot, and they are measured completely. More discussion regarding further data treatment, structure solution and refinement of the three materials, and implications to the SwissFEL experiment can be found in Dejoie *et al.* (2015).
Chapter 10

Conclusion

10.1 Summary

The purpose of this Ph.D. project was to investigate new methods to solve the structures of complex polycrystalline materials. This was achieved by combining different kinds of experimental data and computational methods.

Chapter 5 describes the application of FOCUS, which was originally written to work with XPD data, to ED data. The idea was 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 and tested on four zeolite samples of varying complexity and known structure. This worked remarkably well, and all four structures could be solved in a straightforward manner. The method has since been used to solve the structures of SSZ-45 and SSZ-87, as well as two other materials (not yet published: the silicate SSZ-27 and the germanosilicate CIT-13). For SSZ-45 and SSZ-87, high-quality XPD data were also available. In both cases, the incomplete and comparatively low-quality ED data proved to be more suitable for structure solution than did the XPD data, showing the strength of both the FOCUS algorithm and the ED data.

In Chapter 6 I describe a way of combining ED and XPD data with the goal of creating a data set that is better for structure solution than either one by itself. This goal was only partially achieved. Although repartitioning of the intensities of reflections that overlap in an XPD pattern undeniably improved the data quality for structure solution, it proved to be difficult to choose the appropriate overlap factor. An incorrect value can reduce rather than improve the data quality. The choice of overlap factor, or a better way of assigning overlap groups, requires further investigation. The repartitioning method has yet to be applied to a case where the structure cannot be solved from either the XPD or ED data alone, so whether further investigation is worthwhile remains an open question. Instead, for the further development of this approach, I would suggest trying to combine Laue diffraction data with XPD data. Reflections in Laue diffraction data also overlap, albeit in energy, so the source of the overlap differs from that in XPD. The combination of the two data sets may allow (partial) resolution of the reflection intensities. The XPD data are fully complete, and this helps in the scaling of Laue patterns collected on different crystals to one another. An
advantage is that Laue diffraction is performed using X-rays, and this eliminates the complication of having different form factors for the two data sets.

Chapter 7 is a compilation of crystal structures that were solved in a non-conventional manner during the course of this Ph.D. project. The results show that XPD data by itself sufficed to find the unit cell, as long as the material was pure and the structure ordered. One of the outcomes was the synergy between the charge-flipping and simulated annealing routines for solving the structures of coordination complexes and metal-organic frameworks. The charge-flipping procedure benefits from the presence of heavy elements, but is weak when it comes to locating organic species. However, the molecular arrangement of the ligand or linker is often known beforehand, and this can be used to advantage by the simulated annealing algorithm. By combining the two, first locating the heavy atoms using charge-flipping, and then completing the structure using simulated annealing, a number of structures could be solved from the XPD data alone.

For zeolite structures, more creative solutions were required. For those with ordered structures (SSZ-45, SSZ-87), FOCUS worked very well in combination with RED data. For SSZ-61 and SSZ-70, HRTEM images were essential to the structure solution. Once the framework structures were solved, the problem of finding the organic SDA used in the synthesis had to be faced. For this too, the simulated annealing algorithm offers a practical way of locating the SDA in a more routine manner. This idea was expanded further in Chapter 8. Six zeolite materials with known framework structures were investigated, and the position of the SDA in five of them could be retrieved. Subsequent structure refinements confirmed the arrangements of the SDAs to be sensible. In each of these zeolites, the location of the SDA had been simulated previously using molecular dynamics modeling. In general, the simulated locations compare favorably with those obtained from the structure refinement, but there are also some clear differences. It would be interesting to compare the framework interaction energy of the SDA location determined from the XPD data with that obtained from molecular modeling. Although it is not always possible to model the exact position of the SDA within the zeolite channels accurately, the difference electron density map often gives a good indication of its approximate location. This information could be included in the molecular dynamics modeling as an additional restraint to guide the simulation.

Chapter 9 shows how multi-crystal snapshot data collected with a 4% energy bandwidth can be indexed. Several existing methods for indexing single-crystal data were examined, but none of these proved to be suitable for dealing with our data, so two new approaches were developed based on the idea that the wavelength range is small enough that approximately monochromatic radiation can be assumed. In order to deal with multiple crystals, a greedy set optimization algorithm was employed, and the results show that up to 12 crystals can be indexed at once from a single shot. The fact that single snapshot diffraction patterns from materials with small unit cells can indeed be indexed opens up new possibilities for the structure analysis of polycrystalline materials. Although this work was performed as part of a project to prepare for when SwissFEL comes online in 2017, the method is independent of the data source and can be used with snapshot data collected with any kind of radiation, whether it be monochromatic or polychromatic with a small energy bandwidth (up to 5%).
10.2 Outlook

Much as I would like to be able to recommend a well-defined step-by-step approach for solving complex crystal structures by combining methods, it is difficult to formulate a general procedure for combining the results of different experimental techniques. There is a seemingly endless number of ways that data from different experimental techniques can be combined, and researchers have become exceedingly creative in doing so. Each material comes with its own set of problems and, depending on what kind of data are available, requires a different approach to solve its structure.

As methods evolve, more complex structures become accessible. To stay ahead of the curve, increasingly creative solutions are required to solve the structures of increasingly complex materials. A good example of this is the structure of IM-5 (Baerlocher et al., 2007a), which was solved initially using the charge-flipping algorithm, and required a complicated combination of XPD data with phases extracted from HRTEM images. Later, Sun et al. (2010) showed that its structure could be solved using electron crystallography methods alone, and Xie (2010) developed the 2D-XPD approach that allowed it to be solved from XPD data alone. It turns out that decent three-dimensional ED data and a good algorithm for structure solution are all that are needed to solve this complicated structure in a matter of minutes (Chapter 5.4.4). For me, this example highlights the importance of hybrid methods, as well as their evolution. They are a means to an end, allowing experimental or computational techniques to catch up, and are therefore continually in flux.

This example also highlights the advantage of being able to obtain data from a single crystal. A large number of crystal structures can now be solved routinely from ED data alone (Yun et al., 2015) using direct methods, although some may still resist solution. For example, low data resolution prevented the structure of ZSM-25 from being solved in a conventional manner with direct methods (Guo et al., 2015). I wonder whether FOCUS could have been used. Although direct methods work well for zeolites, FOCUS almost make their structure solution trivial. I have yet to come across a zeolite that cannot be solved using FOCUS and three-dimensional ED data, as long as the framework is not disordered. I am confident that the structure of any ordered zeolite for which ED data can be collected can be solved using FOCUS, regardless of complexity and with low requirements in terms of data quality, resolution, and completeness.

For those materials where single-crystals are available, but the diffraction data cannot be measured because the material is sensitive to the beam, serial crystallography methods offer an interesting alternative. Although our efforts have focused on the 4% energy-bandpass mode that will be offered at SwissFEL, these methods are not necessarily limited to XFELs, and also offer possibilities for micro-crystal diffraction at synchrotron facilities or elsewhere. To demonstrate this, we have recently performed an experiment at the high-energy beamline ID-11 at ESRF (Grenoble, FR). In their setup, a transfocating device is used to focus the entire X-ray beam on the sample to obtain extremely high flux, and this allows diffraction data to be collected on tiny crystallites. In the absence of a monochromator, the beam has a bandwidth of approximately 1% (Vaughan et al., 2011). One of the obstacles of micro-crystal diffraction with such a high flux is that materials are often not stable enough to survive in the beam long enough to collect a complete data set. We are interested to see whether a fo-
cused, unmonochromatized beam like this can be used for structure analysis in a way similar to that described in Chapter 8, i.e. with randomly oriented crystals on a grid. In this way, typical limitations of micro-crystal diffraction can be overcome. Furthermore, synchrotrons are more accessible than XFEL facilities, opening up serial crystallography for a larger number of researchers.

To take this even further, the serial crystallography method may be extended to electron diffraction methods. The electron beam is also focused and very intense, so beam sensitive materials disintegrate before a complete data set can be collected. Preliminary tests by Yunchen Wang (Stockholm University, SE) using my algorithm show that it is possible to index single snapshots of ZSM-5 with a reasonable degree of success.

Then there are disordered materials that remain difficult to analyze, even if single-crystal data are available. Stacking faults or other defects are common in nano- and micro-crystalline materials, and may be one of the reasons why crystals do not grow large enough. Although methods for modeling (DIF-FaX; Treacy et al., 1991) and refining (DISCUS; Proffen and Neder, 1997) XPD profiles are available, materials that are disordered are notoriously difficult to characterize using conventional diffraction methods. Even when high quality single-crystal XRD data are available, analyzing diffuse scattering requires a high degree of expertise and is often limited to qualitative or semi-quantitative analysis. Methods to make such analyses more accessible are still in development (Weber and Simonov, 2012; Simonov et al., 2014). The main obstacle with disordered materials is that the Bragg peaks only contain information about the average structure, and that information contained in the diffuse scattering is hard to extract. Instead, researchers often resort to model building to find a suitable structural model that can then be verified and, in some cases, refined. For this purpose, the use of HRTEM images for structural analysis is well established, and local stacking disorder can often be observed directly (e.g. Figures 7.12 and 7.17). Alternative methods that allow direct probing of the local atomic surface include scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The pair-distribution function (PDF) can be applied to XPD data (usually collected with a specialized setup) to obtain information about short-range order. Then there are spectroscopic methods that probe, for example, specific vibrations (IR and Raman spectroscopy), X-ray absorption, electron spin resonance (ESR), or nuclear magnetic resonance (NMR). IR and Raman spectra are sensitive to specific vibrational, rotational, and other low-frequency modes in a system, making them indirect probes of structure. X-ray absorption spectroscopy (XAS), including both extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) techniques, can reveal information about near-neighbour interatomic distances, coordination numbers, and angles. NMR and ESR are also sensitive to local structure, and yield information about the local symmetry and coordination of the element that is being probed. Each of these methods offers information about short-range interatomic interactions that can be used for structural studies. None of these techniques by itself offers sufficient information to solve a structure unambiguously, but each can deliver valuable information if other more routine options have failed. With the possible exception of PDF and NMR, their use for structure determination in combination with other methods has not yet been well explored.

To solve the structure of a complex material, whether it be disordered or not,
all sources of information should be considered as part of the bigger picture. I hope that the work performed in this project represents another small step towards the development of a broadly applicable, routine approach for combining several experimental techniques and computational approaches effectively to solve difficult structures. Until such a general approach exists, structure solution for such cases will remain a challenge.
Appendix A

Diffraction intensity

A.1 Monochromatic radiation, rotating crystal

For conventional, single-crystal XRD experiments with a rotating crystal, $k_2$ is a constant for all reflections, given by:

$$k_2 = \frac{\lambda^3 \Omega}{V^2}, \quad (A.1)$$

where $\Omega$ is the volume of the crystal, and $V$ is the volume of the unit cell. The Lorentz factor $L$ is dependent on the geometrical setup (Lipson and Langford, 1999), but in its most simple form is given by:

$$L = \frac{1}{\sin 2\theta} \quad (A.2)$$

and the polarization factor $P$ by:

$$P = \frac{1 + \cos^2 \theta}{2}. \quad (A.3)$$

If a monochromator is used, the equation becomes:

$$P = \frac{1 + \cos^2 \theta \cos^2 \theta_M}{2 \cos^2 \theta_M}, \quad (A.4)$$

where $\theta_M$ is the angle of the monochromator. The full equation for the integrated intensity of a reflection is then given by:

$$I_{hkl} = I_0 e^{4 \frac{\lambda^3 \Omega}{m_e^2 c^4 V^2}} \frac{1 + \cos^2 \theta \cos^2 \theta_M |F_{hkl}|^2}{2 \sin 2\theta \cos^2 \theta_M}. \quad (A.5)$$

A.2 Monochromatic radiation, powder

For XPD data, $k_2$ is a constant for each reflection and given by:

$$k_2 = \frac{m_{hkl} \lambda^3 \Omega}{2V^2}, \quad (A.6)$$
where $m_{hkl}$ is the multiplicity of reflection $hkl$, $\Omega$ is the volume of the crystal, and $V$ is the volume of the unit cell. The Lorentz factor for powder diffraction data is given by:

$$L = \frac{1}{\cos \theta \sin^2 \theta}$$  \hspace{1cm} (A.7)

and the polarization factor with a monochromator by:

$$P = \frac{1 - K + K \cos^2 2\theta \cos^2 2\theta_M}{2}$$ \hspace{1cm} (A.8)

where $\theta_M$ is the monochromator angle, and $K$ is the fractional polarization of the beam. For neutrons, $K = 0$, for unpolarized and unmonochromatized X-rays, $K = 0.5$ and $\cos \theta_M = 1$, while for monochromatic or synchrotron radiation $K$ should be determined experimentally. However, for synchrotron sources, $K$ is typically small ($K \sim 0.1$) and incoming radiation hitting the sample is fully plane-polarized, so that Eq. A.8 can be reduced to $P = 1$. For lab sources, typically $2\theta_M = 0^\circ$, which gives $P = \frac{1 + \cos^2 2\theta}{2}$.

Therefore, the full equation for the integrated intensity is

$$I_{hkl} = I_0 \frac{e^4}{m_e^2 c^4} \frac{m_{hkl} \lambda^3 \Omega}{2V^2} \frac{1 - K + K \cos^2 2\theta \cos^2 2\theta_M}{2 \cos \theta \sin^2 \theta} |F_{hkl}|^2$$ \hspace{1cm} (A.9)

for data collected using a laboratory instrument, and

$$I_{hkl} = I_0 \frac{e^4}{m_e^2 c^4} \frac{m_{hkl} \lambda^3 \Omega}{2V^2} \frac{|F_{hkl}|^2}{\cos \theta \sin^2 \theta}$$ \hspace{1cm} (A.10)

for data collected at synchrotron sources.

**A.3 Polychromatic radiation, stationary crystal**

For a stationary crystal that is illuminated with polychromatic radiation, as is the case in a Laue diffraction experiment, or in the experiments described in Chapter 9 where a 4% bandwidth beam is employed, $k_2$ is no longer a constant. Instead, it becomes a function of the wavelength at which a reflection is excited $\lambda_{hkl}$:

$$k_2 = \frac{\lambda_{hkl}^4 \Omega}{4V^2}$$ \hspace{1cm} (A.11)

The Lorentz factor and polarization factors are the same as for the single crystal, monochromatic case (Eq. A.2 & Eq. A.3). The full equation then becomes

$$I_{hkl} = I_0 \frac{e^4}{m_e^2 c^4} \frac{\lambda_{hkl}^4 \Omega}{4V^2} \frac{1 + \cos^2 2\theta}{\sin 2\theta} |F_{hkl}|^2$$ \hspace{1cm} (A.12)

Additionally, for polychromatic radiation, $I_0$ itself is a function of the wavelength, and depends on the source of radiation. The variation of $I_0$ with $\lambda$ can be reconstructed by measuring a known material (Dejoie et al., 2011), or determined independently. The latter will be the case at SwissFEL, where the spectrum of every X-ray pulse will be measured.
Appendix B

LINES

*LINES* is a program for plotting powder diffraction patterns, and was initially developed for interactively modifying the background during the course of a Rietveld refinement with *XRS-82* (Baerlocher, 1982). Background in powder diffraction patterns may arise from scattering of X-rays by the capillary, air, or amorphous material, and can constitute a large part of a diffraction pattern. The modern way of removing backgrounds is by fitting a Chebyshev polynomial (Chebyshev, 1854; Mason and David, 2002) during the course of the Rietveld refinement. In practice, this method is unreliable when doing a Pawley or Le Bail fit, and offers little control over the shape of the background during a Rietveld refinement.

In *XRS-82*, the background can be specified manually in the input file as a list of X and Y coordinates, which are then linearly interpolated and subtracted from the diffraction pattern. Doing so manually is a time-consuming process, so *LINES* was developed specifically in order to make this more convenient, especially considering this procedure is normally repeated several times in order to fine-tune the background. *LINES* was developed to read a diffraction pattern, as well as an *XRS-82* input file, and to present the user with a graphical representation of both. By left-clicking on the plot, the background can be defined interactively. When finished, *LINES* will update the original *XRS-82* input file with the new background.

The background of any file can be corrected with:

```bash
lines SSZ-45.xy --bg_correct 1
```

Then by clicking on the figure, the background can be specified (Figure B.1). By closing the program, a list of X and Y coordinates is printed to console and written to the file *lines.out*. The command line option --bgcorrect 1 tells the program to perform a linear background correction, and print the corrected file to *SSZ-45_corr.xy*. In this way, the original file is never modified.

To perform the background correction with *XRS-82*:

```bash
lines --xrs
```

It is also possible to perform the background correction with *TOPAS*. In order to do so, the observed, calculated and difference plot should be output from *TOPAS* with the following commands:
Figure B.1: Figure showing the background correction in progress. Here, a zoomed in view of the observed (green), calculated (red), background (purple), and difference (teal) plots for SSZ-87 are shown. The red boxed indicate the background points, and can be added and removed with a left or right click, respectively.

```
Out_X_Yobs(x_yobs.xy)
Out_X_Ycalc(x_ycalc.xy)
Out_X_Difference(x_ydiff.xy)
```

Then, to start the background correct procedure:

```
lines SSZ-45.xye --topasbg --bg_correct 1 --bgin lines.out
```

The option `--topasbg` will tell the program to read the observed, calculated and difference plots and `--bg_in lines.out` will load previously saved background points from the file `lines.out`.

Since its inception, many functions for operations performed on powder diffraction data have been implemented. A number of different file formats can be read and visualized in numerous ways. Further options for diffraction pattern manipulation include the options to adjust the wavelength of the diffraction data, or to re-bin, normalize, and smooth them. All the functions are documented in the help file, which can be accessed via `luke --help`.

The program was implemented in Python2.7, and makes use of the `matplotlib` and `NumPy` libraries.
Appendix C

Structure completion

SMILES codes (Weininger, 1988) for all SDAs described in Chapter 8 are shown in Table C.1. A program like Jmol (Hanson, 2010) can be used to generate a three-dimensional model of the molecule from this code, and optimize its coordinates (Figure C.1). The coordinates are exported to a file in .xyz format. Using OpenBabel (O’Boyle et al., 2011), these coordinates can be transformed into a z-matrix in Fenske-Hall (.fh) format. The Fenske-Hall format is slightly different from that used in TOPAS, so a specialized script was written to perform the transformation. Below is an example of the input files used for SSZ-56, and the code that was added to TOPAS to introduce the SDA.

Figure C.1: Three-dimensional representation of the SDA used to synthesize SSZ-56.

<table>
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<td>SSZ-53 c1ccccccc2c<a href="O">N+</a>(C)(O)OCOC2</td>
</tr>
<tr>
<td>SSZ-55 c<a href="O">N+</a>(OCC2(c1ccccccF)c1)OCC2</td>
</tr>
<tr>
<td>SSZ-56 c2ccccc2c(N+)(O)OCC1OCC1OCC1</td>
</tr>
<tr>
<td>SSZ-58 <a href="OCC1">N+</a>(CCOC2CCOC2)1OCC1</td>
</tr>
<tr>
<td>SSZ-59 c2ccccccc2c(N+)(O)OCC1OCC1OCC1OCC2</td>
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<tr>
<td>SSZ-60 <a href="OCC1">N+</a>(CCOC2CCOC2)1OCC1OCC1OCC1OCC1</td>
</tr>
</tbody>
</table>

Table C.1: SMILES syntax used to generate the SDAs in Chapter 8.
### APPENDIX C. STRUCTURE COMPLETION

#### XYZ format

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#### Fenske-Hall format

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### TOPAS code snippet

```plaintext
rigid

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```

Appendix D

LUKE

LUKE is a program for indexing multi-crystal diffraction snapshots collected with an energy bandwidth of up to 5%. The source code of LUKE was written in Python2.7 and has a length of ca. 5900 lines. It makes heavy use of the NumPy, SciPy, Pandas, and tinyarray libraries. Any graphical output is generated using the matplotlib library. CCTBX (Grosse-Kunstleve et al., 2002) is used for the crystallographic computations, and DXTBX (Parkhurst et al., 2014) and FABIO (Knudsen et al., 2013) for reading diffraction images. The program has been tested to work under OS X (10.7+), Windows 7 (or later), and Linux (Ubuntu 14.04 LTS). Development for a GUI for the program, based on the image viewer fabian (Sørensen and Knudsen, 2006), is in progress (Figure D.1).

Input to the program is a list of reciprocal lattice vectors and intensities. It can also read diffraction images directly, if a detailed calibration file is supplied. The coordinate system is based on the one implemented in XMAS (Tamura, 2014). The program offers two modes of operation.

In single-file mode, i.e.:

luke zsm-5_0001.pks -s zsm-5.inp -c calibration.inp

The .pks extension indicates a four-column ascii data file with the xyz coordinates of the reciprocal lattice vectors in the first three columns and the extracted intensity in the fourth column. -s specifies the path to a file containing the crystal information (space group, unit cell parameters) and -c specifies the wavelength range and experimental setup.

In batch mode. A file named file_list.dat listing the paths to the data and relevant crystal/calibration files is needed:

./data/zsm-5_0001.pks zsm-5.inp calibration.inp
./data/zsm-5_0002.pks zsm-5.inp calibration.inp
./data/zsm-5_0003.pks zsm-5.inp calibration.inp
...
./data/zsm-5_0360.pks zsm-5.inp calibration.inp

Then, by running luke, the program will go through all the files sequentially. Output is always in a subfolder ./indexed/. Running luke --template will generate a working example for ZSM-5, including an input file (input.cfg) to
modify the program parameters. The calibration and crystal files are in json format, and an example of each for ZSM-5 is given below.

Calibration file

```json
{
  "chi": 0.0,
  "det_dist": 144.014,
  "det_xcent": 732.312,
  "det_ycent": 1142.11,
  "det_res_x": 1475.0,
  "det_res_y": 1679.0,
  "det_len_x": 253.700,
  "det_len_y": 288.800,
  "omega": -90.0,
  "pitch": -0.165090,
  "rdet": 0.0,
  "roll": -0.18000,
  "yaw": 0.227390,
  "max_wl": "16.9472kev",
  "min_wl": "17.7376kev"
}
```

Crystal file

```json
{
  "name": "zsm5",
  "a": 20.0022,
  "b": 19.8990,
  "c": 13.3830,
  "al": 90.0,
  "be": 90.0,
  "ga": 90.0,
  "spgr": "Pnma"
}
```
Figure D.1: Figure showing the interface for the program \textit{LUKE-GUI}.
Bibliography


