Structure Elucidation of Polycrystalline Materials using X-ray Powder Diffraction and Electron Microscopy Techniques

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Contents

Abstract iii

1 Introduction 1

2 Background 3
  2.1 The Phase Problem in Crystallography 3
  2.2 Structure Determination from X-ray Powder Diffraction Data 5
    2.2.1 Overview 5
    2.2.2 Data Collection and Reduction 6
    2.2.3 Structure Solution Approaches 10
    2.2.4 Structure Completion and Refinement 16
  2.3 Structure Determination by Electron Crystallography 17
    2.3.1 Overview 17
    2.3.2 Relationship Between the Electron Wave Function and the Structure Factor 18
    2.3.3 Parallel Beam Electron Diffraction – SAED and PED 21
    2.3.4 High-Resolution Transmission Electron Microscopy 28
  2.4 The Complementarity of the Two Techniques 28

3 Combining HRTEM Images and XPD Data for Structure Determination 31
  3.1 Introduction 31
  3.2 Experimental 32
  3.3 Phase Extraction and Evaluation 32
  3.4 Improving the Phases Further 39
  3.5 Structure Determination Using Data from Two Sources 43
  3.6 SSZ-74 50
  3.7 Conclusions 53

4 Combining PED and XPD Data for Structure Determination 55
  4.1 Introduction 55
  4.2 Experimental 56
  4.3 PED Data Reduction and Evaluation 58
  4.4 Weak Reflection Elimination 61
  4.5 Phase Retrieval from PED Data 64
  4.6 Combination of the Two Methods 66
  4.7 Test Example 66
  4.8 Conclusions 69
### 5 2D Images Derived from XPD Data and used for Structure Determination

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>71</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>73</td>
</tr>
<tr>
<td>5.3 Phase retrieval using 2D X-ray powder diffraction data</td>
<td>73</td>
</tr>
<tr>
<td>5.4 Structure Determination</td>
<td>74</td>
</tr>
<tr>
<td>5.5 IM-5 Test Case</td>
<td>78</td>
</tr>
<tr>
<td>5.6 SSZ-74 Test Case</td>
<td>81</td>
</tr>
<tr>
<td>5.7 Other Aspects of the 2D-XPD Method</td>
<td>83</td>
</tr>
<tr>
<td>5.8 The 2D-XPD Origin Definition Problem</td>
<td>85</td>
</tr>
<tr>
<td>5.8.1 Using A Three-dimensional Reference Map from pCF</td>
<td>85</td>
</tr>
<tr>
<td>5.8.2 Using Origin Defining Reflections</td>
<td>86</td>
</tr>
<tr>
<td>5.8.3 Using the Plane-group-specific Phase Relationships</td>
<td>87</td>
</tr>
<tr>
<td>5.9 Conclusions</td>
<td>89</td>
</tr>
</tbody>
</table>

### 6 Structure Determination of the Borosilicate Zeolite MCM-70

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Experimental</td>
<td>91</td>
</tr>
<tr>
<td>6.2 Data Analysis</td>
<td>92</td>
</tr>
<tr>
<td>6.3 Powder Charge Flipping Structure Solution</td>
<td>93</td>
</tr>
<tr>
<td>6.4 Structure Refinement</td>
<td>95</td>
</tr>
<tr>
<td>6.5 Discussion</td>
<td>97</td>
</tr>
<tr>
<td>6.6 Conclusions</td>
<td>99</td>
</tr>
</tbody>
</table>

### 7 AM-11

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Experimental</td>
<td>101</td>
</tr>
<tr>
<td>7.2 Data Analysis</td>
<td>103</td>
</tr>
<tr>
<td>7.3 Structure Solution</td>
<td>108</td>
</tr>
</tbody>
</table>

### 8 Conclusions

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8. Conclusions</td>
<td>109</td>
</tr>
</tbody>
</table>

### 9 Suggestions for Future Work

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9. Suggestions for Future Work</td>
<td>111</td>
</tr>
</tbody>
</table>

### References

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>References</td>
<td>113</td>
</tr>
</tbody>
</table>
Abstract

To understand the properties of crystalline materials, whether they are of scientific or industrial importance, structural analysis is essential. If representative single crystals are available, single-crystal X-ray diffraction is the method of choice and a successful structure analysis almost guaranteed. Unfortunately, many important crystalline materials cannot be prepared as single crystals of appropriate size and quality for conventional single-crystal X-ray diffraction studies. In such cases, structural information must be derived from X-ray powder diffraction (XPD) data.

Determining a crystal structure from XPD data is not a trivial matter: not only is the phase information lost during the diffraction experiment, but reflections with similar \( d \)-spacings, which are well separated in a single-crystal measurement, overlap in a powder pattern. This overlap problem strongly hinders structure solution by conventional (single-crystal) crystallographic methods. Although different approaches have been developed over the years to solve crystal structures from XPD data, all have their limitations, especially when the XPD patterns exhibit a high degree of reflection overlap.

To extend the limits of structure determination for polycrystalline materials, another structure characterization technique, electron microscopy (EM), can be used to complement the XPD technique. Compared to XPD, the obvious advantages from EM are: (1) single-crystal electron diffraction data can be obtained from a very tiny crystallite, simply because electrons interact with matter much more strongly than do X-rays; (2) the crystallographic phase information, which is lost in the XPD measurement, can be extracted from high-resolution transmission electron microscopy (HRTEM) images by crystallographic image processing.

With this extra information supplied by electron microscopy, three strategies for combining the two techniques have been investigated. One involves an optimization of the procedure for determining the phases of the structure factors from HRTEM images, and then combining these phases with intensities extracted from the XPD patterns through an optimized strategy for structure solution. The second uses the single-crystal intensities from precession electron diffraction (PED) patterns to better estimate the relative intensities of overlapping reflections in a XPD pattern. The third uses the PED data to derive phase information for combination with XPD data. The main objective of this PhD project was to develop feasible and practical ways of combining information from XPD and EM techniques based on these three strategies.

Crystallographic phase information extracted from HRTEM images has been shown previ-
ously to be very useful in structure determination. In this study, the extremely complex structures of the zeolites TNU-9 and SSZ-74 were used to investigate in more detail how the HRTEM phases from different quality images can best be exploited in structure solution. The most reliable phases extracted from a thin region of crystal are those of low-resolution strong reflections. The dual-space structure solution algorithm termed charge-flipping, which was introduced for single-crystal data in 2004 and adapted to accommodate powder diffraction data in 2007, was optimized for using datasets from XPD and EM. Tests showed that the phases derived from HRTEM images taken along a zeolite’s channel direction can be improved significantly with the single-crystal charge-flipping algorithm, and a recipe for doing this has been suggested. If more than one high quality HRTEM image along different zone axes are attainable, enough phase information can be extracted and they can be used to complement XPD data in reciprocal space for structure solution. If only a few phases can be extracted from a single HRTEM image, using these phases in reciprocal space proved to be less helpful. In such cases, a real-space structure envelope can be generated from these phases and used to facilitate structure solution. In both cases (TNU-9 and SSZ-74), a simple inclusion of all HRTEM phases in powder charge-flipping (pCF) did not yield any correct structures. The correct structures could be found in a straightforward manner, however, if the HRTEM phases were used in an optimized strategy.

Although it has been shown that HRTEM images can be extremely useful in the structure determination process, they are not always easy to obtain, especially if the sample is beam sensitive. To circumvent this problem, the possibility of using the less demanding PED technique in place of HRTEM was investigated. PED data have been exploited in two different ways for this purpose: (1) to identify weak reflections and (2) to estimate the phases of the reflections in the projection. The former is used to improve the partitioning of the reflection intensities within an overlap group and the latter to provide some starting phases for structure determination. In these initial tests, the correct structure was used as a reference to shift the 2-dimensional potential maps to a common origin. The information was incorporated into the pCF algorithm for structure solution. The approaches were first developed using data for the moderately complex zeolite ZSM-5, and then tested on TNU-9. In both cases, including PED data from just a few projections facilitated structure solution significantly.

During the development of these methods to combine XPD and EM techniques, a novel alternative using only XPD data was also developed. The single-crystal charge-flipping algorithm was applied to 2-dimensional projections derived from XPD data to retrieve structure factor phases. As for the PED case, the correct structure was used to fix the origin of 2D-XPD charge-flipping maps. Application of the pCF algorithm to the full 3-dimensional powder diffraction data in conjunction with phases derived from several such (arbitrarily selected) projections was found to have a significant and beneficial effect on the structure solution. The approach was first developed using data collected on TNU-9, and was then tested further using data for IM-5 and SSZ-74. In all three cases, the phase information derived from 2-dimensional subsets of the XPD data resulted in a significant improvement in the electron density maps generated by
the \( pCF \) algorithm. The inclusion of this phase information allowed all three structures to be determined from the XPD data alone.

The key problem in both the PED and 2D-XPD phase retrieval methods lies in the definition of the origin of the 2D charge-flipping maps. A method related to that used for HRTEM images has been developed for this purpose.
Zusammenfassung


Um die Grenzen der Strukturcharakterisierung für polykristalline Materialien zu erweitern und XPD zu ergänzen, kann mit der Elektronenmikroskopie (EM) eine weitere Strukturbestimmungsmethode herangezogen werden. Die offensichtlichen Vorteile von EM im Vergleich zu XPD sind folgende: (1) Gute Einkristall-Elektronenbeugungsdaten können bereits aus sehr kleinen Kristalliten erhalten werden, da Elektronen viel stärker mit Materie wechselwirken als Röntgenstrahlen; (2) Die kristallographische Phaseninformation, die in der XPD-Messung verloren gehen, können aus hochauflösenden Transmissionselektronenmikroskopie (HRTEM)-Bildern mittels kristallographischer Bildverarbeitung extrahiert werden.

Mit dieser durch Elektronenmikroskopie gelieferten zusätzlichen Information wurden drei Strategien zur Kombination der beiden Techniken untersucht. Eine betrifft die Optimierung der Phasenbestimmung der Strukturfaktoren aus HRTEM-Bildern und die Kombination dieser Phasen mit Intensitäten aus den XPD-Daten bei einer optimierten Strukturlösungsstrategie. Die zweite verwendet die Einkristall-Intensitäten aus Präzessionselektronenbeugungs(PED)-Bildern zur besseren Abschätzung der relativen Intensitäten überlappende Reflexe in XPD-Daten. Die dritte nutzt PED-Daten zur Ableitung der Phaseninformation um sie mit den XPD-


Das Hauptproblem sowohl bei der PED- als auch der zweidimensionalen XPD-Methode zur Phasenbestimmung liegt in der Definition des Ursprungs der zweidimensionalen XPD-Elektronendichtekarten. Obwohl keine perfekte Methode entwickelt werden konnte, die in allen Fällen angewendet werden kann, waren einige Ansätze doch teilweise erfolgreich.
Chapter 1

Introduction

Materials in the crystalline state are commonplace and they play a very important role in our daily lives. To understand the properties of these materials, structural information is a prerequisite. Take zeolite catalysts, for example. Detailed knowledge of their structures is crucial to the understanding of their catalytic and adsorption properties. Information obtained from the structural analysis of zeolites can be used not only to explain physicochemical properties of known materials but also to develop synthetic strategies for novel materials with desirable catalytic properties.

Many different techniques have been developed for the structure elucidation of crystalline materials. X-ray diffraction is probably the most important one for deducing the 3-dimensional atomic arrangement. Single-crystal X-ray diffraction, in particular, is now used routinely for crystal structure determination. However, many crystalline materials cannot be prepared as single crystals of appropriate size (~50 µm diameter) and quality for conventional single-crystal X-ray diffraction studies. In such cases, the structural information has to be derived from powder diffraction data.

Determining a crystal structure from X-ray powder diffraction (XPD) data is not a trivial matter: not only is the phase information lost during the diffraction experiment, but reflections with similar d-spacings, which are well separated in a single-crystal measurement, overlap in a powder pattern. This overlap problem strongly hinders structure solution by conventional (single-crystal) crystallographic approaches, because these algorithms assume the reflection intensities are reliable. Although different approaches have been developed over the years to solve crystal structures from XPD data, all have their limitations, especially when the XPD patterns exhibit a high degree of reflection overlap.

To extend the limits of structure determination for polycrystalline materials, another structure characterization technique, electron microscopy (EM), can be used to complement the XPD technique. Compared to XPD, the obvious advantages from EM are: (1) single-crystal electron diffraction data can be obtained from very tiny crystallites, simply because electrons interact with matter much more strongly than do X-rays; (2) the crystallographic phase information, which is lost in the XPD measurement, can be extracted from high-resolution transmission
electron microscopy (HRTEM) images by crystallographic image processing.

With this extra information supplied by electron microscopy, three strategies for combining the two techniques have been investigated. One involves an optimization of the procedure for determining the phases of the structure factors from HRTEM images, and then combining these phases with intensities extracted from the XPD patterns for structure solution. The second uses the single-crystal intensities from electron diffraction patterns, in particular those obtained using the precession technique, to better estimate the relative intensities of overlapping reflections in a XPD pattern. The third uses the precession electron diffraction data to derive phase information for combination with XPD data.

The main objective of this PhD project was to develop feasible and practical ways of combining information from XPD and EM techniques based on these two strategies. Furthermore, the dual-space structure solution algorithm termed charge-flipping, which was introduced for single-crystal data in 2004 and adapted to accommodate powder diffraction data in 2007, was optimized for using datasets from the two sources.
Chapter 2

Background

In this Chapter, the basic theories and techniques that were used are discussed. First, the relationship between a crystal structure and its diffraction pattern (Section 2.1), then the structure determination process using X-ray powder diffraction (XPD) data (Section 2.2) and finally the relevant electron microscopy (EM) techniques (Section 2.3) are described. The iterative dual-space structure solution algorithm charge-flipping and the new electron diffraction technique termed precession electron diffraction (PED), which were used extensively, are emphasized. The complementarity of XPD and EM, which is the motivation of this project, is summarized in Section 2.4.

2.1 The Phase Problem in Crystallography

Ideal crystals have periodic arrangements of atoms in three dimensions. If the positions of the atoms in an ordered crystal lattice can be located, the crystal structure is considered solved. Nowadays, although it is possible, in some cases, to visualize the atomic positions directly from 2-dimensional high-resolution images using high-energy electron microscopy (see Section 2.3), most crystal structures are derived from X-ray diffraction data.

Generally, three types of radiation — X-ray, electron and neutron — are used in diffraction experiments, because their wavelengths are comparable to or smaller than interatomic distances. X-rays are scattered by the electron shells surrounding the atoms, electrons by the electrostatic potential due to the atomic nuclei and their electron clouds, and neutrons by the nuclei of the atoms. The diffraction patterns contain information about the electron density $\rho_{xyz}$, the potential $\phi_{xyz}$, and the nuclear density $\delta_{xyz}$, respectively. Although the interactions with the different radiation sources are different, the maxima of their density distributions (i.e., $\rho_{xyz}$, $\phi_{xyz}$, $\delta_{xyz}$) all correspond to the atom positions in the crystal (Vainshtein, 1964, pp.2-5; Cowley, 1995, pp.77-92). Therefore, determining a crystal structure is equivalent to determine one of the

1Strictly speaking, it is not to be expected that the peaks in these different density distribution maps will be in exactly the same position, or have the same forms. However, the difference in peak positions are negligible for the purpose of structure solution (Cowley, 1967).
three density functions $\eta_{xyz}$ ($\eta_{xyz}$ is used to describe $\rho_{xyz}$, $\phi_{xyz}$ or $\delta_{xyz}$).

The 3-dimensional space in which the diffraction pattern is measured is called reciprocal or Fourier space, whereas the 3-dimensional space defining the crystal structure is called real space. The real-space density distribution functions and their corresponding reciprocal-space diffraction patterns are related to one another via Fourier synthesis (equation 2.1) and Fourier analysis (equation 2.2),

$$\eta_{xyz} = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} F_{hkl} \exp \left[-2\pi i (hx + ky + lz)\right]$$

$$F_{hkl} = V \sum_{x} \sum_{y} \sum_{z} \eta_{xyz} \exp \left[2\pi i (hx + ky + lz)\right],$$

where $V$ is the volume of the unit cell, and $F_{hkl}$ is the structure factor of the reflection $hkl$ and it’s defined as

$$F_{hkl} = \sum_{j=0}^{n} g_{j} t_{j}(s) f_{j}(s) \exp \left[2\pi i (hx_{j} + ky_{j} + lz_{j})\right].$$

Here $n$ is the number of atoms in the unit cell, $s$ is $\sin \theta_{hkl}/\lambda$, $g_{j}$ is the population factor of the $j^{th}$ atom, $t_{j}$ is the atomic displacement factor, and $f_{j}$ is the atomic scattering factor. For different radiation sources, the atomic scattering factors $f_{j}$ are different. The $f_{j}$ for X-rays and electrons are Bragg angle $\theta_{hkl}$ dependent while those for neutrons are constant.\(^2\)

Since the vector $F_{hkl}$ is complex in the general case, it can also be written as

$$F_{hkl} = |F_{hkl}| \exp (i\alpha_{hkl})$$

where $|F_{hkl}|$ is the structure factor amplitude, and $\alpha_{hkl}$ its phase. If the kinematical approximation is used (i.e., with the assumption that the scattering is elastic, the incoming radiation beams are scattered only once, and no interaction between the incoming and scattered beams occurs),\(^3\) the structure factor amplitude is proportional to the square root of the measured diffracted intensity,

$$I_{hkl} \propto |F_{hkl}|^{2}$$

While it is possible to calculate the amplitude of a structure factor from equation 2.5, the

\(^2\)The distributions of electron cloud and electrostatic potential are approximately Gaussian in cross section, so their atomic scattering factors, which are the Fourier transforms of these distributions, are also approximately Gaussian. The nucleus, on the other hand, can be modeled approximately by a delta function weighted by its positive charge $Z$, so that its Fourier transform is constant over all reciprocal space. See Structural Electron Crystallography by Dorset, pp.19 (Dorset, 1995).

\(^3\)X-ray and neutron scattering is generally considered to be kinematic, while in the electron diffraction case it is dynamic. The kinematical assumption can be regarded as the first order approximation of dynamical theory, see Section 2.3.1 for further discussion.
phase information cannot be obtained directly. Therefore a direct inversion of the diffraction pattern to yield the crystal structure via equation 2.1 is impossible. Although both structure factor amplitude and phase are essential for deriving a crystal structure, the phase, which is lost in the diffraction measurement, unfortunately contains more structural information than does the amplitude, because the phase determines where the regions of high density appear in the unit cell, while the amplitude just affects the height of the density peaks. This means, that, the measured intensities can be off by a large amount, but as long as the structure factor phases (e.g. from high-resolution electron microscopy images) are close to the true values, the structure will still be recognizable. The more correct the phases, the higher the tolerance that can be allowed in the amplitudes. On the other hand, the retrieval of structure factor phases using standard crystallographic techniques becomes more difficult as the quality of experimental intensities becomes poorer, because the phases are derived from them.

2.2 Structure Determination from X-ray Powder Diffraction Data

2.2.1 Overview

An ideal powder sample for a diffraction experiment consists of a large number of small, randomly oriented crystallites. Each small crystallite in the powder sample generates a single-crystal diffraction pattern, so an XPD pattern is the sum of millions of randomly oriented single-crystal diffraction patterns. As a result, the information about the relative orientations of the different lattice planes is lost. Therefore reflections overlap in the pattern (Figure 2.1). This leads to ambiguities in the peak positions and individual intensities of these overlapping

Figure 2.1: Two-dimensional single-crystal diffraction pattern (in red) overlaid on the corresponding powder diffraction pattern (in grey). A group of overlapping reflections is indicated with arrows. The diffraction angle 2θ increases radially from the center of the diffraction pattern. (Picture courtesy of Lynne B. McCusker)
reflections, and creates problems in determining the correct lattice parameters, systematic absences, and the individual structure factor amplitudes. Progress in overcoming this intrinsic problem of XPD data relies on finding improved techniques, either experimental or mathematical, for extracting the reflection intensities (see Section 2.2.2), or the development of structure solution approaches that allow the XPD pattern to be used without extracting the intensities (see Section 2.2.3).

The structure determination procedure using XPD data is shown in Figure 2.2. It should be noted that each step depends on the previous one, so a simple mistake made in one step can cause the whole structure determination to fail. In the next sections, these steps are grouped into three stages (i.e., data collection and reduction, structure solution and structure refinement) and are discussed in more detail.

![Flowchart of the procedure for solving crystal structures from X-ray powder diffraction data.](image)

**Figure 2.2:** Flowchart of the procedure for solving crystal structures from X-ray powder diffraction data.

### 2.2.2 Data Collection and Reduction

**Sample Preparation and Data Collection**

The first step for the structure determination process is powder sample preparation and data collection. Care must be taken at this stage that the powder sample contains a large number of crystallites, preferably of comparable size with no preferred orientation. Otherwise the measured intensities will not be representative of the true ones. Although a completely random distribution is difficult to achieve and some corrections are possible at the structure refinement stage, it’s always better to avoid this effect experimentally as much as possible. Usually,
2.2 Structure Determination from X-ray Powder Diffraction Data

powder diffraction data are collected either in reflection mode (Bragg-Brentano geometry) for strongly absorbing materials or in transmission mode (Debye-Scherrer geometry) for samples with lighter elements. The effects of absorption and preferred orientation can be reduced if the sample is loaded in a capillary that rotates during the measurement (Louër, 2002). To obtain good counting statistics throughout the pattern, it is desirable to spend more time at high angles, where the intensities are weaker.

Indexing

When the data collection is finished, the lattice parameters \((a, b, c, \alpha, \beta, \gamma)\) have to be determined. It should be noted that this indexing step is a very important one, because the lattice parameters must be correctly determined before the approaches to structure determination can be applied. Indexing fails easily if the sample contains impurity phases, if there is a large zero-point shift in the pattern, and/or if the peak positions are poorly defined due to reflection overlap, poor instrumental resolution, or poor sample crystallinity.

Generally speaking, the XPD indexing is a routine process, and thousands of XPD patterns have been successfully indexed, thanks to a number of well-established programs (Bergmann et al., 2004; Altomare, Giacovazzo et al., 2008). The most widely used programs are probably ITO (Visser, 1969), TREOR (Werner, Eriksson & Westdahl, 1985) and DICVOL (Boultif & Louër, 1991), which were developed more than twenty years ago. TREOR and DICVOL are still being updated (N-TREOR09: Altomare, Campi et al., 2009; DICVOL06: Louër & Boultif, 2007). Since these programs work in different ways and successful indexing may not always be achieved with one particular program (Werner, 2002), it is desirable to try all three in parallel, using multi-program indexing packages such as CMPR (Toby, 2005) and Crysfire (Shirley, 2004). Apart from these traditional approaches, some alternative methods based on different algorithms have been developed recently [e.g. Profile-based Monte-Carlo program McMaille by Le Bail (2004) and the SVD-based (singular-value-decomposition) algorithm by Coelho (2003)]. These new methods seem to be more tolerant with respect to large zero-point errors and impurity phases, and are well suited for indexing large unit cells.

Space Group Determination

After the XPD pattern has been successfully indexed, the space group symmetry information can then be obtained by identifying the systematic absence conditions. Because of the problems caused by reflection overlap, the space group cannot always be determined uniquely, and generally the subsequent intensity extraction and structure solution procedures have to be carried out separately for each potential space group. While the most common way of assessing the probable space groups is to identify systematic absences manually, two recent probabilistic methods proposed by Markvardsen et al. (2001; algorithm included in the program DASH, David et al., 2006) and Altomare et al. (2004; algorithm included in the program EXPO, Altomare, Camalli
Chapter 2. Background

et al., 2009) make this procedure more reliable and less time consuming. Both approaches are based on the statistical analysis of the reflection intensities extracted from XPD pattern, assuming the space group that has the largest Laue symmetry and no extinction conditions in the allowed crystal system. The probabilities for different extinction symbols are calculated and ranked by the programs (DASH, EXPO), and then the most plausible space groups are constructed from the most likely extinction symbols.

Very recently, Palatinus and van der Lee proposed a totally different strategy (2008; algorithm embodied in the program Superflip, Palatinus & Chapuis, 2007), based on the idea that the determination of the space group from the phased structure factors is easier than from diffracted intensities alone. The space group determination step is performed after the initial structure solution in P1. This alternative method is particularly well suited to small or medium sized structures (Palatinus & Damay, 2009).

Intensity Extraction

Once the lattice parameters have been determined and the space group selected, the diffracted intensity associated with each reflection can be extracted by applying a structure-free whole-profile-fitting technique. This technique is similar to the Rietveld technique (structure-dependent whole-profile-fitting technique, see Section 2.2.4) that is used in the structure refinement stage, but with the reflection intensities rather than the structural parameters being the non-profile variables (David & Sivia, 2002). Two different approaches to intensity extraction have been developed: the Pawley method (Pawley, 1981) and the Le Bail method (Le Bail, Duroy & Fourquet, 1988). Both try to model the whole powder diffraction pattern by refining several parameters that describe the peak profile (includes peak position, peak shape, peak width and background) in a semi-empirical way. The difference in the two methods lies in the fact that the Pawley method treats reflection intensities as free least-squares variables and therefore also provides esd’s, while the Le Bail method keeps the intensities unchanged during the least-squares cycle. In the Le Bail procedure, the intensities are updated after each cycle to the observed intensity values. Initially all peak intensities are set to the same arbitrary value in both procedures.

Both algorithms for determining the integrated intensities of reflections in an XPD pattern have been incorporated into a number of whole-profile-fitting programs (see Table 2.1). It should be noted that even if integrated intensities are not used in the subsequent structure solution step, the intensity extraction procedure is still necessary to establish the appropriate profile parameters.

Because most structure solution methods (see Section 2.2.3) depend heavily on the reliability of the integrated intensities obtained from the XPD pattern, this intensity extraction process is one of the most important steps in the structure determination procedure. However, because of the intrinsic problem of powder diffraction data, the intensities of strongly overlapping reflections are ambiguous, and these reflections need to be treated with care. The most common approach is to set the intensity ratios of overlapping reflections to one (equipartitioning). How-
ever, this can result in the intensities of weak reflections in an overlap group being assigned medium or even large values, and this strongly hinders structure solution.

To improve the estimation of the relative intensities of overlapping reflections, a number of ingenious approaches have been investigated over the years. Algorithms that use the intensities of the non-overlapping reflections to estimate those of the overlapping ones have been developed. These include the Maximum-entropy Patterson map algorithm (David, 1987; 1990), the DOREES method, which involves the analysis of the relations between structure factors derived from direct methods and Patterson function (Jansen, Peshar & Schenk, 1992b), and the Fast Iterative Patterson Squaring (FIPS) method (Estermann et al., 1992; 1993). However, for XPD patterns with a high degree of reflection overlap, these methods tend to fail. In such cases, an experimental approach involving the collection of multiple datasets on the same sample under different conditions can be tried. One possibility is to collect XPD patterns at different temperatures if the material displays anisotropic thermal expansion (Zachariasen & Ellinger, 1963; Brunelli et al., 2003), and a second is to collect data at different orientations if the crystallites in the sample are preferentially oriented (Wessels, Baerlocher & McCusker, 1999; Baerlocher et al., 2004). Whichever method is applied, the purpose is to extract additional information about the relative intensities of overlapping reflections from multiple datasets.

More recently, two novel intensity-partitioning procedures were proposed. They are applied during the structure solution process using the charge-flipping algorithm (Oszlányi & Sütő, 2004; 2005; 2008) (see Section 2.2.3). Wu et al. (2006) performed a repartitioning of intensities in each iteration based on the charge-flipping modification itself, while Barlocher, McCusker & Palatinus (2007) introduced a second electron density modification procedure based on a histogram-matching algorithm (Zhang & Main, 1990) before the repartitioning. The latter was applied in the determination of some very complex zeolite structures (Baerlocher, Gramm et al., 2007; Baerlocher et al., 2008; Sun et al., 2009).

**Table 2.1:** Selected programs used for intensity extraction.

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<thead>
<tr>
<th>Program</th>
<th>Algorithm</th>
<th>Reference</th>
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<td>ALLHKL</td>
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<td>Pawley</td>
<td>Jansen, Peshar &amp; Schenk, 1992a</td>
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<td>Topas</td>
<td>Pawley, Le Bail</td>
<td>Coelho, 2007a</td>
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2.2.3 Structure Solution Approaches

Only at this point can the real structure determination begin. The objective is to derive an approximate description of the arrangement of the atoms in the unit cell. Many different approaches to solving structures from XPD data have been developed and optimized. The methods can be grouped into: (1) conventional reciprocal-space methods, (2) real-space methods, and (3) dual-space methods. All the methods available for powder structure solution can also be used for single-crystal structure solution, but the reverse is not always true. It should be noted that each method has its own strengths and weaknesses, so the selection of the structure solution algorithm for a particular class of structure and particular set of XPD data is of vital importance.

Conventional Reciprocal-space Methods

The conventional Patterson (Patterson, 1934), maximum entropy (Bricogne, 1984; Bricogne & Gilmore, 1990) and direct methods (Hauptman & Karle, 1953; Hauptman, 1991) of structure solution are all reciprocal-space methods that were originally developed for single-crystal data.

The Patterson method is also known as the heavy-atom method, because it can be applied very successfully when a few scatterers dominate the scattering process, e.g. heavy atoms in X-ray diffraction. As suggested by Patterson, the complex structure factors in equation 2.1 can be substituted by the squares of their amplitudes, which are real, and therefore, no phase information is required to calculate the distribution of the following density function:

\[
P_{uvw} = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \exp \left[-2\pi i (hu + kv + lw)\right]
\] (2.6)

Fourier transform of the multiplication of \( F_{hkl} \) and its conjugate \( F_{hkl}^* \) in reciprocal space results in an autocorrelation ("\( \otimes \)") of electron density in real space, so the Patterson function can also be written as:

\[
P_{uvw} = \rho_{xyz} \otimes \rho_{xyz}
\] (2.7)

Thus, although the Patterson function does not reveal the distribution of atoms in the unit cell directly, it gives the distribution of interatomic vectors, all of which begin at a common point – the origin of the unit cell. It is then possible to establish the coordinates of atoms and their scattering power by analyzing coordinates and heights of Patterson peaks.

Direct methods are a class of statistical methods that attempt to derive phases directly from measured intensities. The methods are based on the following postulate: (1) the density map is non-negative everywhere in the unit cell (positivity), and (2) the density map consists of spherical atoms spread evenly throughout the unit cell with approximately zero density between them (atomicity). These two general properties result in special relationships (e.g. triplets) between structure factor amplitudes and their Miller indices.
A very important impetus to the development of direct methods was initiated by Sayre (1952) and interpreted by Cochran (1952, 1955) and Zachariasen (1952). For a structure containing equal resolved atoms, the structure factors are related by the Sayre equation,

\[ F_h = \frac{\theta h}{V} \sum_{h'} F_{h'} F_{h-h'} \]

(2.8)

where \( h = h'k'\ell' \). This equation states that the structure factor for any reflection \( h \) can be calculated as the sum of the products of the structure factors of all pairs of reflections whose indices sum to it. This seems of little use because the calculation of a single reflection requires the knowledge of many others. It should be mentioned, however, that the contribution of any pairs of which one or both are weak will make little contribution and can, at least to begin with, be ignored. A result of this is that if both reflections in the pair are very strong and the reflection being calculated is strong as well, there is a high probability that this relationship alone will give a good indication of the phase of the reflection \( h \) (Cochran, 1952, 1955; Zachariasen, 1952), that is,

\[ S_h S_{h'} S_{h-h'} \approx 1 \quad \text{for centrosymmetric structures} \]  

(2.9)

\[ \alpha_h \approx \alpha_{h'} + \alpha_{h-h'} \quad \text{for noncentrosymmetric structures} \]  

(2.10)

where \( S \) is the sign of the phase. The symbol \( \approx \) has a meaning of “probably equal to”. The probability of these relationships depends on the structure factor amplitudes and is defined as (Cochran, 1955),

\[ P_+ = \frac{1}{2} + \frac{1}{2} \tanh \left[ N^{-1/2} |E_h| E_{h'} E_{h-h'} \right] \quad \text{for centrosymmetric structures} \]  

(2.11)

\[ P_{\alpha h} = \frac{1}{2\pi I_0(k_{hh'})} \exp[k_{hh'} \cos(\alpha_{h'} + \alpha_{h-h'})] \quad \text{for noncentrosymmetric structures} \]  

(2.12)

where \( P_+ \) is the probability of the positive sign for a reflection \( h \), \( N \) is the number of atoms in the unit cell, \( I_0 \) is a Bessel function, and:

\[ N^{-1/2} = \sigma S / \sigma^2, \quad \sigma_m = \sum_{j=1}^{n} Z_j m \]  

(2.13)

\[ E_{hkl} = |F_{hkl}| / \left[ \sum_{j=1}^{n} f_j^2 (s) \right]^{1/2} \]  

(2.14)

\[ k_{hh'} = 2N^{-1/2} |E_h E_{h'} E_{h-h'}| \]  

(2.15)

Here \( Z \) is the atomic number. \( E_{hkl} \) is the normalized structure factor. The notations used in equation 2.14 are the same as those in equation 2.3.
Chapter 2. Background

To derive new phases using these relationships, some starting phases are needed. There are several sources of phase information: (1) phases of certain reflections can be defined to fix the origin of the unit cell; and (2) phases of several strong reflections can be selected for permutation. Direct methods always result in more than one set of phases, and the problem is reduced to selecting the best phase set (Giacovazzo, 1998; pp.113-172).

Usually, a reflection can be used in more than one triplet, and each of the triplets can be used for phase determination. In order to use all triplets to estimate the phases, Karle and Hauptman (1956) introduced a general expression, i.e. the tangent formula, for phase determination from triplets:

\[
\tan \alpha_h = \frac{\sum_h |E_{h'}| |E_{h-h'}| \sin(\alpha_{h'} + \alpha_{h-h'})}{\sum_h |E_{h'}| |E_{h-h'}| \cos(\alpha_{h'} + \alpha_{h-h'})}
\]

(2.16)

Here the sums include all triplets, in which the reflection \( h \) is involved.

The most probable phases evaluated using the tangent formula are finally combined with the normalized structure factor amplitudes \( E_{hkl} \) to calculate a density distribution (\( E \)-map). It is then possible to extract structural information from this density map.

Different from conventional direct methods where the probability analysis is applied to derive phases, the maximum entropy method uses a phase determination procedure based on entropy maximization and likelihood ranking. A detailed description of this method can be found in a review article by Gilmore, Shankland & Dong (2002).

The key problem in using these single-crystal techniques for powder structure solution lies in the derivation of single-crystal-like data from an XPD pattern. All the advanced methods used to partition strongly overlapped reflections can facilitate these methods considerably, and can even make the difference between solving and not solving the structure. These conventional single-crystal structure solution methods have been adapted to powder data in several programs: \textit{EXPO} (Altomare, Camalli \textit{et al.}, 2009), \textit{MICE} (Gilmore, Dong & Bricogne, 1999) and \textit{XLENS} (Rius & Frontera, 2007).

\textbf{Real-space Methods}

The efficiency of conventional reciprocal-space methods is strongly affected by the intensity ambiguity resulting from reflection overlap. However, this problem can be circumvented by applying real-space methods. In these methods, trial structure models, based on prior chemical information (\textit{e.g.} a molecule’s connectivity and known bond lengths and angles), are first generated without involving the experimental data. These models are then moved around within the unit cell by adjusting their positions, orientations and conformations until the best agreement between the experimental and the calculated XPD pattern is obtained. Since the comparison is performed using the whole powder pattern rather than the integrated intensities, the peak overlap problem is bypassed. The global optimization techniques that are commonly used to find the structures associated with the best agreement factor/figure-of-merit (\textit{e.g.}, the weighted profile
Structure Determination from X-ray Powder Diffraction Data

$R_{wp}$ or the full profile $\chi^2$ are Monte Carlo, Grid search, simulated annealing, and evolutionary algorithms. Detailed descriptions of these real-space structure solution methods can be found in the recent review articles by Cerny & Favre-Nicolin (2007) and David (2008).

**Dual-space Methods**

Approaches that work in both reciprocal and real space are called dual-space methods [see *International Tables for Crystallography* (2006). Vol. F, Chapter 16]. Some examples include direct methods combined with simulated annealing (Altomare, Caliandro *et al.*, 2008), the zeolite specific structure solution program *FOCUS* that uses chemical information in real space with experimental structure factor amplitudes in reciprocal space (Grosse-Kunstleve, McCusker & Baerlocher, 1997), *Shake-and-Bake* (Weeks *et al.*, 1994; Sheldrick & Gould, 1995) and *SIR* (Burla *et al.*, 2005), which apply the *positivity* and *atomicity* constraints in both reciprocal space (*via* direct methods) and real space (*via* density modification), and iterative projection techniques such as low-density elimination (Shiono & Woolfson, 1992), difference-map (Elser, 2003), and charge-flipping (Oszlányi & Sütő, 2004; 2005; 2008). Some iterative methods were also developed for phase correction and expansion (Hoppe & Gassmann, 1968; Gassmann & Zechmeister, 1972; Ishizuka, Miyazaki & Uyeda, 1982).

The advantage of these dual-space methods lies in the ability to impose constraints in both spaces. While the definition of the reciprocal-space constraint set (*i.e.*, structure factor amplitudes) is obvious, that of the real-space constraint set (which represent expectations about the structure) may be difficult to quantify. As a result, these methods are iterative and divided into reciprocal-space Fourier synthesis and real-space Fourier analysis steps (Zhang, Cowtan & Main, 2006). The basic idea was first developed in the early of seventies by Gerchberg and Saxton (1971; 1972) for phase determination using images and diffraction patterns measured in electron microscopy experiments. The iterative procedure was performed in both real space and Fourier space. Fienup (1978; 1982) then extended this idea and developed an optimization method called the hybrid input-output (*HIO*) algorithm to deal with the situation where no real-space image is available. Levi and Stark (1984; 1987) later showed that the iterations can be viewed as projections in vector space. This allowed theoreticians to formulate the phase retrieval procedure in a more robust way and eventually generalized the basic Gerchberg-Saxton-Fienup algorithm to a new class of iterative projection algorithms that are now used in many different fields (Millane, 1990; Stark & Yang, 1998; Miao *et al.*, 1999; Zuo *et al.*, 2003; Spence, Weierstall & Howells, 2004; Thibault *et al.*, 2008).

To better understand how these algorithms can be used for crystal structure determination, the fundamental concepts of constraint sets and projections need to be discussed from a crystallographic point of view. Clearly the aim of the algorithms is to find a density map that is physically and chemically meaningful and that reproduces the experimental data. In other words, the algorithms try to find the intersection between two constraint sets, that is (1) the set of structure factors constrained by experimental amplitudes (reciprocal/Fourier-space constraint...
set, \( S_F \)), and (2) the set of densities constrained by positivity, atomicity and other preset conditions (real-space constraint set, \( S_R \)). The search for the intersection can be formulated in terms of projection operators, which transform an arbitrary point in the search space to the nearest point in the constraint set. Depending on how the constraint sets are defined and how these constraints ("projection operator") are applied, the performance of the phase-retrieval algorithms can be quite different.

Of the diverse dual-space methods in crystallography, the charge-flipping structure-solution algorithm that was introduced by Oszlányi and Süttő in 2004 for single-crystal data has proven to be one of the most efficient approaches [see the review by Oszlányi & Süttő (2008), and references therein]. The algorithm itself is very simple (Figure 2.3), it starts by assigning random phases to the structure factor amplitudes derived from the diffraction intensities, and generating an electron density map. Then the signs of all electron density points below some user-defined threshold \( \delta \) (a small positive number) are reversed ("flipped") to produce a perturbed electron density map. From this map, a new set of structure factor amplitudes \(|G_{hkl}|\) and phases are calculated, and the new phases are combined with the measured amplitudes \(|F_{hkl}|\) to produce a new density map. This cycle is repeated until the calculated structure factor amplitudes match the measured ones or until a preset number of cycles has been reached. The flipping threshold \( \delta \) is the central parameter of the algorithm, and its selection is critical to the algorithm’s success. Although no method for predicting the optimal \( \delta \) value for all cases has yet been devised, two empirical methods proposed by Palatinus & Chapuis (2007) and Wu et al. (2004) seem to work properly in many cases. In the first method, \( \delta \) is defined at the beginning of the procedure and then kept fixed. That is: a \( \delta \) value that results in 80% of the pixels in the initial random density being flipped is determined. Ten charge-flipping cycles are performed for a selected \( \delta \) and the ratio of the total charge in the current density and the amount of the flipped charge is calculated. If the ratio is within the range of 0.8 – 1.0, the trial \( \delta \) is accepted and the procedure continues, otherwise \( \delta \) is re-assigned until this criterion fulfilled. In the second method, \( \delta \) is defined as a fraction of all pixels that are to be flipped, so this value changes for each iteration (Wu et al., 2004).

It should be noted that both Fourier-space and real-space constraint sets in the charge-flipping algorithm are non-convex, so no rigorous theorems regarding convergence can be established.

Because some of the measured amplitudes are ambiguous for polycrystalline materials, the Fourier space constraint set is loosely defined. In an attempt to improve the partitioning of the intensities of overlapping reflections and thereby to sharpen the constraint set, two different approaches have been developed (Section 2.2.2). Here we will focus on the powder charge-flipping (pCF) method developed by Baerlocher, McCusker & Palatinus (2007) (Figure 2.3). This pCF method starts in the same way as its single-crystal counterpart. However, after a user-specified number of cycles, the intensities of overlapping reflections are repartitioned. This repartitioning is preceded by an additional perturbation of the electron density map based
2.2 Structure Determination from X-ray Powder Diffraction Data

Figure 2.3: Flow diagram of the single-crystal charge-flipping algorithm (in black) with the modifications added to accommodate powder diffraction data (in blue). [Adapted from Baerlocher, McCusker & Palatinus (2007), courtesy of Lynne B. McCusker]

on histogram matching (Zhang & Main, 1990). The electron density histogram used for this histogram-matching (HM) step simply reflects the chemical composition of the material (i.e., the number and height of the peaks in the map should correspond to the chemical formula). The ratios of the structure factor amplitudes calculated from this HM-modified map are used to repartition the experimental amplitudes in reflection overlap groups, and these are then used as input in subsequent cycles.

Although the iterative projection phase-retrieval procedure is quite standard and successful in optics, this is not the case for crystal structure determination for two reasons. First, the object investigated in optics is non-periodic, so a continuous Fourier transform can be measured sufficiently finely (oversampling) to satisfy the Nyquist criterion (Nyquist, 1928), while for periodic crystals, this is not possible because only the intensities in reciprocal/Fourier space for which the Bragg condition is fulfilled can be measured (undersampling). This means that atomic resolution data (which is not easy to obtain) is usually required to compensate for the undersampling condition. Second, information about the size and shape of a (non-periodic) object (outside the object the scattering density is zero) is normally clear, but it’s difficult to define such a boundary condition for a crystal structure. However, it is possible to construct a structure envelope (Brenner, McCusker & Baerlocher, 1997; 2002) to identify the regions within the unit cell that are most likely to contain atoms. This structure envelope separates regions of
Chapter 2. Background

high electron density from those of low electron density, and can be generated from just a few strong, low-index reflections. It can serve to define internal zero density regions in dual-space structure solution methods such as FOCUS (Grosse-Kunstleve, McCusker & Baerlocher, 1997) and powder charge-flipping (Baerlocher, McCusker & Palatinus, 2007), and it has already proven to be a powerful tool (Gramm et al., 2006; Baerlocher, Gramm et al., 2007; Baerlocher et al., 2008).

2.2.4 Structure Completion and Refinement

When at least the main features of a structure have been obtained, the last step of the structure determination process can begin. Difference Fourier calculations are used to reveal the missing/excess atoms and then the whole structural model is refined using the Rietveld least-squares technique (Rietveld, 1969).

If the starting model is close to the correct one, the structure factor phases should also be close to the true values, so a difference Fourier map $\Delta \rho_{xyz}$ can be calculated using,

$$\Delta \rho_{xyz} = \frac{1}{V_c} \sum_h \sum_k \sum_l (|F_o| - |F_c|) \exp [-2\pi i (hx + ky + lz) + \alpha_c]$$  
(2.17)

where $V_c$ is the calculated volume of the unit cell, $|F_o|$ is the observed structure factor amplitude, and $|F_c|$ and $\alpha_c$ are the structure factor amplitude and phase calculated from the structural model. By visualizing the peaks and troughs in the difference Fourier map, the missing atoms and any extra atoms in the structural model can be located. It should be noted that the intensity partitioning of the overlapping reflections in the powder pattern is estimated by assuming the distribution is the same as that of the model, so the resulting difference Fourier map is doubly biased towards the structural model because both the phases and the intensity partitioning are taken from the model (see equation 2.17) (McCusker et al., 1999).

In Rietveld refinement, the structural parameters (atomic coordinates, occupancy factors, displacement parameters, etc.) together with the profile parameters (the same as those used for intensity extraction) are adjusted using a least-squares procedure to obtain an optimal fit between the experimental pattern and the calculated one. Geometric restraints (e.g., bond distances and bond angles) based on chemical information are often applied in order to guide the refinement towards structurally reasonable results and to prevent disastrous shifts in the atomic positions. For a pattern showing preferred orientation effects, additional model-based corrections (e.g., March-Dollase correction, Dollase, 1986; Spherical harmonics correction, Von Dreele, 1997) must be applied. The progress of the refinement can be monitored either by visualizing the difference between observed and calculated patterns, or by monitoring the corresponding agreement factors.

Further details regarding Rietveld refinement can be found in the book The Rietveld Method edited by Young (1993) and the guidelines outlined by McCusker et al. (1999).
2.3 Structure Determination by Electron Crystallography

2.3.1 Overview

Electron crystallography can be defined as the quantitative use of information obtained from electron microscopy techniques such as electron diffraction (ED) and/or high-resolution transmission electron microscopy (HRTEM) for crystal structure elucidation (Cowley, 1967; Dorset, 1995; Zou, 1995; Weirich, Labar & Zou, 2006; Zou & Hovmöller, 2008).

In a conventional transmission electron microscope (simplified as a 3-lens imaging system in Figure 2.4), the electron beam illuminates a section of the sample selected by an aperture in the image plane of the objective lens. The diffraction pattern of the selected area is obtained by using the first projector lens to image the back focal plane of the objective lens on to the object plane of the second projector lens. This second projector lens then gives a magnified picture of the diffraction pattern on the screen (Figure 2.4(a)). When the diffracted beams together with the transmitted beam are selected by aperture on the back focal plane of the objective lens, a high-resolution image can be obtained (Figure 2.4(b)). A great advantage of TEM is that it allows the diffraction pattern (in reciprocal space) to be correlated with the high-resolution image (in real space). Since both the diffraction pattern and the image contain structural information about the sample, both can be used for structure determination.

![Schematic of TEM](image)

**Figure 2.4:** Schematics of a highly simplified optical ray diagram in TEM (only three lenses are shown): (a) Diffraction Mode; (b) Image Mode. In each case the first projector lens is used to image either the back focal plane or the image plane of the objective lens.

To understand how electron microscopy can serve as a crystallographic tool, a discussion on the relationship between the scattered electron wave function and the crystal structure factor is essential.
2.3.2 Relationship Between the Electron Wave Function and the Structure Factor

As mentioned in Section 2.1, the electrostatic potential distribution that results from electron scattering is the sum of the fields caused by the atomic nuclei and their electron clouds. There are two contributions: one from elastic scattering and the other inelastic scattering. The electron-electron interactions and electron-nucleus interactions via Coulomb forces are elastic, and they produce the most useful structural information in the diffraction pattern and image. The interactions that result in energy loss in the scattered electrons are inelastic, and they cause the chromatic aberrations which blur the image and contribute to the background of the electron diffraction pattern.

To simplify the mathematical derivation of the relationship between the scattered electron waves and the electrostatic potential of the crystal, some approximations have to be made. In the following discussion, it is assumed that the incident radiation is perfectly coherent, the electrons are only elastically scattered, the scattered electron waves are parallel to the incident waves, and the crystal is relatively thin. Most of these derivations below are abstracted from Zou (1999).

Phase-Object Approximation and Dynamical Scattering

Because of the high energy of the radiation used in a TEM (100–300 keV acceleration voltages), the corresponding wavelengths (0.037–0.020 Å) are very small and the radius of the Ewald sphere \((1/\lambda)\) is very large. As a result, a large number of diffracted electron beams (scattered waves) are excited simultaneously, and the wave interactions (not only between the scattered waves and unscattered wave, but also between the scattered waves themselves) must be considered as a whole and described by \(n\)-beam dynamical scattering theory (Cowley, 1995).

Assuming that the electron wave passing through the sample only suffers a phase shift due to the interaction with the crystal potential, while the wave amplitude remains unchanged (phase-object approximation), the wave function at the exit surface of the crystal can be calculated approximately using the phase-grating model introduced by Cowley and Moodie (Cowley & Moodie, 1959; Cowley, 1995),

\[
\psi_{xy}^{EX} = \exp \left( -i \sigma \int_0^t \phi_{xyz} dz \right) = \exp \left( -i \sigma t \phi_{xy} \right) = 1 - i \sigma t \phi_{xy} - \frac{1}{2!} (\sigma t)^2 (\phi_{xy})^2 + i \frac{1}{3!} (\sigma t)^3 (\phi_{xy})^3 + \cdots \tag{2.18}
\]

Here \(\sigma = 2\pi / \{ \lambda_r W [1 + (1 - v^2/c^2)^{1/2}] \} \) is the interaction constant (where \(\lambda_r\) is the relativistic electron wavelength, \(W\) is the accelerating voltage, \(v\) is the velocity of the electron and \(c\) is the velocity of light), \(\phi_{xyz}\) is the crystal potential, \(t\) is the crystal thickness, and \(\phi_{xy}\) is the projection of the potential distribution along the direction \((z\)-axis\) of the incident beam. The exit wave function \(\psi_{xy}^{EX}\) can be viewed as the result of the interference between the unscattered
2.3 Structure Determination by Electron Crystallography

electron wave (direct beam) and a number of scattered waves (diffracted beams) propagating in
different directions. Each scattered wave represents a Fourier component of \( \psi_{xy}^{EX} \), and creates a
diffraction spot in the back focal plane of the objective lens. All plane waves together form an
image in the image plane (Zou, 1995).

From equation 2.18 and equation 2.2 (in two dimensions), the Fourier transform of the exit
wave function \( \Psi_{hk}^{EX} \) and the crystallographic structure factor \( F_{hk} \) can be related in the form

\[
\Psi_{hk}^{EX} \equiv FT(\psi_{xy}^{EX}) \equiv FT[1 - i\sigma t (\phi_{xy}) - \frac{1}{2!} (\sigma t)^2 (\phi_{xy})^2 + i \frac{1}{3!} (\sigma t)^3 (\phi_{xy})^3 + \cdots ]
\]

\[
= \delta_{hk} - \frac{i\sigma t F_{hk}}{V} - \frac{\sigma^2 t^2 (F_{hk}^* F_{hk})}{2! \cdot V^2} + \frac{i\sigma^3 t^3 (F_{hk}^* F_{hk}^* F_{hk}^* F_{hk})}{3! \cdot V^3} + \cdots \quad (2.19)
\]

where \( V \) is the volume of the crystal unit cell. The first term \( \delta_{hk} \) is a Dirac delta function
representing a sharp peak contributed from the direct beam, the following terms represent single
scattering, double scattering, triple scattering, etc., and each term is \( \pi/2 \) out of phase with the
previous one (because \( i = \exp(i\pi/2) \)). The term \( \Psi_{hk}^{EX} \) is also called the dynamical structure factor
(\( \Phi_{hk}^{dyn} \)) in the field of electron crystallography. It is clear from equation 2.19 that: (1) \( \Psi_{hk}^{EX} \) and
\( F_{hk} \) are not linearly related (either in magnitude or in phase angle); and (2) with a decrease
in crystal thickness and a decrease in the interaction constant (by increasing the accelerating
voltage), the significance of the dynamical scattering will be reduced.

Based on equation 2.19, the electron diffraction intensities (without considering the finite
size of the crystal or the curvature of Ewald sphere) are then given by,

\[
I_{hk}^{ED} = |\Psi_{hk}^{EX}|^2 = |\Phi_{hk}^{dyn}|^2 = (A + iB) (A - iB), \quad (2.20)
\]

where

\[
A = -\frac{\sigma^2 t^2 (F_{hk}^* F_{hk})}{2! \cdot V^2} + \frac{\sigma^4 t^4 (F_{hk}^* F_{hk}^* F_{hk}^* F_{hk})}{4! \cdot V^4} + \cdots
\]

\[
B = -\frac{\sigma t F_{hk}}{V} + \frac{\sigma^3 t^3 (F_{hk}^* F_{hk}^* F_{hk}^* F_{hk})}{3! \cdot V^3} + \cdots,
\]

As a reasonable approximation, equation 2.20 can explain most of the experimental obser-
vations that violate the kinematical assumption used in X-ray diffraction (Dorset, 1976; 1980;
1995, pp.137-145). For example, the relative intensities on a continuously excited reciprocal
lattice row is found to change as the crystal is tilted along this reciprocal axis (because the
thickness \( t \) along the direction of the incident beam is different); Some reflections can be af-
fected by dynamical scattering dramatically (i.e., the measured intensity deviates strongly from
the square of the structure factor amplitude) while others are not (because the self-convolution
terms of \( F_{hk} \) are phase-dependent, they can contribute to the intensity in varying degrees for
different reflections).

When the electron waves continue to propagate through the objective lens, they are brought
together onto the image plane where they interfere with the unscattered wave to form an image. The wave function becomes (Zou, 1999),

\[ \psi^{IM}_{xy} = [FT^{-1}(T'_{hk})] \ast \psi^{EX}_{xy} \]  

(2.21)

Here \( T'_{hk} \) is the objective lens transfer function. It contains a damping function \( D_{hk} \) and an exponential function \( \exp (i\chi_{hk}) \) (O’Keefe, 1992),

\[ D_{hk} = \exp \left[ -\pi^2 \frac{\alpha^2 |u|^4}{2} \right] \cdot \exp \left[ -\pi^2 \alpha^2 |u|^2 (\varepsilon + C_s^2 |u|^2)^2 \right] \]  

(2.22)

\[ \chi_{hk} = \pi \varepsilon \lambda |u|^2 + \frac{\pi C_s^2 \lambda^2 |u|^4}{2 \lambda^2} \]  

(2.23)

where \( u = ha^* + kb^* \), \( \Delta \) is the half width of the focus spread, \( \alpha \) is the semi-angle of the incident beam convergence, \( \varepsilon \) is the defocus value, and \( C_s \) is the spherical aberration constant of the objective lens.

As a result, the recorded image intensity distribution becomes,

\[ I^{IM}_{xy} = |\psi^{IM}_{xy}|^2 = |[FT^{-1}(T'_{hk})] \ast \exp (-i\sigma t \phi_{xy})|^2 \]  

(2.24)

It should be noted that, while the structure factor phases are not apparent in the image itself, they may be extracted using equation 2.24 under certain circumstances. Indeed, by using optimized experimental conditions and applying crystallographic image processing (CIP), the low-resolution structure factor phases can be retrieved quite successfully, as will be discussed theoretically in the next section, and demonstrated practically in the next chapter.

**Weak-Phase-Object Approximation and Kinematical Scattering**

If the crystal is thin enough that \( (\sigma t \phi_{xy}) \ll 1 \) is satisfied (weak-phase-object approximation), the exit wave function in equation 2.18 can then be simplified to,

\[ \psi^{EX}_{xy} = 1 - i\sigma t \phi_{xy} \]  

(2.25)

and equation 2.20 becomes,

\[ I^{ED}_{hk} = (\sigma t/V)^2 |F_{hk}|^2 \propto |F_{hk}|^2 \]  

(2.26)

This is the same as equation 2.5, which is used in X-ray diffraction under the kinematical assumption.

The Fourier transform of the \textit{sine} and \textit{cosine} of \( \chi_{hk} \) (equation 2.23) are both real, so the image intensity in equation 2.24 can be rewritten to first order as (Zou, 1999; Spence, 2003,
2.3 Structure Determination by Electron Crystallography

\[ I_{xy}^{1M} = \left| FT^{-1}(T_{hk}') \ast (1 - i\sigma t\phi_{xy}) \right|^2 = 1 + 2\sigma t\phi_{xy} \ast FT^{-1}(T_{hk}) \]  

(2.27)

where

\[ T_{hk} = D_{hk} \sin (\chi_{hk}) \]  

(2.28)

is the imaginary part of the objective lens transfer function \( T_{hk}' \). It is called the phase contrast transfer function (CTF).

Since the crystallographic structure factor is defined in reciprocal space, it is desirable to calculate the Fourier component of the real-space image intensity in equation 2.27,

\[ FT(I_{xy}^{1M}) = \delta + 2 (\sigma t/V) F_{hk} \cdot T_{hk} = \delta + 2 (\sigma t D_{hk}/V) \cdot \sin (\chi_{hk}) \cdot F_{hk} \]  

(2.29)

Thus the phase of \( FT(I_{xy}^{1M}) \) (which is measurable) and the phase of the structure factor can be simply related by the oscillation function \( \sin (\chi_{hk}) \): they are the same if \( \sin (\chi_{hk}) > 0 \) while they are different by \( \pi \) if \( \sin (\chi_{hk}) < 0 \). Note that when \( \sin (\chi_{hk}) = 0 \), the structure factor phase information is lost because \( FT(I_{xy}^{1M}) \) becomes 0.

Although these relationships between the electron wave function and the crystallographic structure factor are highly simplified, they do indicate, in theory, the extent to which the structural information can be extracted from an ED pattern or from a HRTEM image. In the next two sections, the practical aspects of ED and HRTEM techniques that are directly related to this project are discussed briefly.

2.3.3 Parallel Beam Electron Diffraction – SAED and PED

Over the years, several different electron diffraction techniques have been invented and developed for crystal structure analysis. Conventional electron diffraction techniques use a parallel beam of incident radiation, giving single-crystal patterns from the selected area of the crystal. Convergent beam electron diffraction (CBED) uses a convergent beam of electrons to limit the illuminated area of the crystal, the diffraction spots then become discs with their diameters proportional to the convergence angle. Although the CBED technique has been successfully applied for crystal structure analysis in many cases (Spence & Zuo, 1992), its limitation is obvious: this technique is not ideal for studying beam-sensitive crystals due to the large current densities, and not ideal for studying crystals with large unit cells because the diffraction discs will overlap (Weirich, 2003). Therefore, in this study, only parallel beam electron diffraction techniques will be discussed.
Chapter 2. Background

Conventional Selected Area Electron Diffraction

Usually, the crystals used for electron diffraction experiments are very thin, so in reciprocal
space the lattice points turn out to be lattice rods stretched parallel to the thin direction (the
length of the rods is proportional to the inverse of the crystal thickness). This means that the
regions of scattering power around the reciprocal lattice points will be extended parallel to the
electron beam (Figure 2.5). As a result, over a range of angles, the Ewald sphere will still
intercept the reciprocal lattice rod and diffracted intensity will still be generated. This intensity
will depend not only on the structure factor associated with the particular reciprocal lattice point,
but also on the shape transform function and the distance (termed "excitation error", $s_g$) from
the reciprocal lattice point to the Ewald sphere. So the electron diffraction intensity distribution
given by equation 2.20 and 2.26 will be further modified as (Cowley, 1995),

$$I_{ED}'_{hk} = I_{ED}^{hk} \cdot \left[ \frac{\sin (\pi t s_g)}{\pi t s_g} \right]^2$$

(2.30)

where $s_g = \lambda (h a^* + k b^*)^2 / 2$. It is assumed that the other dimensions of the crystal are infinite,
so no extension of the regions of scattering power in the $a^*$ and $b^*$ directions are considered.

Figure 2.5: The Ewald construction for electron diffraction.

For conventional selected area electron diffraction (SAED), the crystal and the incident
electron beam are stationary, and the intensities recorded are sensitive to the intersections of
the Ewald sphere and the reciprocal lattice rods. They differ from the reflection intensities in
a powder diffraction pattern, because the latter correspond to integration over the whole region
of scattering. Because the crystal thickness along the beam direction ($t$ in equation 2.30) is
normally unknown, it’s not easy to apply a geometric correction to the observed intensity to
obtain a true diffraction intensity. Furthermore, due to the spherical aberration of the objective
lens, it is impossible to obtain a SAED pattern from an area of less than about 50 nm in diameter. The resulting SAED intensity is then an average of the intensities over a certain thickness range (Weirich, 2003).

The SAED technique requires that the crystal be aligned carefully such that the incident beam is almost parallel to a zone axis. Otherwise, the intensities of the diffracted spots will not be symmetrical about the central spot. This not only imposes considerable experimental difficulties, but also creates a favorable condition for multiple scattering because many reflections are excited simultaneously.

There are two types of multiple scattering interactions. One is \( n \)-beam dynamical scattering that was discussed in Section 2.3.2 (equation 2.19), and the other is secondary scattering (Cowley, Rees & Spink, 1951). Both can play major role in ED data perturbation if the crystal is not ideally thin (Dorset, 1995, pp.135-152; 2003b). The mechanism of secondary scattering is that strongly diffracted beams behave as the direct beam and form new diffraction patterns centered about themselves. The final pattern can be visualized as the original diffraction pattern with copies of itself superimposed at the positions of the strongly diffracted reflections (Weirich, 2003; Hammond, 2009, pp.396-400). Therefore, instead of measuring the intensity \( I_{hkl} \), one measures (Cowley, Rees & Spink, 1951),

\[
I'_{hkl} = I_{hkl} + mI_{hkl} \ast I_{hkl} + nI_{hkl} \ast I_{hkl} \ast I_{hkl} + \cdots
\]

As a result, the intensity distribution of SAED pattern becomes less differentiated (i.e., strong reflections become weaker and weak reflections become stronger).

Another phenomenon caused by secondary scattering is the violation of extinction rules arising from translation symmetry elements, i.e., glide planes and screw axes that satisfy the Gjønnes-Moodie orientation conditions (Gjønnes & Moodie, 1965). It should be mentioned that this effect is not due to \( n \)-beam dynamical scattering but to secondary scattering (Cowley & Moodie, 1959; Dorset, 1995, pp.146-152).

Despite the fact that SAED intensities are subject to different distortions arising from multiple scattering, sample bending and radiation damage, there have been many cases in which SAED patterns have been used to derive structural information. With careful sample preparation and an optimized data collection strategy, SAED patterns allow unit cell parameters and two-dimensional crystal symmetry to be deduced. Furthermore, by classifying intensities as weak or strong, a number of specialists have been able to apply single-crystal X-ray structure determination approaches (e.g. Patterson method, direct methods and maximum entropy) successfully (Vainshtein, 1964; Cowley, 1967; Dorset, 1995; Dorset, 1998; Gilmore, 2003).

**Precession Electron Diffraction**

Almost 16 years ago, Vincent and Midgley (1994) invented the precession electron diffraction (PED) technique. It was originally devised to complement CBED techniques, but later was also
Chapter 2. Background

adapted to the parallel beam condition. This technique is equivalent to the Buerger precession method used in single-crystal X-ray diffraction, where the crystal is precessed around the incident X-ray beam. In the PED case, however, the incident electron beam (can be convergent or parallel) is deflected and precessed around a stationary crystal to produce a series of off-zone diffraction patterns. This electron beam is then de-scanned in a complementary way under the crystal to integrate all the off-zone patterns to a stationary zone pattern (Figure 2.6).

Compared to conventional SAED, the PED configuration has several useful features:

1. With the tilted illumination, only a few reflections are excited simultaneously, so the possibilities for multiple scattering are reduced and the resulting diffraction intensities are more kinematical in nature.

2. The precession swings the Ewald sphere through the reciprocal lattice rods so the integrated intensities are measured. This also reduces the chaotic oscillatory behavior of intensities as a function of thickness (Sinkler & Marks, 2010).

3. The crystal orientation does not need to be aligned as perfectly as for the SAED technique. Oleynikov et al. (2009) have shown that the tolerance for the sample misalignment is ca. 0.1° for SAED while it is ca. 1° for PED.

A comparison of SAED and PED data recorded on the same crystal, together with the simulated patterns assuming kinematical scattering, is given in Figure 2.7. It is clear from Figure 2.7(a) that multiple scattering effects are present in the SAED pattern. The reflection intensities do not correspond well to those of the kinematical simulation. Although no forbidden reflections appear along the principal axis h00 for the [021] projection, which indicates no or at least a very weak secondary scattering effect, the reflection intensities still suffer from n-beam dynamical scattering. For the [101] projection, a strong secondary scattering effect is observed. Forbidden reflections appear along the principal axis 0k0. The PED patterns, on the other hand, show a reduction both in n-beam dynamical scattering effects in the [021] projection and in secondary scattering effects in the [101] projection.

Although the PED reflection intensities are more reliable than those from a SAED pattern, they are still not ideal. It has been reported that while the non-systematic n-beam dynamical effect (caused by reflections belonging to different reciprocal lattice rows in the projection) is reduced dramatically by PED, the systematic one (caused by reflections belonging to the same reciprocal lattice rows that are excited simultaneously) is not (Gemmi, Calestani & Migliori, 2002; Gjønnes, Hansen & Kverneland, 2004; Own, Subramanian & Marks, 2004). Two corrections to the PED intensities (geometric and dynamical) can be applied before they are used for structure solution. In recent years, different geometric correction terms and different models for PED reflection intensities have been proposed. Two questions are worth mentioning here.

1. Are the geometric (Lorentz) corrections to the PED intensities mandatory?

In terms of the geometric configuration of PED, low-index reflections close to the direct beam are swept more slowly with smaller excitation error than are those with higher indices, so more intensity is sampled per unit time for low-index reflections. Theoretically, a correction
Figure 2.6: The geometry of the precession electron diffraction. The electron beam is tilted off zone using the scan coils and serially precessed. A complementary de-tilt is performed below the specimen by de-scan coils to restore the zone axis pattern. (Picture courtesy of Laurence D. Marks)
Figure 2.7: Electron diffraction patterns for the [021] projection (left) and [101] projection (right) of the zeolite ZSM-5 (space group Pnma). (a) recorded using the SAED technique, (b) simulated assuming kinematical scattering, and (c) recorded using the PED technique. Experimental data were collected at 300 kV on a Philips CM30 electron microscope. The crystal thickness is estimated to be less than 100 nm.
2.3 Structure Determination by Electron Crystallography

must be applied to compensate this effect. However, most of the proposed corrections depend on knowing the true structure factors (Own, 2005; pp.74-99). This is not useful if the structure is unknown. The most widely used Lorentz correction factor is the one that was derived originally by Gjønnes (1997) and later by Gemmi et al. (2002),

\[ C_{\text{Lorentz}} = g \sqrt{1 - \left(\frac{g}{2R}\right)^2} \]  

(2.32)

where \( g \) is reciprocal vector \((g = 1/d_{hkl})\), and \( R \) is the radius of the Laue circle. This phenomenological formula is popular because of its simplicity and the fact that it requires no structural information. Indeed, several structures have been determined from PED data using this correction (Gjønnes, Hansen et al., 1998; Gemmi et al., 2003; 2010; Gemmi & Nicolopoulos, 2007). It has been shown that the application of equation 2.32 can sometimes make the difference between solving and not solving the structure (Gemmi & Nicolopoulos, 2007). Conversely, Weirich et al. (2006) found that the structure determination of Cs\(_2\)Nb\(_{2.54}\)W\(_{2.46}\)O\(_{14}\) failed when equation 2.32 was used, while the structure could be solved without any correction. Dorset et al. (2007) also pointed out that it was unnecessary to perform the Lorentz correction (using equation 2.32) because the quality of their PED data (taken from many zeolites) did not improve.

As might be expected, the precession angle and crystallite thickness are critical parameters. If the crystal under study is thin and the precession angle is relatively large, the geometric correction can be omitted without distorting the PED intensities much.

(2) Are the PED intensities best modeled by a kinematical approximation, a two-beam dynamical approximation or an \( n \)-beam calculations?

There is no doubt that the accurate \( n \)-beam calculation (multislice or Bloch wave) adapted to precession geometry is the best model for interpreting experimental PED intensities (Own, 2005; Own, Marks & Sinkler, 2006; Sinkler & Marks, 2010). The only question is how to apply it before the structure is solved. Reasoning that the effect of precession is to reduce the number of simultaneously excited beams and its limit is the two-beam case in which the direct beam and one diffracted beam are excited, several approximations based on the two-beam theory have been proposed (Gjønnes, Cheng et al., 1998; Gemmi, Calestani & Migliori, 2002; Sinkler, Own & Marks, 2007). The simplest one is to assume that the PED intensity (after geometric correction) is proportional to the structure factor amplitude rather than its square. However, this extremely simplified model does not seem to be applicable in many cases (Own, 2005; Dorset et al., 2007). Once again, the precession angle and crystallite thickness might be the key for selecting the appropriate model. Under favorable conditions (\( i.e. \), thin crystal, larger precession angle), the PED intensity can be modeled using the kinematical approximation and structure determination using these data can be performed quite straightforwardly (White, Eggeman & Midgley, 2010).

Now that PED attachments for existing electron microscopes have become commercially
available, this promising technique has become accessible to a much broader community [see special issues in *Ultramicroscopy* (2007, volume 107), *MRS proceedings* (2009, volume 1184) and *Z. Kristallogr.* (2010, volume 225, 2-3)].

### 2.3.4 High-Resolution Transmission Electron Microscopy

Provided the sample under study is thin enough, the phases of the Fourier components of the image intensities and the phases of structure factors are simply related by the sign of the oscillation function $\sin (\chi_{hk})$ (see equation 2.29). Under Scherzer conditions, *i.e.*, if the defocus value $\varepsilon$ of the objective lens is selected so that equation 2.33 is satisfied (O’Keefe, 1992),

$$
\varepsilon_{\text{Scherzer}} = - (4C_s \lambda / 3)^{1/2}
$$

(2.33)

The objective lens will then give a phase shift of $(\chi_{hk})$ between $-2\pi/3$ and $-\pi/3$ over a large range of resolutions, so $\sin (\chi_{hk})$ will vary smoothly from $-0.8$ to $-1.0$ and $T_{hk} \approx -1$ (Zou, 1999). The structure factors of the reflections that are inside the first crossover [$\sin (\chi_{hk}) = 0$] of the contrast transfer function (CTF) can then be further simplified from equation 2.29 as,

$$
F_{hk} \approx - (V/2\sigma t) \text{FT}(I_{zy}^M)
$$

(2.34)

This means that within the Scherzer resolution (also called "point resolution" of the instrument), all the structure factor phases are shifted by approximately $\pi$ from those of the Fourier components of the image intensities, and their amplitudes are proportional to one another. Since the image intensities can be measured from the digitized experimental HRTEM pictures, approximate structure factors can be calculated. Indeed, even if the HRTEM image is not taken at the optimized defocus value (Scherzer defocus value), once the contrast transfer function is known (see equations 2.22, 2.23 and 2.28), structure factors can still be derived using equation 2.29, although not in a straightforward manner.

The practical procedure for extracting structure information by this crystallographic image processing is summarized in Figure 2.8. Detailed descriptions of the method can be found in Hovmöller (1992), Zou (1995) and Sun *et al.* (2010).

### 2.4 The Complementarity of the Two Techniques

X-ray powder diffraction and electron microscopy techniques have their own strengths and weaknesses. Fortunately, they are remarkably complementary (see Table 2.2):

1. It’s quite straightforward to collect diffraction data from modern X-ray powder diffractometers or from synchrotron radiation sources, but data collection using an electron microscope is not trivial. It requires significant manual intervention and patience to find crystals suitably aligned to obtain a sufficient set of projections.
The Complementarity of the Two Techniques

2.4 The Complementarity of the Two Techniques

Figure 2.8: Flowchart of the crystallographic image processing (CIP) procedure for extracting structural information.

(2) While the XPD data contain all reflections within the $2\theta$ range measured, the EM dataset generally consists of an incomplete set of two-dimensional projections.

(3) Electrons interact much more strongly with matter than do X-rays, so a single-crystal electron diffraction pattern can be obtained from a very tiny crystallite in a powder sample. Such a pattern is that of a single crystal, so there is no reflection overlap. However, as described in Section 2.3, the strong interaction combined with a very short wavelength generally results in complicated multiple scattering effects. This causes the reflection intensities to deviate from the kinematical assumption ($I_{hkl} \propto |F_{hkl}|^2$), even when the PED technique is applied.

(4) While the crystallographic phase information is lost in an XPD pattern, it is possible to extract low resolution phase information directly from HRTEM images, under optimized experimental conditions. This is one of the most promising advantages of the EM over the XPD technique.

Table 2.2: Complementarity of X-ray powder diffraction and electron microscopy.

<table>
<thead>
<tr>
<th></th>
<th>X-ray Powder Diffraction</th>
<th>Electron Microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data collection</td>
<td>Easy</td>
<td>Difficult</td>
</tr>
<tr>
<td>Data set</td>
<td>Complete</td>
<td>Incomplete</td>
</tr>
<tr>
<td>Crystallite size</td>
<td>$\mu$m</td>
<td>$nm$</td>
</tr>
<tr>
<td>Data precision</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Reflection overlap</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Multiple scattering</td>
<td>Rare</td>
<td>Yes</td>
</tr>
<tr>
<td>Phase information</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>
If these two techniques can be combined in an effective way, the course of structure determination can be facilitated and complex structures that cannot be solved by either method alone can be solved (McCucker & Baerlocher, 2009). Since this combination of XPD and EM is quite new, there is considerable potential for further development.
Chapter 3

Combining HRTEM Images and XPD Data for Structure Determination

3.1 Introduction

As described in Chapter 2, the crystallographic phase information that is lost in a diffraction pattern can be partially recovered, from high-resolution transmission electron microscopy (HRTEM) images. In this chapter, the practical aspects of how this phase information can be extracted and used to complement XPD data will be discussed. Three questions are considered here: (1) how are the structure factor phases best extracted from HRTEM images, and how reliable are they; (2) is it possible to improve these 2-dimensional phase sets using crystallographic techniques, and (3) how can HRTEM structure factor phases of different quality be imposed effectively in structure solution programs?

Two complex zeolite structures, TNU-9 (Gramm et al., 2006; [Si$_{192}$O$_{384}$]-TUN; C2/m; $a$ = 28.222 Å, $b$ = 20.012 Å, $c$ = 19.493 Å, $\beta$ = 92.3°) and SSZ-74 (Baerlocher et al., 2008; |(C$_{16}$H$_{34}$N$_{2}$)$_{4}$|[Si$_{92}$O$_{176}$(OH)$_{16}$]-SVR, Cc, $a$ = 20.408 Å, $b$ = 13.304 Å, $c$ = 20.166 Å, $\beta$ = 102.3°), were used for these tests. In the case of TNU-9, the structure was originally solved using the zeolite-specific structure-solution program FOCUS (Grosse-Kunstleve, McCusker & Baerlocher, 1997). For structure solution, 258 phases derived from 3 HRTEM images together with high-resolution X-ray powder diffraction (XPD) data were input to FOCUS, and after 16 days of computing time, the correct model with 24 Si atoms in the asymmetric unit was found. To study how HRTEM phases can be used more efficiently and to find an optimized structure solution strategy using data from the two sources, this structure, together with SSZ-74, were re-investigated using the more general structure solution approach powder charge-flipping (pCF).
3.2 Experimental

Samples of calcined TNU-9 and as-synthesized SSZ-74 were used for the powder diffraction data collections. The high-resolution synchrotron powder diffraction data for TNU-9 were collected at the SRS in Daresbury ($\lambda = 0.99556$ Å, $d_{\text{min}} = 1.15$ Å, 3864 reflections) and those for SSZ-74 at the NSLS in Brookhaven ($\lambda = 0.70035$ Å, $d_{\text{min}} = 0.95$ Å, 3258 reflections). The intensity extractions were performed using the program EXTRACT (Baerlocher, 1990) in the XRS-82 suite of programs (Baerlocher & Hepp, 1982).

Three HRTEM images of TNU-9 were taken by Zheng Liu in Osamu Terasaki’s group at Stockholm University (Gramm et al., 2006), and one of SSZ-74 by Ignatius Y. Chan at Chevron Energy and Technology Company (Baerlocher et al., 2008). The instrumental parameters used to calculate the contrast transfer function (CTF) are given in Table 3.1. Crystallographic image processing (CIP) of the HRTEM images were performed using the CRISP software package (Hovmöller, 1992). HRTEM multislice image simulation and electrostatic potential calculation were performed using the program JEMS (Stadelmann, 2004).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ (Å)</th>
<th>$C_s$ (mm)</th>
<th>$\Delta$ (Å)</th>
<th>$\alpha$ (mrad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNU-9</td>
<td>0.0197</td>
<td>0.6</td>
<td>90</td>
<td>0.50</td>
</tr>
<tr>
<td>SSZ-74</td>
<td>0.0251</td>
<td>0.5</td>
<td>100</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Note: The notations used here are identical to equations 2.22, 2.23 and 2.28.

All calculations involving the charge-flipping algorithm were performed using the program Superflip (Palatinus & Chapuis, 2007) in which a powder-specific charge-flipping ($pCF$) algorithm has been implemented (Baerlocher, McCusker & Palatinus, 2007). Structure factors for the simulations were calculated using the structural data published by Gramm et al. (2006) for TNU-9.

3.3 Phase Extraction and Evaluation

The extraction of structure factor phases from HRTEM images followed the standard CIP procedure: first the digitized HRTEM image was input to the software CRISP and the thinnest area was chosen to avoid multiple scattering (see Figure 3.1, upper right parts of the images), this region was selected to be as homogeneous as possible to improve statistical averaging (Figure 3.2, upper left); then a Fourier transform was applied to this region and a power spectrum generated (Figure 3.2, upper right). Graphically, this power spectrum resembles the electron diffraction pattern taken along the same zone axis, but it also contains structure factor phase information. The CTF was then calculated and corrected from the power spectrum by applying a filter function (Zou et al., 1996) implemented in CRISP. Generally, the defocus value used for the CTF calculation is determined by measuring the "Thon ring" positions in the power
Figure 3.1: High-resolution transmission electron microscopy (HRTEM) images taken along different zone axes of TNU-9. (a) [010]; (b) [001]; and (c) [T10]. (Provided by Zheng Liu in Osamu Terasaki’s group at Stockholm University).

spectrum of an amorphous area of the HRTEM image. However, this is not possible for TNU-9 because there were no amorphous regions available in the three HRTEM images (the upper right corners of the images are empty space). The defocus value could only be estimated by the electron microscopist during TEM operation. In this case it was estimated to be very close to the Scherzer defocus value (Zheng Liu, private communication). After the CTF correction,
the two-dimensional lattice parameters were determined and structure factors extracted (in \( p1 \)). These were used to find the plane group symmetry of the projection (Figure 3.2, below). Finally, structure factors were obtained by imposing the proposed symmetry.

For the case of TNU-9, it was very difficult to determine the unit cell from just three HRTEM images because the geometric relationship between these three projections was not known, so XPD data was used to find the appropriate 3-dimensional lattice parameters. Because there are several impurity peaks present in the XPD pattern, attempts to index the pattern using the software CMPR (with the programs ITO, TREOR, and DICVOL implemented) (Toby, 2005) failed. However, the unit cell could be found with Topas (Coelho, 2003) using the first 20 peaks of the XPD pattern. All of the 10 best unit cells proposed by Topas were \( C \)-centered monoclinic and were only slightly different from one another. The solution with highest figure-of-merit

\[ \text{Figure 3.2: Phase extraction from the HRTEM image of TNU-9 along [001] zone axis using the software CRISP: selection of thin region for analysis (upper left); the power spectrum generated by Fourier transformation from the selected area (upper right); and the determination of plane group symmetry (below).} \]
was assumed. This was also consistent with the 2-dimensional indexing of the power spectra generated from the three HRTEM images. The HRTEM images could then be determined to have been taken along the [010], [001] and [\(\bar{1}10\)] zone axes. There were three possible space groups: \(C2/m\), \(Cm\) and \(C2\). Their projection symmetries along the [010], [001] and [\(\bar{1}10\)] zone axes are shown in Table 3.2.

**Table 3.2:** Projection symmetries for the three possible space groups for TNU-9.

<table>
<thead>
<tr>
<th>Space group</th>
<th>[010]</th>
<th>[001]</th>
<th>[(\bar{1}10)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C2/m)</td>
<td>(p2)</td>
<td>(c2mm)</td>
<td>(p2)</td>
</tr>
<tr>
<td>(Cm)</td>
<td>(p1)</td>
<td>(cm (m \perp b))</td>
<td>(p1)</td>
</tr>
<tr>
<td>(C2)</td>
<td>(p2)</td>
<td>(cm (m \perp a))</td>
<td>(p1)</td>
</tr>
</tbody>
</table>

The most probable space group of the three was selected by checking the projection symmetries of the three HRTEM images (Figure 3.1). This can be done because the structure factors (either amplitudes or phases) obey some specific relationships for each plane group, if the origin is located appropriately (Zou, 1995; pp.39). The crystallographic image processing software **CRISP** does exactly this. It calculates the differences (monitored by a weighted \(R\)-value) between the experimental \(p1\) structure factors (both amplitudes and phases) and their symmetry-imposed forms for each of the plane groups. The plane group that has the lowest \(R\)-value and the highest symmetry is considered to be the most probable one. The \(R\)-values calculated for the phases are more reliable than those calculated for the amplitudes, because the phases are more tolerant to crystal misalignment. For the HRTEM image of TNU-9 along the [001] zone axis, the phase residuals (\(R\)-values) corresponding to \(cm (m \perp a)\), \(cm (m \perp b)\) and \(c2mm\) are 16.0°, 16.2° and 22.7°, respectively (Figure 3.2, right). Reasoning that the plane group \(c2mm\) contains the symmetries of the other two plane groups and its phase residual is only higher by a few degrees, this plane group was considered to be the most probable one. For the other two HRTEM images along the [010] and [\(\bar{1}10\)] zone axes, phase residuals of approximately 17° were found for the plane group \(p2\). Therefore, the most probable space group seemed to be \(C2/m\), the only centrosymmetric space group of the three candidates. It should also be mentioned that most zeolite framework structures are centrosymmetrical [see *Atlas of Zeolite Framework Types* by Baerlocher, McCusker & Olson (2007)].

The symmetry-imposed structure factors for the three HRTEM images were then extracted. To better evaluate what data resolution could be used, plots of the CTF close to the Scherzer defocus value were checked (Figure 3.3). It is clear from Figure 3.3 that when the defocus value is within ± 50 Å of the Scherzer defocus value (~397 Å), the information limit is about 1.4 Å in the ideal case. The resolution of the extracted data was set at 1.5 Å, slightly higher than the information limit. A more conservative option would be to select the data with a resolution 1.8 Å (the first zero crossover of the CTF), since in this resolution range \((d > 1.8 \text{ Å})\) all the phases are simply shifted by \(\pi\).

The comparison between the experimental phases (resolution 1.5 Å) and the correct phases
Chapter 3. Combining HRTEM Images with XPD Data

Figure 3.3: Plots of the CTF close to the Scherzer defocus value. The Scherzer defocus value and the CTF were calculated using equations 2.33, 2.22, 2.23 and 2.28 and the parameters in Table 3.1. The negative part of the vertical axis means that all the phases in this region should be shifted by $\pi$, while the rest remain unchanged.

Careful analysis of the structure factor phase sets from 3 HRTEM images (see Table 3.3 and Figure 3.4) indicated that:
Figure 3.4: Comparison between phases derived from the thinnest regions of the HRTEM images and the correct phases along (a) [010], (b) [001] and (c) [\bar{1}0\bar{1}] zone axes. The incorrect phases are shown in red, and the correct ones in black. The size of the reflection spot indicates its amplitude. The semi- and quarter-circles shown as dashed lines correspond to the resolutions 6 Å, 4 Å, 3 Å, 2.4 Å and 2 Å, respectively from the smallest circle to the largest circle. Reflections covered by these cycles are symmetry independent reflections.
Chapter 3. Combining HRTEM Images with XPD Data

(1) The phases extracted from the thickest region are much worse than those from the thinnest region. While \( \sim 65\% \) (234/360) of the phases are determined correctly from the thinnest region, only about half (188/381) are from the thicker region. This is a more or less random distribution, because the phases can only be 0° or 180°. If the dataset with 1.8 Å rather than 1.5 Å is considered, the phase correctness is 68% (183/269) for the thinnest region and 48% (139/290) for the thickest region. It appears that even when the same HRTEM image is used, the selection of the region has a significant impact on the phase extraction. As might be expected, the dynamical scattering effect plays an important role in this difference. As the sample thickness increases, the weak-phase-object approximation (WPOA, see equation 2.25) becomes less valid.

(2) When the thinnest region is used, the phases of the low-resolution reflections and of the strong reflections are more likely to be correct. For example, a total of 30 reflections in the three projections have \( d \)-spacings larger than 6 Å, and 28 of them were phased correctly. This high correctness (93%) is reduced to 78% (93/120), if reflections with \( d \)-spacings larger than 3 Å are considered. Similarly, of the 29 strongest reflections (with amplitudes larger than 200), only 2 were phased incorrectly. If reflections with amplitudes larger than 50 are considered, the correctness is reduced to 71% (94/133). Thus the most reliable phases extracted from a thin region are those of low-resolution and/or strong reflections. This does not hold for phases extracted from thicker regions.

(3) If the total amplitude of correctly phased reflections is considered, the correctness for the [010], [001] and [110] projections are 81%, 78% and 64%, respectively. One reason for this large range (64% – 81%) can probably be attributed to the difference in the thickness for the different projections. Indeed, computer simulation showed that the sample thickness for the three projections are approximately 4 nm, 4 nm and 14 nm, respectively (Gramm et al., 2006). Other factors might be inherent to a specific projection (Figure 3.5). For example, the [010] projection is along a channel direction, so there are larger regions of very low potential and the contrast is higher and clearer (Figure 3.5, left), and the [001] projection has the highest symmetry (c2mm), so the additional constraint on the phase relationships may help (Figure 3.5, middle).

![Figure 3.5: The 2-dimensional electrostatic potential calculated for TNU-9 along the [010] projection (left), [001] projection (middle) and [110] projection (right). Each picture shows 2 × 2 cells along the corresponding projection.](image-url)
(4) The number of correct phases in the resolution range 1.8 Å – 1.5 Å is 56% (51/91), and the correctness weighted by amplitude is 60%. This means that the phases in this resolution range are indeed less useful. Nevertheless, they are still better than random.

Although the HRTEM images of TNU-9 are of high quality, 35% of the phases (resolution to 1.5 Å) are determined incorrectly. Some of the errors can be attributed to the following factors:

(1) Dynamical scattering. As already discussed in Chapter 2, the simple relationship between the Fourier transform of the image intensity and the structure factor phase (equation 2.29) is derived using the weak-phase-object approximation (assuming purely kinematical scattering). This assumption is not correct, because dynamical scattering can only be reduced (using thinner sample and higher accelerating voltage), but not eliminated completely (Dorset, 1995; pp.140).

(2) The contrast transfer function (CTF). As can be seen from Figure 3.3, the uncertainty in the defocus value makes the CTF correction approximate, even if it is close to the Scherzer defocus value. While the reflections with d-spacings above 1.8 Å are not sensitive to the defocus value, those with lower d-spacings are. For TNU-9, the Scherzer defocus value was assumed for the CTF calculation, and this may not be exactly correct. This may explain why the phases in the resolution range 1.8 Å – 1.5 Å are less correct.

(3) Crystal tilt. This is a very common phenomenon observed in HRTEM images. Zou and Hovmöller discussed the effect of crystal tilt over ten years ago (Zou, 1995; pp.50-55; Hovmöller & Zou, 1999). They pointed out that in many HRTEM images of thin crystals, the main reason that the images do not look quite like the projected potential is because the crystals are tilted, not because of thickness or defocus effects (Hovmöller & Zou, 1999). Although crystal tilt affects the amplitudes most, the phases can also be distorted, especially if the tilt is extreme. In the case of TNU-9, all three images show some crystal tilt effects. For example, the tilt effect in the [010] projection is shown in Figure 3.6. The tilt axis identified by CRISP from the power spectrum (reciprocal space, Figure 3.6(a)) can be used to determine the direction of distortion in the HRTEM image (real space, Figure 3.6(b)), because these two directions are perpendicular to each other. From the correct projected potential (Figure 3.6(b)), one can see that the image is indeed stretched along the direction recognized by CRISP. Although CRISP can find the tilt axis, there is no way to compensate for this effect in the plane groups p1 and p2 (in plane groups with higher symmetry, symmetry averaging can be used).

3.4 Improving the Phases Further

To see if the 2-dimensional experimental phase sets could be improved by applying crystallographic phase-retrieval techniques, extensive tests were performed using the charge-flipping algorithm implemented in the program Superflip (see Table 3.4).
Figure 3.6: Crystal tilt effect in the HRTEM image of TNU-9 along the [010] projection. (a) The power spectrum of the HRTEM image, and (b) An enlarged thin region of the HRTEM image with the correct projected potential overlaid. The tilt axis identified by CRISP is shown as a white line in (a), and the distorted direction observed in the HRTEM image as a yellow line in (b).

Table 3.4: Charge-flipping input parameters tested for TNU-9 HRTEM images.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2-dimension, 3-dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ value</td>
<td>determined by Superflip, fixed at 0</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>300, 500, 1000</td>
</tr>
<tr>
<td>Input phases enforced for</td>
<td>1, 2, 3, 4, 5, 10 cycles</td>
</tr>
</tbody>
</table>

The test procedure was simple: structure factor amplitudes and phases extracted from a single HRTEM image were input to Superflip, and then the p1 potential maps generated by the program were Fourier transformed to obtain the phases of the corresponding reflections. These phases were then converted to 0 or π, whichever was closest, and were compared with the correct phases.

As might be expected, the performance of charge-flipping changed dramatically with different input datasets and parameters. However, some general trends could be observed:

1. Charge-flipping corrects the phases for the [010] projection much more efficiently than for the [001] and [110] projections. One possible explanation is that charge-flipping works better when a large fraction of the space has near zero density (Oszlányi & Sütő, 2008). As mentioned before, the [010] projection is along a channel direction, so the regions of very low potential are much larger in this projection than in the other two (see Figure 3.5).

2. The reflections used for the tests are 2-dimensional because they were extracted from 2-dimensional HRTEM images, so the Fourier iteration procedure could be performed in a 2-dimensional environment. However, these reflections can also be assigned 3 Miller indices and used in the conventional 3-dimensional environment. Both cases were tested in this study. For all the tests, the potential modification procedures performed in 3 dimensions provide more (or at least comparable) correct phases than those performed in 2 dimensions.
3.4 Improving the Phases Further

(3) The central parameter of charge-flipping, i.e., the potential modification threshold (the \( \delta \) value), affects the performance of the algorithm most. Although the method proposed by Palatinus and Chapuis (2007) for determining the \( \delta \) value is very robust when 3-dimensional datasets are used, it failed to find an optimal \( \delta \) value for the projection data. All tests, whatever the combination of input parameters, showed that the algorithm works better when \( \delta \) is set to 0 rather than to the value determined by Superflip.

In these initial tests it was found that the phase sets from the HRTEM images along \([001]\) and \([\bar{1}10]\), which have less empty space, were not improved by charge-flipping, while the phase set from the \([010]\) HRTEM image was improved significantly (Figure 3.7) by using optimized Superflip input parameters (see Figure 3.8). With this simple charge-flipping correction, the number of correct phases increased from 70% (89/127) to 80% (102/127), and the correctness weighted by amplitude from 81% to 93%.

\[\text{Figure 3.7: TNU-9 potential map along [010] projection calculated using structure factors extracted from HRTEM images (a) before and (b) after charge-flipping correction. Although the map shown in (a) is already quite good, the improvement of the map shown in (b) is obvious. The 10-, 6- and 5-rings of the framework structure can be seen from (b) very clearly.}\]

To see if this correction could also be applied in other cases, it was tested on HRTEM images taken on the zeolite IM-5 (Baerlocher et al., 2007). The input structure factor amplitudes and phases were taken from the publication of Sun et al. (2010, Supplementary materials, Table S1). These were extracted from 3 HRTEM images of IM-5 along \([100]\), \([010]\) and \([001]\) after crystallographic image processing. By using exactly the same Superflip input parameters (Figure 3.8), the initial HRTEM phases were improved significantly (Table 3.5). Note that the \([100]\) and \([001]\) projections are those along the zeolite’s channels. Once again, charge-flipping corrected the phases of the projections with more empty space more effectively.
Table 3.5: Number of correct phases before and after charge-flipping correction for IM-5.

<table>
<thead>
<tr>
<th></th>
<th>[100] zone Corrected</th>
<th>[010] zone Corrected</th>
<th>[001] zone Corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>81/133 (61%)</td>
<td>24/34 (71%)</td>
<td>65/114 (57%)</td>
</tr>
<tr>
<td>Correct</td>
<td>106/133 (80%)</td>
<td>28/34 (82%)</td>
<td>90/114 (79%)</td>
</tr>
</tbody>
</table>

$\sum$ amplitudes with correct phases / $\sum$ all amplitudes

|                  | 72%                   | 80%                   | 66%                   |

Figure 3.8: Superflip input file used for HRTEM phase correction.
3.5 Structure Determination Using Data from Two Sources

To use the phase sets extracted from 2-dimensional HRTEM images in combination with 3-dimensional XPD data, the individual projections must be merged. It should be noted that phase values are relative. They change with the origin of the unit cell. For the space group C2/m, the origin can be located in any one of 4 positions: (0, 0, 0), (0, 0, 1/2), (1/2, 0, 0) or (1/2, 0, 1/2). Assuming that the initial phase set extracted from each HRTEM image corresponds to the origin at (0, 0, 0), the phase sets corresponding to the other 3 origins could be calculated by

\[ \alpha_{xyz}^{hkl} = \alpha_{hkl}^{000} + 2\pi (hx + ky + lz), \]

where \( x, y \) and \( z \) are the coordinates of the new origin and \( \alpha_{hkl}^{000} \) is the initial phase set. There are 2 different phase sets for the [010] and [001] projections, and 4 for the [\( 1 \overline{1} 0 \)] projection. The phases of the reflections common to different projections were compared (see Table 3.6).

**Table 3.6:** Comparison of the phases of common reflections.

<table>
<thead>
<tr>
<th></th>
<th>[010] Set 1</th>
<th>[010] Set 2</th>
<th>[001] Set 1</th>
<th>[001] Set 2</th>
<th>[( 1 \overline{1} 0 )] Set 1</th>
<th>[( 1 \overline{1} 0 )] Set 2</th>
<th>[( 1 \overline{1} 0 )] Set 3</th>
<th>[( 1 \overline{1} 0 )] Set 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 1</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>0 0 3</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>0 0 5</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>0 0 7</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>0 0 9</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>0 0 11</td>
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<td>0</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>1 1 0</td>
<td>180</td>
<td>0</td>
<td>180</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>3 3 0</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>0</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7 7 0</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>9 9 0</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>180</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>11 11 0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tbody>
</table>

Although some reflections are missing in Table 3.6, and not all phases of common reflections could be matched perfectly in the different projections, it is still straightforward to merge the phase sets from the three HRTEM images. Three of the four reflections common to the [010] and [\( 1 \overline{1} 0 \)] projections have the same phases if the appropriate phase sets (e.g. [010] set 1 and [\( 1 \overline{1} 0 \)] set 2) are selected. Only 007 differs, and it is neither a high \( d \)-spacing nor a strong reflection. The situation is analogous for the [001] and [\( 1 \overline{1} 0 \)] projections (e.g. [001] set 1 and [\( 1 \overline{1} 0 \)] set 2).

The phases obtained from the 3 HRTEM images were then combined with the structure factor amplitudes extracted from X-ray powder diffraction (XPD) data, and used as input to the powder charge-flipping (pCF) algorithm in the program Superflip (see Chapter 2 for the discussion of pCF).

There are three different ways (2 in reciprocal space and 1 in real space) of combining the phase information with XPD data in the pCF procedure:
(1) "Reflection-list" option: The phases can be added directly to the XPD reflection list. These phases will be used instead of random phases for the corresponding reflections. The phases of all other reflections are still random. The number of cycles for which these phases are kept can be specified.

(2) "Model-map" option: The phases can be used to generate an electron density map, which is then Fourier transformed to produce phases for all reflections instead of random phases. These phases are allowed to vary by some percentage (adjustable) in a random fashion to create multiple starting phase sets.

(3) "Structure-envelope" option: The phases of a few high d-spacing, strong reflections can be used to generate a low-resolution density map. This map can be used as a structure envelope (Brenner, McCusker & Baerlocher, 1997; 2002) to identify the regions within the unit cell that are most likely to contain atoms. As discussed in Chapter 2, this structure envelope separates regions of high electron density from those of low density, and can serve to define zero density regions (e.g. pores in a zeolite structure). In addition to the flexibility of choosing different high d-spacing reflections to generate an envelope, there are 3 control parameters that can be specified in Superflip: the density threshold that defines the envelope, the cycle in which the envelope constraint should first be imposed, and the frequency with which the constraint should be applied.

All these options for using phases were tested extensively to establish which is the most effective. Fifty pCF runs, each with 600 iterations, were performed separately for various combinations of these parameters (see Table 3.7). The histogram-matching/repartitioning step was first imposed after 10 cycles and then every 10 cycles thereafter.

<table>
<thead>
<tr>
<th>Table 3.7: Charge-flipping input parameters tested for TNU-9.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input phases in resolution (total number)</td>
</tr>
<tr>
<td>6 Å (24), 3 Å (106), 2.4 Å (157), 1.8 Å (252), 1.5 Å (340)</td>
</tr>
<tr>
<td>Input phases enforced for</td>
</tr>
<tr>
<td>1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100,</td>
</tr>
<tr>
<td>150, 200, 250, 300 cycles</td>
</tr>
<tr>
<td>Input phases varied by</td>
</tr>
<tr>
<td>5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%</td>
</tr>
<tr>
<td>Structure envelope</td>
</tr>
<tr>
<td>2-dimensional, 3-dimensional</td>
</tr>
</tbody>
</table>

Generally, for ab initio structure solution, the pCF solutions in Superflip are ranked according to an \( R_{SF} \) value that compares the experimentally measured structure factor amplitudes (\(|F_{hkl}|\)) with those derived from the charge-flipped map (\(|G_{hkl}|\)):

\[
R_{SF} = \frac{\sum_{hkl} \left| |G_{hkl}| - |F_{hkl}| \right|}{\sum_{hkl} |F_{hkl}|} \tag{3.1}
\]

But in this case the structure was already known, so a reference map calculated from the true structure was used to evaluate the correctness of all the electron density maps produced. For
this purpose the agreement factor $R_{map}$

$$R_{map} = \frac{\sum |\rho_{map} - \rho_{ref}|}{\sum \rho_{ref}}$$ (3.2)

was calculated for each run.

Before starting the analysis of the results, a rough classification of the quality of pCF density maps (according to their $R_{map}$ values) is needed: For TNU-9, a density map with an $R_{map}$ value above 70% does not contain enough structural information to be interpreted (Figure 3.9(a)), a map with an $R_{map}$ value around 60% can be interpreted, at least partially by an experienced crystallographer with intuition (Figure 3.9(b)), a map with an $R_{map}$ value around 50% can be considered an acceptable/solvable map, because most of the Si atoms and many O atoms can be located (Figure 3.9(c)), and a map with an $R_{map}$ around 40% can be considered to be a very good map with almost all of the Si atoms and O atoms located and with chemically sensible electron densities (i.e., higher densities for Si) (Figure 3.9(d)).

![Figure 3.9: TNU-9 electron density maps of different quality generated from pCF. (a) – (d) correspond to $R_{map}$ values of 70.15%, 61.13%, 51.32% and 40.63%, respectively.](image)

Figure 3.10 shows the results ($R_{map}$-value distribution) of pCF runs in which HRTEM phases were added to the XPD input reflection list. It is clear from the figure that with different number of phases and different number of cycles with these phases fixed, the performance of pCF changed significantly.

In the first two cases (resolution 1.5 and 1.8 Å, Figure 3.10 (a) and (b)), the $R_{map}$ values first dropped continuously as the number of cycles with the phases fixed was increased from 1 cycle to 50 cycles, the $R_{map}$ values then increased again as the number of cycles increased further. It is, of course, beneficial to keep correct phases longer while allowing incorrect ones
Figure 3.10: Correctness of the electron density maps ($R_{\text{map}}$, see equation 3.2) generated by $p\text{CF}$ for TNU-9 with HRTEM phases fixed for different numbers of cycles. (a) – (e) show the $R_{\text{map}}$ values of the 50 $p\text{CF}$ runs using 340, 252, 157, 106 and 24 input phases (corresponding to resolutions of 1.5, 1.8, 2.4, 3 and 6 Å), respectively. In each case, the $R_{\text{map}}$ values are arranged in ascending order.
to change. Finding the number of cycles that best balances the two is important for structure solution. Nevertheless, even with optimal input parameters, the density maps produced were not good enough to be interpreted.

With a resolution of 2.4 and 3 Å (Figure 3.10 (c) and (d)), the \( R_{\text{map}} \) values continued to drop as the number of cycles with fixed phases was increased from 1 to 300. This is different from the previous cases. The reason may lie in the fact that the phases derived for higher \( d \)-spacings are more reliable (recall Table 3.3). When the input phases were fixed for 50 cycles or more, some of the resulting electron density maps were interpretable. The 3 Å phase set yielded more interpretable density maps than did the 2.4 Å phase set.

When only the lowest-resolution phases (6 Å) were included (Figure 3.10 (e)), no significant improvement was found for any of the test parameters. It appears that the small number of phases (24) is insufficient to change the \( pCF \) runs much despite the fact that these phases are the most reliable ones.

Figure 3.11 shows the results of \( pCF \) runs in which the "Model-map" option for combining HRTEM phases was used. Surprisingly, no improvement was detected, and the \( R_{\text{map}} \) values became even worse in most cases.

![Figure 3.11](image.png)

Figure 3.11: Correctness of the electron density maps \( (R_{\text{map}}) \) generated by \( pCF \) for TNU-9 with starting phases generated from a density map calculated from (a) 1.5 Å data, and (b) 1.8 Å data. In each case the starting phase sets were allowed to vary in a random fashion by different amounts.

Figure 3.12 shows the results of \( pCF \) runs in which phases were input in the form of the structure envelopes. Two envelopes, one generated from 9 phases (6 Å) from a single HRTEM image (along \([010]\)) and the other from 24 phases (6 Å) from all 3 HRTEM images, were used for these tests (Figure 3.13). In each case, different numbers of cycles for starting the envelope constraint were selected, and then the constraint was applied every 10 cycles thereafter. It is clear from Figure 3.12 that the \( pCF \) structure solution did not improve much whichever
envelope or parameter was used. Just a few electron density maps with $R_{\text{map}}$-values slightly above 60% were produced (with no structure envelope, the best $R_{\text{map}}$-value was around 70%).

**Figure 3.12:** Correctness of the electron density maps ($R_{\text{map}}$) generated by $pCF$ for TNU-9 with a structure envelope constraint imposed. Structure envelope generated from (a) 9 phases (resolution 6 Å) from one HRTEM image (along [010]), and (b) 24 phases from all 3 HRTEM images (see Figure 3.13). In each case, the $R_{\text{map}}$ values for the 50 $pCF$ runs are arranged in ascending order.

**Figure 3.13:** Structure envelopes generated from (a) 9 phases (6 Å) from a single HRTEM image along [010], and (b) 24 phases (6 Å) from all 3 HRTEM images. Atoms would be expected on the pink side (high electron density) of the surface.

As discussed before, by including the phases derived from 2.4 Å- or 3 Å-resolution HRTEM data in the XPD reflection list and keeping them fixed initially in $pCF$, it is possible to solve the structure of TNU-9 from the best density maps produced by $pCF$. Reasoning that if all three options for combining phases are used simultaneously, the structure solution might be further facilitated. A new strategy was tested: (1) a model map was generated from *all of the HRTEM phases* to exploit the full information obtained from HRTEM images, (2) *the more reliable phases* (i.e., lower resolution data) were added to the XPD reflection list and kept fixed, with the hope that these phases could guide structure solution in the correct direction, (3) a structure
envelope constraint generated from the most reliable phases (i.e., lowest resolution data) was applied to make the electron density maps cleaner. The $R_{map}$-value distributions using this recipe are shown in Figure 3.14. As expected, the $R_{map}$ values of these new pCF electron density maps improved. Most of the maps obtained would be interpretable and a few of them would be suitable for automatic interpretation.

Further improvement can be achieved by performing a second series of pCF runs using one of the best density maps (according to $R_{SF}$ value, see equation 3.1) as a "Model map" to generate new phase sets for all reflections (Figure 3.14). With these new pCF runs, all 50 maps have $R_{map}$ values below 45%, and most of them can be interpreted directly. It seems that the "Model-map" option works better for "repairing" density maps than for generating initial phase sets.

![Figure 3.14: Correctness of the electron density maps ($R_{map}$) generated by pCF for TNU-9 with (a) no phase information included; (b) 3 Å HRTEM phases used; (c) the optimized strategy of including phases: (1) a model map generated from all the HRTEM phases (1.5 Å) was used to calculate starting phase set for all input reflections, this phase set was allowed to change up to 10% by a random fashion; (2) all 3 Å HRTEM phases were directly added to the XPD reflection list; (3) a structure envelope was generated from all 6 Å phases from all three HRTEM images, the envelope constraint was first imposed after 10 cycles and then every 10 cycles thereafter. Further improvement can be achieved by a second series of pCF runs using one of the best density maps (according to $R_{SF}$ value) as a "Model map" to generate a new phase set for all input reflections. The results are shown in (d).]

It appears that even though the same phase information is used, the different ways of exploiting this information can affect the structure solution significantly.
3.6 SSZ-74

The high-silica zeolite SSZ-74 has been shown to be a good catalyst for a wide variety of reactions (Zones, Burton & Ong, 2007). The elucidation of its framework structure, however, proved to be difficult. Like many zeolitic materials, SSZ-74 is polycrystalline, so its structure had to be derived from powder diffraction data and/or using electron microscopy techniques.

The synchrotron XPD pattern could be indexed on a monoclinic unit cell ($a = 20.507$ Å, $b = 13.394$ Å, $c = 20.099$ Å, $\beta = 102.2^\circ$), and the systematic absences indicated that the most probable space groups were $C2/c$ or $Cc$. Initial attempts to solve the structure from these data proved to be very difficult, so electron microscopy data was included. In contrast to TNU-9, where HRTEM images along three different directions were obtained, only one was available for SSZ-74 (Figure 3.15). Indexing of the power spectrum generated from HRTEM image indicated that it had been taken along the [110] zone axis.

Using an amorphous area close to the thin region of the crystal, the defocus value could be determined by measuring the "Thon ring" positions in the power spectrum (Figure 3.16 (a)). The CTF was then calculated using this defocus value (Figure 3.16 (b)) and the image was corrected using the CIP program CRISP.

There were only two possible plane group symmetries for this projection, i.e. $p2$ (corresponds to $C2/c$) and $p1$ (corresponds to $Cc$). The phase residual provided by CRISP for the plane group $p2$ was about $21^\circ$, which indicated this projection symmetry was possibly true. However, since only 29 low-resolution (about 3.3 Å) phases could be extracted and used for this calculation, this $R$ value is not completely persuasive. Both $p2$ and their original $p1$ phases are listed in Table 3.8.
Figure 3.16: The CTF of the HRTEM image of SSZ-74. The defocus value was determined by measuring the "Thon ring" positions in the power spectrum shown in (a), this value was used to calculate the CTF curve shown in (b).

Table 3.8: Structure factors extracted from HRTEM image of SSZ-74 along [110] zone axis.

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</table>
Assuming the space group \( C2/c \), intensities were extracted from the XPD pattern using the program \textit{EXTRACT} in the \textit{XRS-82} suite of programs. Attempts to solve the structure by adding these 29 HRTEM phases to the XPD reflection list in the \textit{pCF} algorithm were then performed. As might be expected, the electron density maps from these \textit{pCF} runs were not much different from those generated from the XPD data alone. This is similar to the TNU-9 case in which 24 phases from low resolution (6 Å) data were used. The small number of phases are not sufficient to improve the \textit{pCF} runs significantly. A structure envelope, constructed using all 29 phases and assuming \( p2 \) symmetry (see Figure 3.17), was then used.

![Figure 3.17](image.png)

\textbf{Figure 3.17:} Structure envelope generated from the HRTEM image of SSZ-74 along [110] zone axis. Inner surface are highlighted in yellow, and outer surface in pink. Densities surrounded by the inner surface are considered to be 0.

Although \( C2/c \) symmetry was assumed for the intensity extraction, the symmetry-equivalent reflections were expanded and treated independently of one another in the \textit{pCF} algorithm. Initially, 50 \textit{pCF} runs of 600 cycles each were performed in default mode, and no symmetry was imposed during the \textit{pCF} runs because the space group was not clear. The 29 input HRTEM phases were kept for the first 150 cycles and allowed to change freely afterwards. The histogram-matching procedure and the structure envelope constraint were both started in the 10th cycle and then repeated every 10 cycles. The method proposed by Palatinus and van der Lee (2008) for determining the space group symmetry from the final electron density map generated in \( P1 \) was also applied. In 50 \textit{pCF} runs, the space group \( Cc \) was found 39 times, but \( C2/c \) was not found at all. Furthermore, all of the 10 best density maps (according to \( R_{SF} \) value) showed \( Cc \) symmetry. This is a strong indication that the non-centrosymmetric space group \( Cc \) is the correct one.
Another 50 \textit{pCF} runs were then performed with \textit{Cc} symmetry imposed, and the previous best density map was used as a "Model map" to generate new starting phase sets. These phases were allowed to change up to 10\% in a random fashion. Although the electron density maps generated in \textit{P1} were already quite good, those obtained from the second series of \textit{pCF} runs with symmetry averaging were better. The 10 best maps were averaged, and from this map, the positions of all 23 Si atoms and many O atoms in the asymmetric unit could be determined directly (Figure 3.18).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3_18.png}
\caption{Powder charge-flipping (\textit{pCF}) electron density map generated for SSZ-74. The refined framework structure is overlaid for comparison (Si: yellow; O: red).}
\end{figure}

\section{3.7 Conclusions}

Crystallographic phase information extracted from HRTEM images has proven to be extremely useful in structure determination. In this chapter, the extremely complex structures of the zeolites TNU-9 and SSZ-74 were used to investigate how to exploit the HRTEM phases of different quality to maximum effect. Detailed analysis of HRTEM images showed that the most reliable phases extracted from thin regions of a crystal are those of low-resolution, strong reflections. The phases derived from HRTEM images taken along a zeolite’s channel direction can be improved significantly with the single-crystal charge-flipping algorithm, provided that the optimal input parameters are used. If high quality HRTEM images along different zone axes are available, the phase information can be used beneficially to complement XPD data in reciprocal space. If, however, only a few phases can be extracted from a single HRTEM image, using
these phases in reciprocal space proved to be less useful. In such cases, a real-space structure envelope generated from these phases was found to be more valuable for structure solution. The dual-space structure-solution algorithm charge flipping, has been optimized for using datasets from these two sources. In both cases (TNU-9 and SSZ-74), a simple inclusion of all HRTEM phases into powder charge-flipping did not yield the correct structure. However, the correct structures could be found in a straightforward manner when the HRTEM phase information was used through an optimized strategy.
Chapter 4

Combining PED and XPD Data for Structure Determination

4.1 Introduction

Although it has been shown that high-resolution transmission electron microscopy (HRTEM) images can be extremely useful in the structure determination process (Gramm et al., 2006; Baerlocher, Gramm et al., 2007; Baerlocher et al., 2008), they are not always easy to obtain. To circumvent this problem, the feasibility of using another, less demanding, electron microscopy technique, namely precession electron diffraction (PED), to augment the X-ray powder diffraction data was explored.

As mentioned in Chapter 2, the key problem in structure determination from X-ray powder diffraction (XPD) data arises from the fact that reflections with similar 2θ values, though unrelated from a structural point of view, overlap in the powder pattern. As a result, their individual intensities are ambiguous, and this hinders structure solution. In this study, we consider the viability of using one or more single-crystal PED patterns (free of reflection overlap) to supplement the high-resolution XPD pattern.

Two possibilities for combining the information from the two sources were investigated. In one case, the PED data were simply used to identify the weak reflections in selected projections, with the hope that this information would lead to a more correct partitioning of some of the overlapping reflections in the powder pattern. In the second case, the single-crystal charge-flipping structure solution algorithm of Oszlányi and Sütő (2004, 2005, 2008) was applied to the two-dimensional PED data for selected zones to obtain phases for the contributing reflections. These phases were then included in the starting phase sets for the application of the powder charge-flipping (pCF) algorithm (Baerlocher, McCusker & Palatinus, 2007) to the XPD data. This approach resembles that used previously for the combination of XPD data with phases derived from HRTEM images (see Chapter 3).

To develop the two approaches, both simulated and experimental data for the moderately
complex zeolite ZSM-5 (van Koningsveld et al., 1987; Pnma; \(a = 20.022 \text{ Å, } b = 19.899 \text{ Å, } c = 13.383 \text{ Å, } \) 38 atoms in the asymmetric unit, 288 atoms in the unit cell) were used. The methods were then tested using experimental data for the very complex zeolite TNU-9 (Gramm et al., 2006; C2/m; \(a = 28.222 \text{ Å, } b = 20.012 \text{ Å, } c = 19.493 \text{ Å, } \beta = 92.3^\circ\)).

4.2 Experimental

Samples of as-synthesized ZSM-5 and calcined TNU-9 were used for the powder diffraction data collections. The initial crystal sizes in the powders were estimated by LEO 1530 scanning electron microscope (SEM) (Figures 4.1 and 4.2). For the electron diffraction measurements, both were calcined and prepared using the grinding-dispersing approach (Zvyagin, 1967, pp.66-67; Pan, 1996): they were crushed using a mortar and pestle, dispersed in ethanol to form a suspension mixture, and disaggregated with ultrasound. A few drops of the suspension were then put on a TEM grid with holey carbon film and allowed to dry. Samples from various suspension concentrations were prepared and checked by SEM, and the most suitable one (i.e., with less aggregation and optimum crystal size) was selected for further investigation. Experience shows that the smaller the crystallities, the more dilute the suspension should be.

Because the typical morphology of microcrystallites prepared by the grinding-dispersing approach is wedge-shaped (Figure 4.3(a)), the thinnest region is close the edge of the crystal. Such regions were selected for recording the electron diffraction patterns (Figure 4.3(b)).
Figure 4.3: TEM bright field image of ZSM-5 microcrystallite. (a) The wedge-shaped morphology of a ZSM-5 microcrystallite prepared by the grinding-dispersing approach. (b) The thinnest region of the microcrystallite shown in (a) selected by the diffraction aperture.

The experimental electron diffraction patterns were collected at 300 kV ($\lambda = 0.0197$ Å) on a Philips CM30 electron microscope equipped with a side-entry goniometer stage (tilt range ± 25°), a ‘SpinningStar’ precession unit (NanoMegas, Belgium) and a 16 bit Gatan 794 CCD camera. A beam stop was used to avoid saturation and exposure times were selected such that the diffraction intensities lay within the linear response range of the detector. The adjustment of the eucentric height and sample focus was followed by an alignment of the ‘SpinningStar’ scanning coil control at two pivot points, which correspond to the image and diffraction planes of the objective lens. The patterns used for the tests were recorded with a precession angle smaller than 1.6°, because an appreciable amount of spot splitting and spiral distortion appeared in the pattern when higher precession angles were used.

The intensities were extracted using the program ELD (Zou et al., 1993a) in the CRISP software package (Hovmöller, 1992), and the "shape-fitting" method (Zou et al., 1993b) implemented in ELD was used to estimate the intensities of the electron diffraction spots. Phases from PED projections were derived using the single-crystal charge-flipping algorithm in the program Superflip.

The high-resolution synchrotron powder diffraction data for ZSM-5 were collected on the Swiss Norwegian Beamline (SNBL) at the ESRF in Grenoble ($\lambda = 1.1011$ Å). The XPD data of TNU-9 used here is the same as that used in the previous chapter. The intensity extractions were performed using the program EXTRACT in the XRS-82 suite of programs.

The powder charge-flipping ($pCF$) algorithm implemented in the program Superflip was used for structure solution. Structure factors for the simulations were calculated using the structural data published by van Koningsveld et al. (1987) for ZSM-5 and by Gramm et al. (2006) for TNU-9.
Chapter 4. Combining PED Data with XPD Data

4.3 PED Data Reduction and Evaluation

Experimental PED patterns of ZSM-5 were recorded along four zone axes ([010], [01\bar{2}], [02\bar{T}] and [10\bar{T}]) (Figure 4.4). Although the crystallite thicknesses for the PED measurements spanned

![Figure 4.4: Precession electron diffraction patterns for ZSM-5 (left) and their simulated counterparts (right) for the [010], [01\bar{2}], [02\bar{T}] and [10\bar{T}] projections.](image)
a large range because of the wedge-shaped morphology (Figure 4.3), the thickest sides were estimated to be less than 100 nm.

For each PED pattern, reflection intensities of Friedel pairs were compared. The pattern showing the least discrepancy between Friedel equivalents was selected for subsequent analysis (monitored by \( R_{\text{Friedel}} = \sum |I_{hkl}| - |I_{-h,-k,-l}|/\sum |I_{hkl}| \)). Since there were a number of missing reflections in the pattern because of the large beam stop, the next step of data reduction was to apply a constraint such that

\[
I_{hkl} = I_{-h,-k,-l} = \max (I_{obs}^{hkl}, I_{obs}^{-h,-k,-l})
\]  

(4.1)

The initial estimations of the symmetries of the four PED patterns (Figure 4.4, left) were \( p2gg \) for the \([010]\) projection and \( p2mm \) for the other three projections. This can be checked either by a qualitative visual inspection, or quantitatively, by comparing the intensities of possible symmetry-equivalent reflections (Figure 4.5). Note that as a result of Friedel’s law, an inversion center is always present in the ED pattern, so if a projection contains a 2-fold axis or a mirror plane, the resulting ED pattern will have the symmetry \( 2mm \). These symmetry-equivalent reflection intensities were then averaged for further analysis.

![Figure 4.5: Comparison between intensities of the symmetry-equivalent reflections in the [010], [012], [021] and [101] projections.](image)

59
Chapter 4. Combining PED Data with XPD Data

For simplicity, the structure-factor amplitudes were calculated using the kinematical assumption, and no geometrical corrections were applied (see Chapter 2, Section 2.3.3). The PED amplitudes were scaled to the simulated ones by applying a least-squares fit to the data. Although the experimental patterns look qualitatively similar to the simulated ones (Figure 4.4), there is considerable scatter in the amplitudes (Figure 4.6). Take the [010] projection (Figure 4.6) for example. The $R$ value for the agreement between the two is only 0.51 ($R = \sum \frac{|F_{hkl}^{\text{calc}} - k|F_{hkl}^{\text{obs}}|}{\sum |F_{hkl}^{\text{calc}}|}$, where $k$ is a scale factor determined by least-squares calculation). Similar scatter is observed in ten other [010] patterns collected over a period of time under different conditions. Data collected with a precession angle of $1.2^\circ$ appear to be slightly better ($0.51 \leq R \leq 0.53$) than those collected with a precession angle of $0.8^\circ$ ($0.55 \leq R \leq 0.57$). The reproducibility is also better with the higher precession angle ($0.15 \leq R_{\text{merge}} \leq 0.17$ at $1.2^\circ$ versus $0.19 \leq R_{\text{merge}} \leq 0.22$ at $0.8^\circ$).

Figure 4.6: Comparison between experimental (PED) and calculated structure factor amplitudes for ZSM-5 along the [010], [01\overline{2}], [02\overline{1}] and [10\overline{1}] projections. The $R$ values for these 4 projections are 0.51, 0.42, 0.38 and 0.45, respectively.
4.4 Weak Reflection Elimination

Although it was hoped initially that all the PED data could be used directly to supplement the XPD data, this proved not to be possible, because (1) the PED intensities are still distorted from the kinematical case (see Figure 4.6), and (2) the atomic scattering factors (and therefore the structure factors) for X-rays and electrons are not strictly proportional to one another (see for example Figures 4.7 and 4.8). However, the scattering factors do show the same general trend. Dorset et al. (1998) exploited this similarity to scale a set of SAED patterns to one another using an XPD pattern as a reference. In our case, it was reasoned that reflections that are weak in the ED pattern should also be weak in the X-ray diffraction pattern, at least for materials with a single dominant scatterer such as organic materials and zeolites (Figure 4.8).

Figure 4.7: Atomic scattering factors of Si and O for X-rays and electrons.

Figure 4.8: Comparison between the calculated structure-factor amplitudes of ZSM-5 for X-rays and electrons.
A very simple and conservative procedure was applied to take advantage of the PED data. They were used to identify the weak reflections in a projection, and then these reflections were eliminated from the XPD intensity extraction. Generally, the intensity ratios of overlapping reflections are set to one (equipartitioning), so weak reflections in an overlap group can be assigned medium or even large structure-factor amplitudes. It was hoped that by eliminating these weak reflections from consideration, a more correct partitioning of the remaining reflections in the group would be obtained (Figure 4.9).

![Equi-partitioned, Correct partitioned, Re-partitioned](image)

**Figure 4.9:** The effect of weak reflection elimination on intensity extraction. The true intensities of three reflections (160, 130, 10) under a single peak are shown in the centre. On the left is a conventional equi-partitioning (100, 100, 100), and on the right, equi-partitioning after the weak reflection has been eliminated (150, 150, 0).

Initial tests of this weak reflection elimination (WRE) approach were performed on the zeolite ZSM-5 using both simulated and experimental PED patterns along four zone axes ([010], [012], [02T] and [10T]). In order to identify which reflections should be considered to be weak, an amplitude threshold had to be defined. It is important to note that, unlike the simulated data, the experimental PED intensities derived from different projections are not on the same scale, because they are taken with different illumination conditions, exposure times and crystal thicknesses (Gemmi, Calestani & Migliori, 2002). Therefore, it is not sensible to set the same threshold value for all four data sets. Attempts to scale the patterns to one another using common reflections were not very satisfactory, so it was considered to be better to treat each projection independently. The threshold for each projection was chosen for both the simulated and the experimental data by examining a plot of the amplitude distribution (Figure 4.10) and selecting a value such that the reflections to be eliminated were in the range of the tail of the profile. To evaluate how sensitive the structure solution is to the choice of this threshold, ten values ranging from 10 to 100% of the average amplitude were tested. For each threshold, the reflections defined to be weak were eliminated from the $hkl$ list and the remaining reflection intensities were re-extracted. Each of the 20 modified data sets (ten simulated and ten experimental) were then used as input for 100 runs of the $pCF$ algorithm.
4.4 Weak Reflection Elimination

Figure 4.10: Experimental (PED) and calculated structure-factor amplitudes for the [010] projection arranged in ascending order. The average $|F_{hkl}|$ value for the PED data is indicated with a dashed line. Plots for the other three projections shown in Figure 4.4 are similar.

To evaluate the correctness of the electron density maps produced in the $pCF$ runs, the ten best maps according to the $R_{SF}$ values (equation 3.1) were compared with a reference map calculated from the true structure, and an average of the $R_{map}$ values (equation 3.2) was calculated (Figure 4.11). The correctness of the maps was found to be substantially better for threshold values within the 30–80% range and relatively stable within this range. It is apparent from these comparisons that the WRE method can improve the electron density maps produced by Superflip significantly. In contrast to $pCF$ electron density maps generated without WRE, those generated with WRE (30–80% range) revealed the positions of all 12 Si and 26 O atoms in the asymmetric unit clearly. It appears that even this simple modification of the data set has a significant impact on the structure solution.

Figure 4.11: Effect of the weak reflection threshold value (% of the average $|F_{hkl}|$ for both PED and calculated data) on the correctness of the electron density maps ($R_{map}$) generated by $pCF$. The point for each threshold value reflects the average $R_{map}$ for the ten best $pCF$ maps (lowest $R_{SF}$ values).
4.5 Phase Retrieval from PED Data

Precession electron diffraction data have already been used in combination with direct methods (Weirich, Portillo et al., 2006) and maximum entropy methods (Dorset et al., 2007; Gilmore et al., 2008a,b) to determine two-dimensional structures. This is an indication that the reflection intensities are reliable enough and have sufficient resolution for the phasing process to succeed. For three-dimensional structures, of course, a single projection is insufficient to solve the structure, but it was reasoned that if the phases for selected projections could be determined from PED data, these phases could be used in combination with X-ray powder diffraction data in the same way as those derived from electron microscopy images. In this study, the charge-flipping algorithm (2004, 2005) rather than direct methods or maximum entropy methods was used for the phase retrieval step.

The simulated and experimental electron diffraction data for ZSM-5 that were used to develop the weak reflection elimination approach were also used for these tests. The phase retrieval procedure was extremely simple and automatic. 100 charge-flipping runs, each with 500 iterations, were performed on each of four two-dimensional data sets (289 reflections for the [010] projection, 162 reflections for [01\(\bar{2}\)], 124 reflections for [02\(\bar{1}\)] and 246 reflections for [10\(\bar{1}\)]). For simplicity, the correct structure was used to generate a 3-dimensional reference map to align the charge-flipping potential maps. In this way, all the potential maps had the same origin position as the reference map. For each projection, the five potential maps with the best \(R_{SF}\) value were averaged. Then a Fourier transform was applied to calculate the phases of the corresponding reflections. Even though the symmetry of the map at this stage was \(P1\), the space-group symmetry was imposed for this transformation to ensure that only phases consistent with a centrosymmetric space group were obtained. A comparison of these phases with the correct ones is given in Table 4.1.

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<th>[10(\bar{1})] zone</th>
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</tr>
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<td>&gt; 5</td>
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<td>133/203</td>
<td>47/69</td>
<td>46/69</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>191/289</td>
<td>166/289</td>
<td>96/162</td>
<td>90/162</td>
</tr>
<tr>
<td>(\sum) amplitudes with correct phases / (\sum) all amplitudes</td>
<td>83%</td>
<td>73%</td>
<td>74%</td>
<td>74%</td>
</tr>
</tbody>
</table>

Table 4.1: Number of correct phases derived from the charge-flipping runs on electron diffraction data for ZSM-5.

It is readily apparent from Table 4.1 that the phases of the stronger reflections are more likely to be correct than are those of the weaker reflections. If the total amplitude that is correctly
phased is considered, this is more than 70% for all four zones, even for the experimental data. These numbers are similar to those obtained for phases derived from HRTEM images. The potential map generated from the PED amplitudes and the charge-flipping phases for the [010] projection of ZSM-5 is shown in Figure 4.12. It should be mentioned that a previous study on the determination of the phases for the [010] projection of ZSM-5 from electron diffraction data is somewhat puzzling. Phase determination from 100 kV SAED data with direct methods worked reasonably well (Dorset, 2003a), while the analyses of 300 kV PED data with the maximum entropy program MICE were less satisfactory (Dorset et al., 2007) until histogram matching was used to sort the trial solutions (Gilmore et al., 2008a). In our study, however, it can be seen from the projection of the structure that is overlaid in Figure 4.12 that the major features are reproduced in the potential map. Thus, it would appear that the phases from PED projections might be as useful as those from an HRTEM image.

To test this, the 594 phases derived from the four PED charge-flipping runs were included in each starting phase set of 3042 reflections for $pCF$ runs using the XPD data. All phases were allowed to change during the procedure. 100 $pCF$ runs of 500 iterations were performed. As might be expected, the additional phase information resulted in electron density maps much closer to the true one. The final $R_{\text{map}}$ values dropped from 56.7% with just random phases in the starting phase set to 18.0% with the inclusion of the phases derived from the PED data.

![Figure 4.12: Two-dimensional density map for the [010] projection generated from the PED structure-factor amplitudes and charge-flipping phases. The corresponding framework structure model is overlaid in the left hand for comparison (Si, green; O, red).](image)
4.6 Combination of the Two Methods

To evaluate the effect of combining the weak reflection elimination and phase retrieval approaches, a series of tests using one to four PED data sets were performed. The weak reflection threshold was simply chosen to be half the average amplitude. The results of these pCF runs are summarized in Table 4.2. It is clear from the electron density maps generated with and without the PED data that the PED data contribute significantly to the correctness of the map. Not only are all the atoms visible in the map, but their electron density ratios also better reflect the different sizes of Si and O, so (automatic) interpretation becomes easier (Figure 4.13).

Table 4.2: Comparison of pCF runs using both WRE and phase information for ZSM-5.

<table>
<thead>
<tr>
<th>PED data used</th>
<th>Number of weak reflections eliminated</th>
<th>Number of phases supplied</th>
<th>$R_{map}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>0</td>
<td>56.7</td>
</tr>
<tr>
<td>[010]</td>
<td>136</td>
<td>79</td>
<td>34.2</td>
</tr>
<tr>
<td>[010] + [012]</td>
<td>227</td>
<td>109</td>
<td>33.9</td>
</tr>
<tr>
<td>[010] + [012] + [02T]</td>
<td>292</td>
<td>138</td>
<td>24.7</td>
</tr>
<tr>
<td>[010] + [012] + [02T] + [10T]</td>
<td>412</td>
<td>182</td>
<td>16.7</td>
</tr>
</tbody>
</table>

Figure 4.13: Powder charge-flipping electron density maps for ZSM-5 generated (a) using XPD data alone, and (b) using XPD data and four PED patterns (combined weak reflection elimination and phase retrieval). The framework structure of calcined ZSM-5 is overlaid for comparison.

4.7 Test Example

As mentioned in Chapter 3, the structure of TNU-9 ([Si$_{192}$O$_{384}$]) is one of the most complex zeolite structures known. It was originally solved by combining high-resolution XPD data with phases derived from HRTEM images in the zeolite-specific structure solution program FOCUS (Grosse-Kunstleve et al., 1997). To test the methods described in the previous sections, the
structure was re-investigated using the $pCF$ algorithm supplemented with information derived from PED data.

Initial attempts to solve the structure using XPD data alone were not successful. The electron density maps with the best $R_{SF}$ values showed neither clear pores nor framework atom positions (Figure 4.14a). Comparison of this map with the correct one yields an $R_{map}$ value of

![Figure 4.14: Powder charge-flipping electron density maps for TNU-9 generated (a) using XPD data alone, (b) using XPD data and five PED patterns (combined weak reflection elimination and phase retrieval), and (c) using the map in (b) as a seed for a second $pCF$ run. The framework structure of calcined TNU-9 is overlaid for comparison.](image-url)
Chapter 4. Combining PED Data with XPD Data

78.8%. PED data were then used for weak reflection elimination and phase retrieval. For each PED projection, a plot of the amplitude distribution was examined to evaluate the appropriate amplitude threshold for WRE, and in each case, a value of half of the average amplitude was chosen. Using the procedure described in Section 4.4 and 4.5, weak reflections were eliminated from the XPD hkl list and the intensities of the remaining reflections re-extracted, and phases were derived from different PED projections using the single-crystal algorithm in Superflip.

A series of pCF tests combining these data showed that the structure could be solved when five PED patterns ([001], [100], [102], [10\bar{1}] and [021] projections) were used (Figure 4.15). With these five patterns, 323 weak reflections could be eliminated and 176 phases derived. Then, 100 pCF runs of 600 iterations each were performed. The input phases were enforced for the first 50 iterations and were then allowed to change like the rest. The electron density maps with the best $R_{SF}$ values showed significant improvement over those generated using the XPD data alone. The peaks in the electron density maps were more spherical and the main features of the pore system appeared (Figure 4.14b, $R_{map} = 51.3\%$). Although the best map showed the positions of 23 of the 24 Si atoms in the asymmetric unit and many of the O atoms, the height of the peaks did not reflect the relative scattering powers of Si and O. Therefore, this map was used as a seed in Superflip to generate 100 new starting phase sets by allowing the phases calculated from the seed map to vary by up to 20% in a random fashion. The best electron density maps resulting from this second series of pCF runs showed all 24 Si atom positions and more realistic electron densities for Si and O (Figure 4.14c, $R_{map} = 39.2\%$).

Figure 4.15: Precession electron diffraction patterns for TNU-9 for the [001], [100], [102], [10\bar{1}] and [021] projections.
Although the solution of the structure of TNU-9 was not quite as simple as that of ZSM-5, the additional information from the PED data did make structure solution possible. The increased difficulty can probably be attributed to three factors: (1) the complexity of the structure (twice as many atoms in the unit cell), (2) the degree of reflection overlap (92.6% for TNU-9 versus 87.9% for ZSM-5) and (3) the lower resolution of the X-ray data (1.15 Å for TNU-9 versus 0.99 Å for ZSM-5). The charge-flipping algorithm is known to be particularly sensitive to the resolution of the data. Nonetheless, the structure could be solved in a relatively straightforward manner.

4.8 Conclusions

By supplementing X-ray powder diffraction data with precession electron diffraction data, it is possible to facilitate the solution of the crystal structures of polycrystalline materials. Such PED data are considerably easier to obtain than high-resolution electron microscopy images and appear to contain similar information. PED data can be used to identify weak reflections in the X-ray powder diffraction pattern and thereby improve the reflection intensity extraction, and/or to obtain phase information for those reflections in the projection. The amount of correct phase information retrieved by applying a simple charge-flipping procedure to the two-dimensional single-crystal PED data is comparable to that that can be derived from an HRTEM image. In this initial investigation, we wanted to keep things as simple as possible, so no corrections were applied to the PED data. However, studies evaluating the effect of applying different corrections to the data are in progress. It should also be mentioned that at the time of developing these methods, we used the correct structures as references to shift the origins of the 2-dimensional potential maps. A further investigation on how to locate the origins of 2-dimensional maps without using a correct model is discussed in Chapter 5.

In this chapter, the application of these two approaches to two zeolite structures of different complexities using the powder charge-flipping algorithm in the program Superflip have been discussed. The methods are generally applicable (i.e., not zeolite specific), so it should be possible to apply them to many other polycrystalline materials. Furthermore, introducing information from PED data to the structure solution procedure is not restricted to charge flipping. It could also be used to advantage in other programs (e.g., in the form of better intensities in a direct-space global-optimization program or as starting phases for direct methods trials). The precession electron diffraction technique offers a relatively simple route to valuable information that can be used to complement that in a powder diffraction pattern.
Chapter 5

2D Images Derived from XPD Data and used for Structure Determination

5.1 Introduction

The combination of X-ray powder diffraction (XPD) and electron microscopy (EM) techniques has been shown to be a powerful one for determining the structures of polycrystalline materials that resist solution by more conventional methods (McCusker & Baerlocher, 2009; Sun et al., 2009). In particular, it has been demonstrated that phase information derived from high-resolution transmission electron microscopy (HRTEM) images can be extremely useful in the structure determination process. However, such images are not always easy to obtain. Therefore, the possibility of using the less-demanding, precession electron diffraction (PED) technique in place of HRTEM was investigated (Xie, Baerlocher & McCusker, 2008). This was discussed in the previous chapter.

Although the reflection intensities measured in a PED experiment are less affected by multiple scattering than are those obtained using the more conventional selected area electron diffraction technique, they are still not completely kinematical (Own, Marks & Sinkler, 2006). Even so, application of the charge-flipping algorithm (Oszlányi & Sütő, 2004; 2005) to these less-than-ideal data was found to yield phase information comparable to that that can be derived from a HRTEM image. Reasoning that the deviations of PED reflection intensities from the ideal ones are comparable in magnitude (though for different reasons) to those of reflection intensities derived from XPD data (see Figure 5.1), we wondered if the charge-flipping algorithm would yield similar results if XPD structure factor amplitudes for a specific projection were used in place of the PED amplitudes. While the reflection intensities measured in a powder diffraction experiment are kinematical, they are often ambiguous because reflections with similar diffraction angles (d-spacings) overlap and their relative contributions to the total intensity cannot be determined. Therefore, the intensity measured for a group of overlapping reflections is usually simply equipartitioned over all contributing reflections. If such reflection intensities
derived from an XPD pattern could be used in place of those from a PED measurement, the advantages would be considerable. Not only would the PED experiment itself become superfluous, but the projections could be selected arbitrarily and would not be dependent on finding a crystallite with the appropriate orientation. In other words, the more complicated electron microscopy experiments, whether HRTEM or PED, could be replaced with a very simple powder diffraction data collection.

Figure 5.1: Comparison between calculated and experimentally measured structure factor amplitudes for the [100] projection of TNU-9. (a) PED and (b) XPD data. The experimental amplitudes were scaled to the calculated ones by applying a least-squares fit to the data. The correlation coefficient between the experimental and calculated structure factors is 0.88 for the PED and 0.85 for the XPD data.

To test this hypothesis, an approach analogous to the one used previously for PED data was explored. The single-crystal, charge-flipping, structure-solution algorithm was applied to two-dimensional subsets of the reflection intensities extracted from the full powder diffraction
5.2 Experimental

The data of TNU-9 and SSZ-74 that were used here are the same as those used in previous chapters. High-resolution XPD data of calcined IM-5 were collected on the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The HRTEM images of IM-5 were taken by Zhanbing He in Xiaodong Zou’s group at Stockholm University (Baerlocher et al., 2007).

The XPD intensity extractions were performed using the program EXTRACT in the XRS-82 suite of programs. All calculations involving the charge-flipping algorithm were performed using the program Superflip.

5.3 Phase retrieval using 2D X-ray powder diffraction data

The procedure used to retrieve the phases from the two-dimensional X-ray powder diffraction (2D-XPD) data was quite simple. First, the full set of reflection intensities was extracted from the powder diffraction pattern in a standard manner using the Le Bail method (Le Bail, Duroy & Fourquet, 1988) with an equipartitioning of overlapping reflections. Then all reflections belonging to the same zone were selected and phase retrieval was performed using Superflip. This algorithm has proven to be quite effective not only with X-ray and neutron diffraction data (Oszlányi & Sütő, 2008; and references therein), but also with two- (Wu & Spence, 2005; Spence et al., 2008; Xie, Baerlocher & McCusker, 2008; Eggeman, White & Midgley, 2009) and three-dimensional (Mugnaioli, Gorelik & Kolb, 2009) electron diffraction data.

Initial tests were performed with the zeolite TNU-9. First, reflection intensities were extracted from the measured powder diffraction pattern assuming the space group $C2/m$. Then 2D-XPD subsets corresponding to twelve arbitrarily selected zones ([001], [010], [100], [01T], [10T], [1T0], [01Z], [02T], [10Z], [20T], [1Z0] and [2Z0]) were taken from this list. For comparison, calculated single-crystal structure factor amplitudes were also generated for each zone. A straightforward charge-flipping phase-retrieval procedure was then applied to both the measured
and the simulated data. Each 2D-XPD dataset was input to the program Superflip with one hundred runs (each with a different seed for the random phase generation) of 300 cycles each. Then for each projection, the ten electron density maps with the best Superflip $R$ values ($R_{SF}$), defined in equation 3.1, were averaged. In these initial tests, the 2D maps were matched to a calculated 3D reference map to ensure that all maps had the same origin before they were summed. This point is revisited in Section 5.8. Finally, a Fourier transform was applied to this averaged map to calculate the phases of the contributing reflections. Because the Fourier transformation was performed in $p1$ (i.e. no symmetry assumed), the phases were not restricted to $0$ and $\pi$ as they would have been if the space group information ($C2/m$) had been enforced, so they were then converted in a subsequent step to $0$ or $\pi$, whichever was closest. A summary of the phases retrieved from the projections along the channel direction $[010]$ and along the non-channel directions $[100]$ and $[001]$ is given in Table 5.1. For comparison, the phases derived from HRTEM images (see Chapter 3) and from PED data (see Chapter 4) are also included in the table.

It is readily apparent from Table 5.1 that the number of correct phases derived from 2D-XPD data is similar to that obtained from PED data. Indeed, the results in both cases are almost as good as those obtained for calculated single-crystal data. It should be noted that the resolution of 2D-XPD and PED data included here is 1.15 Å, while the resolution of HRTEM data is only 1.50 Å, so the total number of reflections in the 2D-XPD and PED datasets is about twice that from the HRTEM images. Even so, the correctness of the phases derived from 2D-XPD and PED data is only slightly worse than that of the phases extracted from HRTEM images.

For all four types of data, whether 2D-XPD, HRTEM, PED or simulated, the phases of the stronger reflections are much more likely to be correct than are those of the weaker ones. For example, more than 85% of the reflections with calculated amplitudes above 800 are phased correctly, while only slightly more than 50% of the reflections with amplitudes below 200 are. Even though incorrect amplitudes, whether from PED or from XPD data, were used for the phase retrieval, it is the reflections that are in fact stronger (i.e. higher calculated amplitudes) that are most likely to be phased correctly.

It had been expected that a projection along a channel direction might be phased more correctly (as is the case for HRTEM images), because the contrast is higher and there are larger regions of zero electron density. However, there is no strong indication that the effectiveness of the phase retrieval process is dependent on the projection selected.

### 5.4 Structure Determination

To evaluate the effect of using the phases retrieved from 2D-XPD data in structure solution, phases derived from three to twelve projections (586-1361 reflections, see Table 5.2) were included in the starting phase sets for $pCF$ runs using the full set of XPD data for TNU-9 (3577 reflections).
Table 5.1: Number of correct phases derived from the charge-flipping runs using calculated single crystal (Calc), 2D-XPD, HRTEM and PED data for TNU-9. Note that the resolution of the HRTEM images is 1.50 Å, while for the other data it is 1.15 Å.

<table>
<thead>
<tr>
<th>Calculated amplitudes (for X-ray)</th>
<th>Number of correct phases/number of reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[010] zone</td>
</tr>
<tr>
<td></td>
<td>Calc 2D-XPD HRTEM PED*</td>
</tr>
<tr>
<td>&gt; 800</td>
<td>18/21 18/21 15/16 3/3 3/3</td>
</tr>
<tr>
<td>&gt; 400</td>
<td>84/95 65/95 33/41 11/14 11/14</td>
</tr>
<tr>
<td>&gt; 200</td>
<td>135/185 129/185 59/76 21/30 22/30</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>205/323 201/323 89/127 75/125 71/125</td>
</tr>
</tbody>
</table>

\[ \sum \text{amplitudes with correct phases} / \sum \text{all amplitudes} \]

76% 69% 77% 70% 71% 71% 76% 71% 77% 72%

* No data available for this projection.
Table 5.2: Phase information from 2D-XPD projections used for the TNU-9 pCF tests.

<table>
<thead>
<tr>
<th>2D-XPD data used</th>
<th>Number of projections</th>
<th>Number of phases derived</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(1) [001] + [010] + [100]</td>
<td>3</td>
<td>586</td>
</tr>
<tr>
<td>(2) (1) + [010] + [100] + [110]</td>
<td>6</td>
<td>1094</td>
</tr>
<tr>
<td>(3) (2) + [010] + [100] + [110]</td>
<td>9</td>
<td>1293</td>
</tr>
<tr>
<td>(4) (3) + [020] + [200] + [210]</td>
<td>12</td>
<td>1361</td>
</tr>
</tbody>
</table>

In the initial tests, the HM/repartitioning step was first imposed after 50 cycles and then every 10 cycles thereafter. The phases derived from the 2D-XPD projections were enforced for the first 50 cycles, and were then allowed to change like the rest. One hundred pCF runs of 500 cycles were performed with these parameters. To monitor the results, the electron density map produced for each run was compared with a reference map generated from the true structure, and an agreement factor $R_{\text{map}}$ (see equation 3.2) was calculated.

With the phase information from different 2D-XPD projections included in the pCF runs, electron density maps much closer to the true one were produced (Figure 5.2). When phases derived from six or more 2D-XPD datasets were included, the $R_{\text{map}}$ values dropped from 80% (with just random phases in the starting phase set) to 50%. In the case of TNU-9, this makes the difference between solving and not solving the structure. While it would be difficult, if not impossible, to extract the structure from the electron density maps generated by pCF without

![Figure 5.2](image-url)

**Figure 5.2:** Correctness of the electron density maps ($R_{\text{map}}$) generated by pCF for TNU-9 with starting phases from 0-12 projections. In each case, the $R_{\text{map}}$ values for the 100 pCF runs are arranged in ascending order. For these tests, the 2D-XPD phases were kept fixed for 50 cycles and histogram matching and repartitioning of the reflections was also started after 50 cycles.
any starting phase information (Figure 5.3 (a)), it might be possible if phases from six 2D-XPD projections were included. The positions of 21 of the 24 Si atoms in the asymmetric unit and many of the O atoms could be located directly from those electron density maps. With the phases from 9 projections, 2 of the 3 missing Si atoms could also be found (Figure 5.3 (b)), and that is certainly sufficient to complete the structure using standard Fourier techniques.

![Figure 5.3](image)

**Figure 5.3:** Powder charge-flipping electron density maps generated for TNU-9. (a) starting with random phases, and (b) starting with phases derived from nine 2D-XPD projections. The refined framework structure is overlaid for comparison.

It should be noted that adding even more 2D-XPD datasets did not necessarily improve the maps further. In fact, for this test with TNU-9, including twelve projections (light blue line in Figure 5.2) actually caused the correctness of the final pCF electron density maps to deteriorate slightly. To evaluate how sensitive the Superflip structure solution was to the choice of input parameters, and to check if the higher $R_{map}$ values obtained with 12 projections were caused by a selection of inappropriate parameters, a series of tests were performed (see Table 5.3).
Table 5.3: \( pCF \) input parameters tested for TNU-9.

<table>
<thead>
<tr>
<th>Datasets with phases included from</th>
<th>3, 6, 9, 12 projections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input phases enforced for</td>
<td>1, 2, 3, 10, 20, 25, 30, 40, 50, 75, 100 cycles</td>
</tr>
<tr>
<td>HM/repartitioning started after</td>
<td>1, 2, 3, 10, 20, 30, 40, 50, 100, 150 cycles</td>
</tr>
</tbody>
</table>

Although some interesting differences were observed in the \( R_{\text{map}} \) values when the numbers of cycles before the initial repartitioning step (1-100) and the release of the imposed phases (1-150) were varied, the general trend shown in Figure 5.2 that 9 projections gave the optimum \( R_{\text{map}} \) values remained unchanged. It seems that there are just too many incorrect phases introduced (and kept) when more projections are used.

In general, keeping the number of cycles for the initial repartitioning and the release of the imposed phases the same seemed to yield the best results. A surprising result was that using a very low number (1-3) improved the overall performance significantly (Figure 5.4). Apparently the phases from the 2D-XPD data are correct enough to allow a sensible repartitioning from the outset, and the correct phases are stable enough to persist without reinforcement.

5.5 IM-5 Test Case

The structure of the zeolite IM-5 was solved originally using the \( pCF \) algorithm in conjunction with high-resolution XPD data and phases derived from HRTEM images (Baerlocher et al., 2007). Inclusion of 95 phases and a structure envelope defining the channels along the [100]
and [001] directions in the initial pCF runs proved to be insufficient for structure solution. Only by calculating the phases for a partial model derived from the HRTEM data and using those as seeds to generate starting phase sets for pCF runs could the structure be solved. To test the method described in the previous sections, this extremely complex structure was re-investigated using the pCF algorithm supplemented with phase information derived from 2D-XPD data.

Reflection intensities were extracted from the powder diffraction pattern in the space group Cmcm, and, as reported in the original paper, attempts to solve the structure using just these amplitudes and random phases were not successful. The electron density maps with the best Superflip $R$ values showed neither clear pores nor framework atom positions. A typical map generated in this way yielded an $R_{map}$ value of 86.1% (Figure 5.5a). Then 2D-XPD subsets for several different projections were generated for phase retrieval (see Table 5.4), and the same procedure as that described in Section 5.4 was followed. The density map generated from the (equipartitioned) XPD amplitudes and the 2D-XPD charge-flipping phases for the [001] projection of IM-5 is shown together with the HRTEM image taken along the same projection in Figure 5.6.

(a)

(b)

Figure 5.5: Powder charge-flipping electron density maps generated for IM-5. (a) starting with random phases, and (b) starting with phases derived from twelve 2D-XPD projections and then using the resulting map as a seed. The refined framework structure is overlaid for comparison.

It can be seen that both the 2D-XPD map and the HRTEM image show similar structural features and that the main pore systems are reproduced in both cases. If the 2D-XPD phases are combined with the correct (calculated) amplitudes, an almost perfect projection is obtained
Table 5.4: Comparison of $pCF$ runs using phase information from 2D-XPD projections for IM-5.

<table>
<thead>
<tr>
<th>2D-XPD data used</th>
<th>Number of projections</th>
<th>Number of phases derived</th>
<th>$R_{map}(%)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>0</td>
<td>86.1</td>
</tr>
<tr>
<td>(1) [001] + [010] + [100]</td>
<td>3</td>
<td>727</td>
<td>71.7</td>
</tr>
<tr>
<td>(2) (1) + [011] + [101] + [110]</td>
<td>6</td>
<td>1205</td>
<td>72.4</td>
</tr>
<tr>
<td>(3) (2) + [012] + [102] + [201]</td>
<td>9</td>
<td>1439</td>
<td>64.4</td>
</tr>
<tr>
<td>(4) (3) + [021] + [120] + [210]</td>
<td>12</td>
<td>1510</td>
<td>60.5</td>
</tr>
<tr>
<td>(5) using the electron density map from (4) as a seed to generate new starting phase sets</td>
<td></td>
<td>52.6</td>
<td></td>
</tr>
</tbody>
</table>

* average of the ten maps with the best Superflip $R$ values.

(Figure 5.6b). This demonstrates that the retrieved phases are in fact very good despite the fact the amplitudes used to derive them suffered from severe overlap. For this projection, 80% of the reflections (234 out of 295) were overlapping with other reflections of the full 3D data set. It should be noted that the resolution of the HRTEM image is only ca. 2.0 Å, whereas that of the 2D-XPD projection is 1.1 Å (295 reflections), and this difference in resolution can be seen quite clearly in Figure 5.6. A similar density map calculated for the [010] projection down the long axis of the crystal structure (using 2D-XPD amplitudes and phases) is given in Figure 5.7 to show that the phase retrieval also works very well for projections without channels.

![Figure 5.6](image_url)

A series of $pCF$ runs using centrosymmetric phases derived from three to twelve projections were performed. The results of these $pCF$ runs are summarized in Table 5.4. Although the best $R_{map}$ value, obtained with 12 projections, is rather high ($R_{map} = 60.5\%$), only 2 of the 24 Si atoms in the asymmetric unit are missing from the electron density map, and the main pore system can be seen clearly. Further improvement could be achieved by applying a second series of $pCF$ runs using the previous map as a seed to generate new starting phase sets (Figure 5.5b, $R_{map} = 52.6\%$). The best electron density maps resulting from this second series of $pCF$ runs
showed all Si atom positions and most of the O atom positions.

![Figure 5.7: Two-dimensional projection of IM-5 along the [010] direction (the 57.2 Å axis of the structure) generated from XPD amplitudes and 2D-XPD phases. The corresponding projection of the framework structure is overlaid for comparison.](image)

It is clear from the electron density maps generated with and without phases from 2D-XPD data, that the 2D-XPD phases contribute significantly to the correctness of the map (Figure 5.5). With this 2D-XPD approach, the structure could be solved without the benefit of information from HRTEM images.

### 5.6 SSZ-74 Test Case

The structure of the zeolite SSZ-74 is a most unusual one because its framework contains perfectly ordered Si vacancies (Baerlocher et al., 2008). With 23 Si atoms in the asymmetric unit, it is one of the most complex zeolite framework structures known. Furthermore, SSZ-74 crystallizes in the non-centrosymmetric space group $Cc$, so it was expected to be a good test for the 2D-XPD approach.

The structure could not be solved from the electron density maps produced in the initial $pCF$ runs starting with random phases (Figure 5.8a, $R_{\text{map}} = 72.3\%$). Data for 2D-XPD projections along the main zone axes (i.e., [001], [010] and [100]) were used to derive 386 non-centrosymmetric phases, by following the procedure outlined for TNU-9 (Section 5.4). When these phases were included in 100 $pCF$ runs of 500 iterations, the electron density maps with the best Superflip $R$ values showed significant improvement over the initial one. The peaks in the electron density maps became more spherical and the main features of the structure appeared. However, these maps still could not be interpreted directly ($R_{\text{map}} = 48.8\%$). Therefore, phases from three more 2D-XPD projections along [01T], [10T] and [1T0] were derived. With the
inclusion of a total of 867 starting phases from these six projections, the electron density map generated by the $pCF$ algorithm was of sufficient quality to allow most of the atoms in the unit cell to be found, and the $R_{map}$ value decreased to 36.2%. This map was then used as a seed in $Superflip$ to generate 100 new starting phase sets, and the best maps from this second series of $pCF$ runs showed all 23 Si atoms and a clearly ordered Si vacancy (Figure 5.8b, $R_{map} = 32.4\%$). Unlike TNU-9 and IM-5, the structure of SSZ-74 is non-centrosymmetric, so in this case no restraints were imposed on the $P1$ phases after the 2D-XPD phase retrieval, though the 2D maps were shifted to a common origin. Apparently, even these non-centrosymmetric phases were correct enough to facilitate the $pCF$ structure solution.

**Figure 5.8**: Powder charge-flipping electron density maps generated for SSZ-74. (a) starting with random phases, and (b) starting with phases derived from six 2D-XPD projections and then using the resulting map as a seed. The refined framework structure with terminal O atoms shown in red is overlaid for comparison. The Si vacancy is circled in (b). For clarity, the level of the electron density has been chosen to show mainly the heavier Si atoms.
5.7 Other Aspects of the 2D-XPD Method

It was not obvious why 2-dimensional subsets of the full XPD dataset should yield more correct phases than the dataset itself, so again a series of tests were carried out. Five charge-flipping runs with identical input parameters but different seeds for random phase generation were performed using the full 3-dimensional XPD data for TNU-9 (with histogram matching and repartitioning after 50 cycles), and for 2-dimensional subsets along the zone axes [001], [010] and [100]. Five hundred cycles were performed for each run. The phases of the reflections belonging to the three projections were retrieved, and the results are shown in Figure 5.9. For all three projections and all $|F_{hkl}|$ thresholds (based on calculated amplitudes), the average correctness of the phases from the 2D-XPD data is significantly better than that from the full 3-dimensional XPD data, with just one exception ([010] projection with structure factor amplitudes larger than 600). Furthermore, the results from the five runs on the full XPD data extend over a markedly larger range of $R_{map}$ values than do those from the 2D-XPD data. It appears that the phases derived from the 2D-XPD data are not only better on average than those derived from the full 3D-XPD data, but also more reproducible.

![Figure 5.9](image)

**Figure 5.9:** Correctness of the phases derived from charge-flipping runs using 2D-XPD data (●) and the full 3D-XPD data (◇) for TNU-9. The symbols indicate the average value of five charge-flipping runs and the bars the associated minima and maxima. The numbers are the number of reflections above the corresponding $|F_{hkl}|$ (calculated) threshold.

When the 2D-XPD approach was first developed, the default mode of *Superflip* was chosen to generate the 2D-XPD maps. That is to say, the key parameter in the charge-flipping algorithm, *i.e.*, the density flipping ratio ($\delta$ value), was determined automatically by the program. However, subsequent tests have shown that the quality of the 2D maps can be improved significantly if the $\delta$ value is set to 0 rather than to the value determined by *Superflip*. As an example, Figure
5.10 shows the difference in $R_{map}$-values (equation 3.2) between the TNU-9 2D-XPD maps generated using different $\delta$ values.

![Graph showing differences in $R_{map}$ values](image)

**Figure 5.10:** Correctness of the electron density maps ($R_{map}$) generated by charge-flipping for TNU-9 with the $\delta$ value determined automatically by *Superflip* and fixed to 0. In each case, the $R_{map}$ values are arranged in ascending order.

Another series of tests were performed using 2D-XPD data with different resolutions. Surprisingly, the $R_{map}$-values improved when lower resolution data were used (Figure 5.11). This may due to the fact that the percentage of the number of reflections that overlap is reduced with lower resolution, so the data are more reliable.

![Graph showing $R_{map}$ values for different resolutions](image)

**Figure 5.11:** Correctness of the electron density maps ($R_{map}$) generated by charge-flipping for TNU-9 with different 2D-XPD data resolution along the [100] (left), [010] (middle) and [001] projections (right). In each case, the $R_{map}$ values are arranged in ascending order.
5.8 The 2D-XPD Origin Definition Problem

In the initial tests of the 2D-XPD method, described in the previous sections, the correct structure was used to generate a 3D reference map to align the 2D electron density maps from the 2D-XPD charge-flipping runs. In this way, all the 2D maps generated had the same origin as the reference map. Therefore, the 2D maps from the same projection could be summed, and the phases derived from the different projections could be compared with the correct ones easily. The phases of reflections common to two or more zones, were simply averaged (in \( P_1 \)), and for centrosymmetric structures, all phases were then further converted to 0 or \( \pi \), whichever was closest.

Of course, if the structure is not known, no such reference map can be generated, so a different method for defining the origin must be used. Furthermore, it was found by Lukas Palatinus that aligning the 2D maps to a correct map does more than just shift them to a common origin. For example, he could show that shifting 100 random electron density maps (generated from 100 sets of random phases) to a correct density map and adding them together produced a map with a very low \( R_{\text{map}} \) value. In our case, however, only 10 2D-XPD maps were used to produce an averaged map (see Section 5.3) and summing 10 random maps, even if they are correctly aligned, will not produce a correct map. The phases for the individual maps are clearly not random. Nevertheless, the fact that 2D maps generated with \( \delta = 0 \) are of sufficiently high quality that the summation of several maps is no longer necessary (see Section 5.7) simplifies the origin definition problem.

Tests based on three different strategies have been performed. Although no completely foolproof method has been found yet, some promising approaches have emerged. These are outlined in the following sections. For all of these tests, the 2D charge-flipping runs were performed using a \( \delta \) value of 0.

5.8.1 Using A Three-dimensional Reference Map from \( pCF \)

If a 3D electron density map generated by \( pCF \) can replace the correct structure as a reference map, then the 2D-XPD origin definition problem can be bypassed. A procedure for finding a 3D reference map was tested. One hundred \( pCF \) runs were performed to produce 100 \( P_1 \) electron density maps. The one showing both a low \( R_{SF} \) value and good agreement with the proposed space group symmetry was selected. This map was then shifted to the origin determined by Superflip.

Three centrosymmetric structures, ZSM-5, TNU-9 and IM-5, and one non-centrosymmetric structure, SSZ-74, were checked. For the case of ZSM-5, the initial \( pCF \) map was already quite good (see for example Figure 4.13(a)), so it was no problem to use this map as a reference to align the 2D (either PED or 2D-XPD) maps. In the case of SSZ-74, all of the 7 best \( pCF \) maps (according to \( R_{SF} \)-value) showed \( Cc \) symmetry. The map with the lowest \( R_{SF} \) value could be used as a reference, and all the generated 2D-XPD maps, either from the same projection
or from different projections, could be shifted to the same origin. Thus, the method could be applied to these two structures successfully without having a 2D-XPD origin definition problem. However, this method failed, with TNU-9 and IM-5. The reason is simple: even the best $R_{SF}$ map was not good enough to allow Superflip to determine the origin correctly.

### 5.8.2 Using Origin Defining Reflections

If the 3D $pCF$ maps cannot be used to align the 2D maps, then the origin of each 2D map has to be defined. The origin defining procedure that is used in direct methods (see Ladd & Palmer, 2003, pp.423-425; Dorset, Roth & Gilmore, 2005) was tried. A small number of phases were assigned to reflections with appropriate index parity to define the origin (for a non-centrosymmetric structure, only one phase is assigned) before the charge-flipping iterations.

Unfortunately, this procedure, which works so successfully in direct methods, proved to fail easily in charge-flipping. The reason may lie in that in direct methods, the origin defining reflections are used to derive new phases, so they are all consistent, while in charge-flipping, no such phasing tree is used. The small number of defined phases are not enough to fix the origin during charge-flipping iterations.

If a few more phases of strong reflections could be derived from the origin defining reflections, a low resolution 3D electron density map could be generated and this might be used as a reference map to align 2D maps. A test along these lines was performed for TNU-9. The phases of the two origin defining reflections $60\overline{5}$ and $351$ were assigned. These phases together with 50 non-overlapping strong reflections in the 2.7 Å XPD dataset were input to the program SayPerm (Brenner, 1999), where the Golay error-correcting code (Golay, 1949) was chosen for phase permutation. In this code the signs of 24 additional reflections are permuted. The 10 most reliable phases suggested by SayPerm were then used to generate a low resolution 3D electron density map. This map was finally modified by changing all the negative densities to zero (Figure 5.12).

![Figure 5.12](image-url)

**Figure 5.12:** The low resolution 3D reference map generated for TNU-9 along [100] (left), [010] (middle) and [001] (right) projections. The correct framework structure is overlaid for comparison.
One hundred 2D-XPD charge-flipping runs using this map as a reference were performed on the [100], [010] and [001] projections. The low resolution reference map allowed the 2D-XPD maps along the [001] and [100] directions to be aligned nicely (Figure 5.13). For the [010] projection, however, some 2D maps had the correct origin while some did not (Figure 5.14). The smeared densities of the reference map along the [010] projection might be the reason for the origin misalignment.

![Figure 5.13](image1.png)  
**Figure 5.13:** A typical 2D-XPD map (in blue) along the [001] projection (*left*) and the [100] projection (*middle*). The low resolution reference map (in white) is overlaid for comparison.

![Figure 5.14](image2.png)  
**Figure 5.14:** Two 2D-XPD maps along the [010] projection. The left one has the same origin as the correct structure while the right one does not.

### 5.8.3 Using the Plane-group-specific Phase Relationships

Finally, a method similar to the phase extraction procedure used for HRTEM images (see Section 3.3) was tested. The initial phase set was first extracted from the 2-dimensional $P1$ map generated by *Superflip*, then new phase sets corresponding to different hypothetical origin positions were calculated using \( \phi_{hkl}^{xyz} = \phi_{hkl}^{initial} + 2\pi (hx + ky + lz) \). The origin that yielded the phases that best fulfill the specific phase relationships for the proposed symmetry was considered to be the correct one. This was monitored using the \( R_\phi \) value,

\[
R_\phi = \frac{\sum_{hkl} |F_{hkl}| \Delta \phi_{hkl}}{\sum_{hkl} |F_{hkl}|},
\]  
(5.1)
where \( \phi_{hkl} \) is the phase error for the reflection \( hkl \).

The idea of using the plane-group-specific phase relationships to find the origin worked for the case of TNU-9 and IM-5 (see for example Figure 5.15). However, there are no reliable criteria for distinguishing good solutions from bad ones in 2D-XPD charge-flipping runs. The \( R_{SF} \) values are not very reliable in the 2D case. For most of the projections tested, the higher \( R_{\phi} \) values generally correspond to poor maps. For a few projections (for example, the [001] projection of TNU-9), however, this is not the case, because there is a tendency towards a "Uranium-atom" solution (this happens in charge-flipping, see Coelho, 2007b) where the majority of the density is concentrated on the mirror plane (Figure 5.16). Fortunately, "Uranium-atom" solutions can be identified by comparing the maximum density values of the 2D maps: those with unusually high maximum density values are most probably "Uranium-atom" solutions.

Figure 5.15: A TNU-9 2D-XPD map along the [010] projection before (left) and after (right) shifting the origin. The correct framework structure is overlaid for comparison.

Figure 5.16: TNU-9 2D-XPD maps along the [001] projection showing a "Uranium-atom" solution (left) and a correct solution (right).

Initial tests on TNU-9 and IM-5 have shown that the following recipe can be applied to identify good 2D maps and to define a correct origin:

1) Use lower resolution 2D-XPD data for the charge-flipping runs. As mentioned in Section 5.7, the powder data are more reliable with lower resolution because the overlap problem is less
Conclusions

It has been demonstrated that although many of the reflection intensities derived from a powder diffraction pattern are ambiguous because of reflection overlap, they can still be used for phase retrieval in two dimensions. By applying a single-crystal charge-flipping algorithm to 2-dimensional subsets of the extracted intensities, phases as reliable as those obtained from HRTEM images or from PED data can be obtained. These phases can then be used in conjunction with the powder charge-flipping algorithm and the full 3-dimensional powder diffraction data to facilitate structure solution. The advantages of this 2D-XPD approach are twofold: (1) X-ray powder diffraction data are considerably easier to obtain than are HRTEM images or PED patterns, and (2) the selection of a 2-dimensional projection is not dependent on finding a crystallite with the appropriate orientation, but can be chosen arbitrarily.

Three materials with the extremely complex zeolite framework structures, TNU-9, IM-5 and SSZ-74, were used to test the method. In all three cases, the phase information derived from 2D-XPD data resulted in a significant improvement of the electron density maps generated by the pCF algorithm. The inclusion of this phase information allowed all three structures, which could not be solved starting from random phases, to be determined from X-ray powder diffraction data alone. The 2D-XPD approach appears to offer a remarkably simple and powerful method for solving the structures of complex polycrystalline materials.

Furthermore, it is possible to generate a 2-dimensional image of the structure that is of similar or even higher quality than that of a good HRTEM image from the 2D-XPD phases and the XPD amplitudes. This means that gross features of the structure, such as a zeolite’s pore system, can be seen without having to solve and refine the crystal structure or obtain an HRTEM image.
Chapter 5. 2D Images Derived from XPD Data and used for Structure Determination

The key problem of this method lies in the definition of the origin of the 2-dimensional electron density maps. Preliminary tests of a method related to that used for HRTEM images are promising. Further tests are necessary but it appears that using plane-group-specific phase relationships with low-resolution 2-dimensional data will allow the problem to be overcome.
Chapter 6

Structure Determination of the Borosilicate Zeolite MCM-70

In 2005, Dorset and Kennedy reported the crystal structure of the borosilicate zeolite MCM-70 (Dorset & Kennedy, 2005), whose synthesis had been patented two years earlier (Dinghra & Weston, 2003). However, the structure analysis was complicated by the fact that the peak shapes in the X-ray powder diffraction (XPD) pattern exhibited anisotropic line broadening and were difficult to model. During the course of the Rietveld refinement, extra-framework species, whose positions were not easy to interpret, were found in the electron density maps generated for both as-synthesized and dehydrated samples. The geometries of the framework structures in both cases were distorted. There also appeared to be a large amount of K in the structure for the relatively small amount of B in the framework. Finally, although the $^{29}$Si MAS NMR spectrum was indicative of a non-random distribution of B in the framework structure, this was not apparent in the crystal structure analysis.

With the aim of clarifying some of these details, a fresh structure determination was undertaken on a new polycrystalline sample of MCM-70 synthesized using an optimized strategy. Because the powder charge-flipping ($pCF$) structure-solution algorithm mentioned in previous chapters has proven to be remarkably powerful for zeolite framework structures (Baerlocher et al., 2007; 2008; Sun et al., 2009; McCusker et al., 2009), this approach was also applied to MCM-70.

6.1 Experimental

The as-synthesized sample of MCM-70 was prepared by Lisa Gibson and Allen W. Burton from Chevron Energy and Technology Company. Details of the synthesis can be found in Xie et al. (2009).

High-resolution X-ray powder diffraction (XPD) data were collected on the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.
Data collection parameters are given in Table 6.1. The morphology of the MCM-70 crystallites is shown in Figure 6.1.

Table 6.1: High-resolution XPD Data Collection for MCM-70

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synchrotron Facility</td>
<td>SNBL (station B) at ESRF</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.49719 Å</td>
</tr>
<tr>
<td>Diffraction Geometry</td>
<td>Debye-Scherrer</td>
</tr>
<tr>
<td>Analyzer Crystals</td>
<td>Si 111</td>
</tr>
<tr>
<td>Sample</td>
<td>Rotating 1.0 mm capillary</td>
</tr>
<tr>
<td>2θ range</td>
<td>1.0 - 43.0°</td>
</tr>
<tr>
<td>Step size</td>
<td>0.003° 2θ</td>
</tr>
<tr>
<td>Time per step</td>
<td></td>
</tr>
<tr>
<td>1.0 - 10.5° 2θ</td>
<td>1.5 s</td>
</tr>
<tr>
<td>10.5 - 22.5° 2θ</td>
<td>3.0 s</td>
</tr>
<tr>
<td>22.5 - 43.0° 2θ</td>
<td>4.5 s</td>
</tr>
</tbody>
</table>

Figure 6.1: Scanning electron micrograph of MCM-70 crystals.

6.2 Data Analysis

The diffraction pattern could be indexed on a primitive orthorhombic unit cell \((a = 13.316 \, \text{Å}, b = 4.658 \, \text{Å}, c = 8.698 \, \text{Å})\) using the program \textit{TREOR} implemented in the software \textit{CMPR}. A careful examination of the diffraction pattern indicated that \(h0l\) reflections with \(h + l = 2n + 1\) were systematically absent, as in the original work of Dorset and Kennedy (2005), the two most probable space groups were expected to be \textit{Pmnm} (centrosymmetric, standard setting \textit{Pmmn}) or \textit{Pmn2}_1 (non-centrosymmetric).

Assuming the centrosymmetric space group \textit{Pmnm}, reflection intensities were extracted from the powder pattern to a minimum \(d\)-spacing of 0.77 Å \((\text{ca. 37.6° 2θ})\) using the Le Bail
method with the program *EXTRACT* in the XRS-82 suite of programs. To optimize the partitioning of overlapping reflections as far as possible, the extracted intensities were repartitioned using the fast iterative Patterson squaring (*FIPS*) method (Estermann & Gramlich, 1993). In this case a reflection whose 2\(θ\) value was within 0.25 FWHM (full width at half-maximum) of that of a neighboring reflection was defined as overlapping. Of the 685 reflections in *Pmnm*, 283 were non-overlapping, and the remainder formed 154 overlap groups.

6.3 Powder Charge Flipping Structure Solution

Although *Pmnm* symmetry was used for the intensity extraction, the charge-flipping algorithm works in the space group *P1*. That is, symmetry-equivalent reflections are expanded and treated independently of one another. The expanded reflection list was then used as input to the *pCF* structure solution algorithm that is implemented in the program *Superflip*. An approximate chemical composition of K\(_2\)Si\(_{11}\)O\(_{22}\) was used for the histogram matching step.

Initially, 100 *pCF* runs of 600 cycles each were performed in default mode: the flipping threshold \(δ\) was determined by *Superflip* automatically at the beginning of the iteration and then kept fixed during the iteration, the overall isotropic Debye-Waller factor \(B_{iso}\) was set to zero, and no symmetry was imposed during the *pCF* runs because the space group was not clear. The histogram-matching procedure was started at the 30th cycle and then repeated every 10 cycles. The *Superflip* input file is shown in Figure 6.2.

During the initial *pCF* runs, the method proposed by Palatinus and van der Lee (2008) for determining the space group symmetry from the final electron density map generated in *P1* was applied. In 100 *pCF* runs, the space group *Pmn2\(_1\)* was found 83 times, but *Pmnm* was not found at all. Furthermore, 8 of the 10 best density maps (according to the *Superflip R* value) showed *Pmn2\(_1\)* symmetry. This is a strong indication that the non-centrosymmetric space group *Pmn2\(_1\)* is the correct one. Another 100 *pCF* runs were then performed with *Pmn2\(_1\)* symmetry imposed. Although the electron density maps generated in *P1* appeared to be quite interpretable, those obtained from the second series of *pCF* runs with symmetry averaging were slightly better. The 10 best maps were averaged, and from this map, not only could the positions of all atoms in the asymmetric unit (4 T atoms, 2 extra-framework atoms, and 7 O atoms) be determined directly from the 15 highest peaks in the density map, but also the peak heights were consistent with the different types of atoms (Figure 6.3). The electron density at one of the tetrahedrally coordinated framework atom (T-atom) sites was significantly lower than at the other three, so it was assumed that this site probably contained a substantial amount of B. The T–O bond distances from this site were also found to be shorter than those from the other three, as would be expected for a higher B content (B–O, ca. 1.47 Å; Si–O, ca.1.61 Å).
Figure 6.2: The initial Superflip input file for MCM-70.

Figure 6.3: pCF electron density map for MCM-70 generated with Pmn2_1 imposed. The stick model of the final structure is overlaid for comparison (Si: blue; B: light blue; O: red; K: green).
6.4 Structure Refinement

To begin with, the four T atoms were refined as Si atoms with occupancies set arbitrarily at 0.95, 0.95, 0.95, and 0.3 to reflect the probable high B content in the latter. The distance between the two extra-framework-atom positions (ca. 2.75 Å) was too short to allow simultaneous occupation by K, so each of these sites was initially assigned as K with an occupancy of 0.5. This model appeared to give a reasonable fit to the diffraction pattern ($R_F = 0.103$, $R_{wp} = 0.310$, $R_{exp} = 0.048$), so it was used as a starting point for Rietveld refinement using the XRS-82 suite of programs.

Geometric restraints were placed on the bond distances and angles of the framework atoms throughout the refinement (see Table 6.2), but their relative weight with respect to the powder diffraction data was reduced as the refinement progressed.

<table>
<thead>
<tr>
<th>Table 6.2: Crystallographic Data for MCM-70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Composition</td>
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<tr>
<td>Unit Cell</td>
</tr>
<tr>
<td>$a$</td>
</tr>
<tr>
<td>$b$</td>
</tr>
<tr>
<td>$c$</td>
</tr>
<tr>
<td>Space Group</td>
</tr>
<tr>
<td>Number of Observations</td>
</tr>
<tr>
<td>Number of Contributing Reflections</td>
</tr>
<tr>
<td>Number of Geometric Restraints</td>
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<tr>
<td>$Si-O$ 1.60(1) Å</td>
</tr>
<tr>
<td>$B-O$ 1.48(1) Å</td>
</tr>
<tr>
<td>$O-Si-O$ 109.5(1.0)$^\circ$</td>
</tr>
<tr>
<td>$O-B-O$ 109.5(1.0)$^\circ$</td>
</tr>
<tr>
<td>$Si-O-Si$ 145(8)$^\circ$</td>
</tr>
<tr>
<td>$Si-O-B$ 145(8)$^\circ$</td>
</tr>
<tr>
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<tr>
<td>Number of Profile Parameters</td>
</tr>
<tr>
<td>$R_F$</td>
</tr>
<tr>
<td>$R_{wp}$</td>
</tr>
<tr>
<td>$R_{exp}$</td>
</tr>
</tbody>
</table>

Once the positions had been refined, the occupancies of the Si and K atom positions were also allowed to vary. These refinements indicated that the fourth T site was, indeed, fully occupied with B and that the other three were pure Si. The total occupancy of the K(1) and K(2) positions, however, consistently refined to a value above 1.0. Reasoning that the excess electron density might be from water (a K–O distance of 2.75 Å would be reasonable), water was added at each K position. Because a previous difference electron density map with the K atoms removed from the model had shown only single spherical peaks at the two positions, the water molecules were constrained to have coordinates identical to those of the respective K atoms, and the total occupancy at each site [K(1)/Ow(2) and K(2)/Ow(1)] was constrained to be
not more than 1.0. This refinement not only reduced the \( R \) values significantly but also yielded a chemically reasonable structure. The occupancies of K at K(1) and K(2) refined to 0.58 and 0.42, respectively. Using the atomic scattering factors for oxygen, the remaining electron density at each position refined to 0.42 and 0.58 for Ow(2) and Ow(1), respectively.

Refinement of this structural model with the chemical formula \( [K_2(H_2O)_2][Si_{10}B_2O_{24}] \) converged with \( R_F = 0.072 \) and \( R_{wp} = 0.135 \). All displacement factors were refined isotropically, and those for similar atoms were constrained to be equal to keep the number of parameters to a minimum. Neutral scattering factors were used for all atoms. Details of the refinement are given in Table 6.2, and selected bond distances and angles, in Table 6.3. The fit of the profile calculated from the final model to the experimental data is shown in Figure 6.4, and the final atomic parameters are given in Table 6.4.

### Table 6.3: Selected Bond Distances (Å) and Angles (°) for MCM-70

<table>
<thead>
<tr>
<th>Bond</th>
<th>Min</th>
<th>Max</th>
<th>Avg</th>
<th>Bond</th>
<th>Min</th>
<th>Max</th>
<th>Avg</th>
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<td>1.61</td>
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<td>109.5</td>
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<td></td>
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<td>K(2)—O(2)</td>
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<tr>
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<td></td>
<td>K(2)—Ow(2)</td>
<td>2.77(2)</td>
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</tbody>
</table>

**Figure 6.4:** Observed (top), calculated (middle), and difference (bottom) profiles for the Rietveld refinement of as-synthesized MCM-70. The profiles in the inset have been scaled up by a factor of 5 to show more detail. Tick marks indicate the positions of reflections.
Table 6.4: Atomic Parameters for MCM-70

<table>
<thead>
<tr>
<th>Atom</th>
<th>Multiplicity</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$ (Å²)</th>
<th>Site occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1)</td>
<td>4</td>
<td>0.2051(3)</td>
<td>0.6366(8)</td>
<td>0.3318(8)</td>
<td>0.014(b)</td>
<td>1.00</td>
</tr>
<tr>
<td>Si(2)</td>
<td>4</td>
<td>0.2977(3)</td>
<td>0.1346(8)</td>
<td>0.1726(8)</td>
<td>0.014</td>
<td>1.00</td>
</tr>
<tr>
<td>Si(3)</td>
<td>2</td>
<td>0.5</td>
<td>0.5817(9)</td>
<td>0.916(1)</td>
<td>0.014</td>
<td>1.00</td>
</tr>
<tr>
<td>B(4)</td>
<td>2</td>
<td>0.0</td>
<td>0.918(2)</td>
<td>0.603(1)</td>
<td>0.014</td>
<td>1.00</td>
</tr>
<tr>
<td>O(1)</td>
<td>4</td>
<td>0.0944(4)</td>
<td>0.512(1)</td>
<td>0.315(1)</td>
<td>0.009(c)</td>
<td>1.00</td>
</tr>
<tr>
<td>O(2)</td>
<td>4</td>
<td>0.2135(5)</td>
<td>0.896(1)</td>
<td>0.208(1)</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>O(3)</td>
<td>2</td>
<td>0.5</td>
<td>0.923(1)</td>
<td>0.957(1)</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>O(4)</td>
<td>4</td>
<td>0.2886(6)</td>
<td>0.407(1)</td>
<td>0.294(1)</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>O(5)</td>
<td>4</td>
<td>0.2733(3)</td>
<td>0.251(2)</td>
<td>0.0</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>O(6)</td>
<td>4</td>
<td>0.4101(4)</td>
<td>0.007(1)</td>
<td>0.194(1)</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>O(7)</td>
<td>2</td>
<td>0.5</td>
<td>0.402(2)</td>
<td>0.070(1)</td>
<td>0.009</td>
<td>1.00</td>
</tr>
<tr>
<td>K(1)</td>
<td>2</td>
<td>0.0</td>
<td>0.477(2)</td>
<td>0.893(2)</td>
<td>0.054(d)</td>
<td>0.58(1)</td>
</tr>
<tr>
<td>K(2)</td>
<td>2</td>
<td>0.0</td>
<td>0.045(2)</td>
<td>0.112(2)</td>
<td>0.054</td>
<td>0.42</td>
</tr>
<tr>
<td>Ow(2)</td>
<td>2</td>
<td>0.0</td>
<td>0.477</td>
<td>0.893</td>
<td>0.054</td>
<td>0.42</td>
</tr>
<tr>
<td>Ow(1)</td>
<td>2</td>
<td>0.0</td>
<td>0.045</td>
<td>0.112</td>
<td>0.054</td>
<td>0.58</td>
</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are the $esd$'s in the units of the least significant digit given. Values without an $esd$ were not refined.
$^b$–$^d$ Thermal parameters with the same superscript were constrained to be equal.

6.5 Discussion

The framework structure of MCM-70 can be described in terms of pairs of edge-sharing 4-rings. These pairs, arranged in a centered (in projection) rectangle in the $ac$ plane, are linked together to form 10-rings, and are connected to one another along the $b$-axis in a zigzag manner to form a 3-dimensional, 4-connected net with a 1-dimensional, 10-ring channel system (Figure 6.5).

Figure 6.5: The framework structure of MCM-70 showing the edge-sharing 4-ring pairs and the 10-ring channels. Bridging O atoms have been omitted for clarity. The B position is shown in gray.
The extra-framework K\(^+\) ions are located in the 10-ring channels. Because the K\(^+\) ions at K(1) and K(2) cannot coexist in the same channel, 58% of the channels have K\(^+\) ions at K(1) and water molecules at Ow(1), and 42% have K\(^+\) ions at K(2) and water molecules at Ow(2) (Figure 6.6). The two K sites are very similar to one another (related by a pseudo inversion center). In both cases, the K\(^+\) ions are located opposite 8-ring pockets in the walls of the 10-ring channels, where they coordinate to five O atoms of the framework and one water molecule (Table 6.3, Figure 6.7). The water molecules, in turn, are at hydrogen bonding distances from framework O atoms.

**Figure 6.6:** The structure of MCM-70 viewed down the \(b\)-axis showing a possible arrangement of the extra-framework atoms. Three channels are shown with K\(^+\) ions at K(1) and water molecules at Ow(1), whereas the other two are shown with K\(^+\) ions at K(2) and water molecules at Ow(2) to reflect the 58% and 42% occupancy factors.

The structure is very similar to that reported earlier by Dorset and Kennedy (Dorset & Kennedy, 2005). The major differences are that (1) the B atoms in the framework structure of the material used in this study are clearly ordered and (2) the K\(^+\) ions are found in two (rather than one) closely related, but crystallographic distinct, positions in the 10-ring channels. The sample described here has a much higher percentage of B in the framework structure (Si/B 5:1 vs 40:1 in the previous work). Apparently, this higher B concentration has led to a more crystalline material with a simple stoichiometry ([K\(_2\)(H\(_2\)O)\(_2\)][Si\(_{10}\)B\(_2\)O\(_{24}\)]), a clear ordering of B in the framework structure, and the appropriate number of K\(^+\) ions in the channels to balance the charge of the borosilicate framework.

The framework topology itself is centrosymmetric, but because the B atoms are ordered, the inversion center is violated and the structure crystallizes in the non-centrosymmetric space.
6.6 Conclusions

The powder charge-flipping structure-solution algorithm has allowed the structure of the zeolite MCM-70 to be elucidated in a quite straightforward manner. The framework structure for the borosilicate zeolite MCM-70 originally proposed by Dorset and Kennedy, with a 1-dimensional, 10-ring channel structure, has been confirmed. Optimization of the synthesis conditions for this material resulted in a more crystalline/homogeneous sample, and structural characterization of this sample using X-ray powder diffraction technique has allowed some of the ambiguities in the earlier study to be resolved. In particular, the boron has been shown to be completely ordered, fully occupying one of the four tetrahedral sites in the framework structure. The remaining three
sites are pure Si. For each B atom in the framework, there is a $K^+$ counterion in the channels. These $K^+$ ions partially occupy two very similar sites in different 10-ring channels, where they bond to five framework O atoms and one water molecule.
Chapter 7

AM-11

The novel microporous niobium silicate AM-11 (Aveiro-Manchester microporous solid no. 11) was first synthesized and reported in 1998 (Rocha et al., 1998). Although this material shows promising catalytic performance (Phillippou et al., 2001; Brandão et al., 2001, 2002; Dias et al., 2006), its properties cannot be fully understood without detailed crystal structure information. The AM-11 samples were polycrystalline, and all attempts to solve the structure from X-ray powder diffraction data to date have failed. In view of the encouraging results obtained by supplementing X-ray powder diffraction (XPD) data with precession electron diffraction (PED) data (see Chapter 4), this old problem of AM-11 was re-examined using this new combination.

7.1 Experimental

Samples of calcined and as-synthesized AM-11 were kindly provided by Antonió Moreira dos Santos from the University of Aveiro. The morphology of both the calcined and the as-synthesized samples were established from scanning electron micrographs (Figure 7.2): the calcined sample has extremely long needle-like crystallites, while the as-synthesized one has plate-like crystallites. High resolution XPD data for both samples were collected on the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Data collection parameters are given in Table 7.1. A comparison of the two XPD patterns shows that they are almost identical (Figure 7.1). As the data for the calcined sample had better statistics, this pattern was analyzed first.

For the electron diffraction (ED) measurements, samples were prepared using the grinding-dispersing approach that was described in Chapter 4: AM-11 powders were crushed for about 15 minutes using a mortar and pestle, they were then suspended in ethanol and disaggregated with ultrasound for about 30 minutes. 3-6 drops of the suspension were put on a TEM grid with holey carbon film and allowed to dry. Because the AM-11 crystals (the calcined sample) has a long needle-like shape even after crushing (checked by SEM again), it was suspected that it would be difficult to find one oriented with its needle-axis perpendicular to the holey carbon
Table 7.1: High-resolution X-ray Powder Diffraction Data Collection for AM-11.

<table>
<thead>
<tr>
<th>AM-11 (calcined)</th>
<th>AM-11 (as-synthesized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synchrotron Facility</td>
<td>SNBL (station B) at ESRF</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.5004 Å</td>
</tr>
<tr>
<td>Diffraction Geometry</td>
<td>Debye-Scherrer</td>
</tr>
<tr>
<td>Analyzer Crystals</td>
<td>Si 111</td>
</tr>
<tr>
<td>Sample</td>
<td>Rotating 1.0 mm capillary</td>
</tr>
<tr>
<td>$2\theta$ range</td>
<td>1.0 - 33.0$^\circ$</td>
</tr>
<tr>
<td>Step size</td>
<td>0.005$^\circ$ 2$\theta$</td>
</tr>
<tr>
<td>Time per step</td>
<td>1.0 - 33.0$^\circ$ 2$\theta$: 14.5 s</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.1: Comparison of the high-resolution X-ray powder diffraction patterns for calcined and as-synthesized AM-11.

film. Therefore, after putting the suspension onto the TEM grid, a filter paper was used to suck the solvent gently from the other-side of the film, with the hope that some needles would attach themselves to the edge of the carbon holes.

The experimental ED patterns were collected at 300 kV ($\lambda = 0.0197$ Å) on a Philips CM30 electron microscope equipped with side-entry goniometer stage (tilt range $\pm 25^\circ$), a ‘Spinning Star P020’ precession unit (NanoMegas, Belgium) and a 16 bit Gatan 794 CCD camera. Exposure times were selected such that the diffraction intensities lay within the linear response range of the detector. The precession electron diffraction (PED) patterns were recorded with a precession angle close to 1$^\circ$. The intensities were extracted using the program ELD (Zou et al., 1993a) in the CRISP software package (Hovmöller, 1992), and the "shape-fitting" method (Zou et al., 1993b) implemented in ELD was used to estimate the intensities of the electron diffrac-
tion spots. Phases from PED projections were derived using the single-crystal charge-flipping algorithm in the program *Superflip*.

**Figure 7.2:** Scanning electron micrographs of the calcined sample (left) and the as-synthesized sample (right) of AM-11.

### 7.2 Data Analysis

The XPD pattern of the calcined sample could be indexed with 3 different unit cells (Figure 7.3, Table 7.2).

**Figure 7.3:** XPD indexing of calcined AM-11. (a) XPD pattern; (b), (c) and (d) show the pattern indexed on the orthorhombic, hexagonal and monoclinic cells listed in Table 7.2, respectively.
A careful examination of these unit cells indicated that they were closely related to one another (see Table 7.2). For example, the hexagonal unit cell has twice the volume of the orthorhombic unit cell and four times that of the monoclinic unit cell. The primitive monoclinic cell is equivalent to the $B$-centered orthorhombic cell (Figure 7.4).

**Table 7.2:** Different unit cells indexed from XPD pattern.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Orthorhombic</th>
<th>Hexagonal</th>
<th>Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>23.676</td>
<td>27.298</td>
<td>12.415</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>13.635</td>
<td>27.298</td>
<td>13.635</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.483</td>
<td>7.483</td>
<td>7.483</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90</td>
<td>90</td>
<td>107.54</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
<td>120</td>
<td>90</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>2415.679</td>
<td>4829.120</td>
<td>1207.818</td>
</tr>
</tbody>
</table>

| Relations       | $a_o \approx \sqrt{3}b_o$ | $a_h \approx a_o / \sin 60^o$ | $a_m \approx \sqrt{a_o^2 + c_o^2}/2$ |
|                | $\approx b_o / \cos 60^o$ | $\beta_m \approx \arcsin(2a_m / \sqrt{a_o^2 + c_o^2})$ | |
|                | $V_h \approx 2V_o$ | $V_m \approx (1/2)V_o$ | |

**Figure 7.4:** The geometric relationships between the orthorhombic (top), the hexagonal (middle) and the monoclinic (bottom) unit cells of AM-11. (a), (b) and (c) correspond to the projections perpendicular to the $c$-, $b$- and $a$-axis, respectively.

To solve this indexing ambiguity, single-crystal electron diffraction patterns taken along different zone axes were used (Figure 7.5). Although the precision of ED indexing is relatively low due to the imperfect sample alignment, camera length calibration and instrument distortions, information regarding the approximate magnitudes of the two principal lattice vectors and the angle between them allows the zone axis and systematic absences to be determined. These results are listed in Table 7.3. The unit cell appears to be orthorhombic (see Table 7.2), and the most probable extinction symbols (space groups), according to Table 7.3, are: (1) $Pnna$ ($Pnnm$) or $Pnn$- ($Pmm2$ or $Pnnm$); (2) $P$-na ($P2na$ or $Pmna$) or $P$-$n$- ($Pmm2_1$ or $P2_1nm$ or $Pmmn$). All of these are consistent with the XPD data.
Figure 7.5: Electron diffraction patterns for AM-11: (a) and (b) are SAED patterns, the rest are PED patterns. Note that (b) was taken along a very thick region of the sample [perpendicular to the needle direction (or close to the needle direction)], so it should be used with caution.
Table 7.3: Summary of indexing and symmetry determination from the electron diffraction patterns of AM-11.

| Systematic | Symmetry | Possible Angles between Zones | Directions of 2 Vectors | Zonal Axes
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic</td>
<td>1 + $2n = 000$</td>
<td>00 06 = $\phi$</td>
<td>[000] = 100 V 010</td>
<td>[010] = 100 V 010</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1 + $2n = 1 + i$</td>
<td>00 06 = $\phi$</td>
<td>[111] = 101 V 010</td>
<td>[011] = 101 V 010</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>1 + $2n = 2$</td>
<td>00 06 = $\phi$</td>
<td>[110] = 101 V 010</td>
<td>[010] = 101 V 010</td>
</tr>
</tbody>
</table>

Although most 000 with $h = 2n + 1$ are absent, a few did appear in this pattern.

Although most 000 with $h = 2n + 1$ still appeared in this pattern.

The angle did not match the measured value.
Assuming the centrosymmetric space group \( Pnma \), XPD reflection intensities were extracted to a minimum \( d \)-spacing of 0.90 Å (ca. 32.3° \( 2\theta \)). A reflection whose \( 2\theta \) value was within 0.25 FWHM of that of a neighboring reflection was defined as overlapping.

Precession electron diffraction data along [100], [10\( \overline{1} \)], [1\( \overline{2} \)0] and [1\( \overline{2} \)1] were used for weak reflection elimination (WRE). Since AM-11 contains two strong scatterers (Nb and Si), a very rough estimate was made to see if WRE could be performed without problem. The compound \( H_5\text{NbSi}_4\text{O}_{13} \), which has a composition similar to that of AM-11, was used for the test. A comparison between the structure factors calculated for X-rays and electrons for this material showed that most of the weak reflections in electron diffraction are still weak in X-ray diffraction (Figure 7.6).

![Figure 7.6: Comparison between the calculated structure-factor amplitudes of \( H_5\text{NbSi}_4\text{O}_{13} \) for X-rays and electrons.](image)

For each PED projection, a plot of the amplitude distribution was examined to evaluate the appropriate amplitude threshold for WRE, and in each case, a value of half of the average amplitude was chosen, this resulted in 217 weak reflections being identified. Using the procedure described in Chapter 4, weak reflections were eliminated from the XPD \( hkl \) list and the intensities of the remaining reflections re-extracted. 121 rather than 217 reflections were eliminated, because: (1) the PED data resolution was slightly higher than that of the XPD data; (2) the non-overlapping XPD reflections were not eliminated, even if they were weak; and (3) the XPD intensities were extracted assuming the space group \( Pnma \) (which may not be correct), so some reflections which were identified as weak from PED data were absent from the XPD \( hkl \) list.
7.3 Structure Solution

One hundred $pCF$ runs of 500 cycles each were performed, and the histogram-matching procedure was started at the 10th cycle and then repeated every 10 cycles. An approximate chemical composition of $\text{Na}_8\text{Nb}_8\text{Si}_{32}\text{O}_{88}$ was used for the histogram matching step. Initially, no symmetry was imposed during the $pCF$ runs because the space group was not clear. The $P1$ electron density maps generated from Superflip, however, were not satisfactory. Only when the symmetry was imposed (assuming $P2na$) could the electron density maps be interpreted, albeit, only partially (Figure 7.7 (a)). The starting model built from these maps is shown in Figure 7.7 (b) ($R_F = 0.19$, $R_{wp} = 0.67$). Currently, the interpretation of this model and the subsequent difference Fourier analysis/Rietveld refinement are in progress.

Figure 7.7: The electron density map (assuming $P2na$) generated by powder charge-flipping is shown in (a), the starting model built from (a) is shown in (b) (Si, blue; Nb, light blue; O, red; Na, yellow).
Chapter 8

Conclusions

The main objective of this PhD project was to examine how X-ray powder diffraction (XPD) and electron microscopy (EM) techniques could be used to solve the structures of complex polycrystalline materials. Three strategies for combining the two techniques were investigated. One involved an optimization of the procedure for determining the phases of the structure factors from high-resolution transmission electron microscopy (HRTEM) images. These phases were then combined, through an optimized strategy, with the intensities extracted from the XPD pattern for structure solution. The second used the single-crystal intensities from precession electron diffraction (PED) patterns to better estimate the relative intensities of overlapping reflections in a XPD pattern. The third used the PED data to obtain phase information for combination with XPD data.

The extremely complex structures of the zeolites TNU-9 and SSZ-74, were used to investigate how to take maximum advantage of phase information derived from HRTEM images of different qualities. Analysis showed that the most reliable phases extracted from a thin region of the crystal are those of low-resolution strong reflections. The phases derived from HRTEM images taken along a zeolite’s channel direction can be improved significantly with the single-crystal charge-flipping algorithm, and a recipe for doing this has been suggested. If high quality HRTEM images along different zone axes are attainable, enough phase information can be extracted to be useful as additional information in reciprocal space. If, however, only a few phases can be extracted, using these phases in reciprocal space proved to be less helpful. In this case, a real-space structure envelope was more beneficial to the structure solution process. The dual-space powder charge-flipping (pCF) algorithm was optimized for using data from both XPD and EM techniques simultaneously. In both cases (TNU-9 and SSZ-74), a simple inclusion of all HRTEM phases in pCF did not yield any correct structures. However, the correct structures could be found in a straightforward manner if the HRTEM phases were used through the optimized strategy mentioned above.

HRTEM images can be extremely useful in the structure determination process, but they are not always easy to obtain. Therefore, the possibility of using the less demanding electron microscopy technique, precession electron diffraction (PED), to replace HRTEM was investigated.
PED data were exploited in two different ways for this purpose. In one case, the PED data were simply used to identify the weak reflections in the available projections, with the hope that this information would lead to a more correct partitioning of some of the overlapping reflections in the powder pattern. In the second case, the charge-flipping method was applied to the two-dimensional PED data to obtain phases for the contributing reflections. The phases obtained were then included along with the XPD intensities as input to the pCF algorithm. These approaches were first developed using data for the moderately complex zeolite ZSM-5, and then tested on TNU-9. In both cases, including PED data from just a few projections facilitated structure solution significantly. In these initial tests, the correct structure was used as a reference to align the PED potential maps so that they had the same origin.

In view of the success in retrieving phase information from PED data, an alternative approach requiring only XPD data was developed. The single-crystal charge-flipping algorithm was applied to 2-dimensional projections derived from the 3-dimensional XPD data to retrieve structure factor phases. As for the PED case, the correct structure was used in the tests to fix the origin of 2D-XPD charge-flipping maps. Combining the phases derived in this way with the full 3-dimensional XPD data was found to have a significant and beneficial effect on the structure solution. The approach was first developed using data collected on TNU-9, and was then tested further using data for IM-5 and SSZ-74, two similarly complex zeolites. In all three cases, the phase information derived from 2-dimensional subsets of the XPD data resulted in a significant improvement in the electron density maps generated by the pCF algorithm. The inclusion of this phase information allowed all three structures to be determined from the X-ray data alone.

The key problem in both the PED and 2D-XPD phase retrieval methods is the definition of the origin of the 2-dimensional charge-flipping maps. A method related to that used for HRTEM images has been developed for this purpose. Preliminary tests showed that using plane-group-specific phase relationships with low-resolution 2-dimensional data will allow this problem to be overcome.
Chapter 9

Suggestions for Future Work

The potential of the methods discussed in previous chapters has been demonstrated, but further development can be envisioned.

(1) It is known that structure factors for X-ray and electron diffraction experiments are neither identical nor strictly proportional to one another, because the atomic scattering factors for the two sources are different. Therefore, care must be taken when structure factors (phases and amplitudes) obtained from ED are applied to X-ray data. It has been shown in this thesis that for materials with a single dominant scatterer such as zeolites, the structure factors (in particular their phases) for both sources are comparable. Therefore the phase information derived from EM can be combined with X-ray powder diffraction (XPD) data directly, and the weak reflection elimination (WRE) procedure can be performed without problem. However, the viability of these methods is not clear if the material contains more than one strong scatterer. A very rough estimate could be made by comparing the structure factors calculated for both sources for a known structure with a composition similar to that of the material of interest, but more systematic investigation of this potential limitation would be worthwhile.

(2) It has been shown that the phase information extracted from HRTEM images is far from perfect, even if the images are of "high" quality (Chapter 3, see also Sun et al., 2010). If the HRTEM phase set could be corrected and/or expanded, the usefulness of these HRTEM images in structure solution could be improved. Initial tests have shown that the charge-flipping algorithm is able to correct the phases from the HRTEM images taken along a zeolite’s channel direction very efficiently. An investigation of the possibility of using charge-flipping for phase extension would be of interest. The dual-space method developed by Gassmann et al. (Hoppe & Gassmann, 1968; Gassmann & Zechmeister, 1972) and Ishizuka et al. (1982) for phase correction and phase extension might also be tried.

(3) In this study, a very conservative approach, i.e. weak reflection elimination (WRE), was used to combine precession electron diffraction (PED) intensities with XPD intensities. If the relationship between the atomic scattering factors (and therefore structure factors) for X-rays and electrons is better understood, and the quality of PED data can be further improved, more quantitative ways of combining the two datasets can be tried. That is, the full PED data rather
Chapter 9. Suggestions for Future Work

than just weak reflections might be used to repartition the intensities of overlapping reflections.

The quality of PED data can be improved in different ways. At the time the methods described here were developed, PED data could only be recorded with a precession angle ca 1°. Now the new generation of the DigiStar PED attachment has been installed on the FEI Tecnai F30 electron microscope, the precession angle can reach 4° or more. Therefore more kinematical PED intensities can be expected. The new electron diffraction tomography techniques developed in Kolb's group at the University of Mainz, and in Zou and Hovmöller's group at Stockholm University, allowed a large number of 3-dimensional ED data to be collected automatically. This data would be ideal for combination with XPD data for difficult structure solutions.

For simplicity, the PED intensities used in this study were calculated assuming kinematical scattering, and no geometrical corrections were applied. However, ideal kinematic conditions are not achieved with the precession electron diffraction technique, and at least in theory geometrical corrections are indeed necessary. Therefore, an evaluation of the effect of applying different corrections to the data are worthwhile. The grinding-dispersing approach for sample preparation is not satisfactory in many cases, because the samples prepared in this way are usually wedge-shaped and are only thin close to the edge. The kinematic conditions are normally not fulfilled if a large surface is illuminated by the beam. Samples with more homogenous and smaller thicknesses can be obtained using the "ultramicrotomy" method, and this would be worth investigating.

(4) The origin definition problem needs to be investigated further. The idea of using origin defining reflections to generate a low resolution 3-dimensional reference map, and of using the plane-group-specific phase relationships to define the origin were partially successful. The problem is that there are no reliable criteria for distinguishing good solutions from bad ones in 2-dimensional charge-flipping runs. A recipe has been suggested to find good 2D maps with the correct origin and this is worth testing in more detail. Investigation on how to combine the two partially successful ideas would also be helpful.

(5) Initial tests showed that the 2-dimensional single-crystal and 3-dimensional powder charge-flipping algorithms can be affected significantly by input parameters. Therefore, a systematic analysis of the influence of these different parameters on the structure solution should be undertaken. Better figures of merit to identify the best solutions also need to be developed.
References


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