Molecular Sieves
Science & Technology

Structures and Structure Determination

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Preface to the Series

Following Springer's successful series *Catalysis – Science and Technology*, this series of monographs has been entitled *Molecular Sieves – Science and Technology*. It will cover, in a comprehensive manner, all aspects of the science and application of zeolites and related microporous and mesoporous materials.

After about 50 years of prosperous research, molecular sieves have gained a firm and important position in modern materials science, and we are witnessing an ever increasing number of industrial applications. In addition to the more traditional and still prevailing applications of zeolites as water softeners in laundry detergents, as adsorbents for drying, purification and separation purposes, and as catalysts in the petroleum refining, petrochemical and chemical industries, novel uses of molecular sieves are being sought in numerous laboratories.

By the beginning of 1999, the Structure Commission of the International Zeolite Association had approved approximately 120 different zeolite structures which, altogether, cover the span of pore diameters from about 0.3 nm to 2 nm. The dimensions of virtually all molecules (except macromolecules) chemists are concerned with fall into this same range. It is this coincidence of molecular dimensions and pore widths which makes zeolites so unique in adsorption and catalysis and enables molecular sieving and shape-selective catalysis. Bearing in mind that each zeolite structure can be modified by a plethora of post-synthesis techniques, an almost infinite variety of molecular sieve materials are nowadays at the researcher's and engineer's disposal. In many instances this will allow the properties of a zeolite to be tailored to a desired application. Likewise, remarkable progress has been made in the characterization of molecular sieve materials by spectroscopic and other physico-chemical techniques, and this is particularly true for structure determination. During the last decade, we have seen impressive progress in the application of quantum mechanical ab initio and other theoretical methods to zeolite science. The results enable us to obtain a deeper understanding of physical and chemical properties of zeolites and may render possible reliable predictions of their behavior. All in all, the science and application of zeolites is a flourishing and exciting field of interdisciplinary research which has reached a high level of sophistication and a certain degree of maturity.

The editors believe that, at the turn of the century, the time has come to collect and present the huge knowledge on zeolite molecular sieves. *Molecular Sieves – Science and Technology* is meant as a handbook of zeolites, and the term "zeo-

lites" is to be understood in the broadest sense of the word. While, throughout the handbook, some emphasis will be placed on the more traditional alumosilicate zeolites with eight-, ten- and twelve-membered ring pore openings, materials with other chemical compositions and narrower and larger pores (such as sodalite, clathrasils, $AlPO_4-8$, VPI-5 or cloverite) will be covered as well. Also included are microporous forms of silica (e.g., silicalite-1 or -2), alumophosphates, gallophosphates, silicoalumophosphates and titaniumsilicalites etc. Finally, zeolite-like amorphous mesoporous materials with ordered pore systems, especially those belonging to the M41S series, will be covered. Among other topics related to the science and application of molecular sieves, the book series will put emphasis on such important items as: the preparation of zeolites by hydrothermal synthesis; zeolite structures and methods for structure determination; post-synthesis modification by, e.g., ion exchange, dealumination or chemical vapor deposition; the characterization by all kinds of physico-chemical and chemical techniques; the acidic and basic properties of molecular sieves; their hydrophilic or hydrophobic surface properties; theory and modelling; sorption and diffusion in microporous and mesoporous materials; host/guest interactions; zeolites as detergent builders; separation and purification processes using molecular sieve adsorbents; zeolites as catalysts in petroleum refining, in petrochemical processes and in the manufacture of organic chemicals; zeolites in environmental protection; novel applications of molecular sieve materials.

The handbook will appear over several years with a total of ten to fifteen volumes. Each volume of the series will be devoted to a specific sub-field of the fundamentals or application of molecular sieve materials and contain five to ten articles authored by renowned experts upon invitation by the editors. These articles are meant to present the state of the art from a scientific and, where applicable, from an industrial point of view, to discuss critical pivotal issues and to outline future directions of research and development in this sub-field. To this end, the series is intended as an up-to-date highly sophisticated collection of information for those who have already been dealing with zeolites in industry or at academic institutions. Moreover, by emphasizing the description and critical assessment of experimental techniques which have been used in molecular sieve science, the series is also meant as a guide for newcomers, enabling them to collect reliable and relevant experimental data.

The editors would like to take this opportunity to express their sincere gratitude to the authors who spent much time and great effort on their chapters. It is our hope that *Molecular Sieves - Science and Technology* turns out to be both a valuable handbook the advanced researcher will regularly consult and a useful guide for newcomers to the fascinating world of microporous and mesoporous materials.

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Hellmut G. Karge
Jens Weitkamp

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Preface to Volume 2

Once a new natural zeolite is found or a new molecular sieve synthezised, via one or the other of the methods described in Volume 1 for example, the researchers face the task of confirming that a novel structure has come into their hands. However, beyond this basic problem, questions soon arise concerning rather detailed and subtle structural features.

The classical method of determining crystal structures is X-ray diffraction. Thus, in Chapter 1 of the present volume, *H. van Koningsveld* and *M. Bennett* provide the reader with information about the enormous progress which has been made in X-ray structure analysis of zeolites. To a large extent, this is due to outstanding developments in both experimental techniques and methods of data evaluation, such as the application of synchrotron radiation and Rietveld analysis. New methods now enable crystallographers to study very small single crystals or crystallite powders. This is extremely important with respect to most of the synthetic micro- and mesoporous materials since the size of primary particles is usually in the μm range. The authors stress that, in the context of reliable structure analysis, the determination of the unit cell and space group is of paramount importance. Modern tools now allow researchers to study subtle effects on zeolite structures such as those caused by framework distortions, dealumination, isomorphous substitution or cation and sorbate location.

The study of structures containing light atoms is the particular domain of neutron scattering, even though this is not its only advantage. The authors of Chapter 2, *A. N. Fitch* and *H. Jobic* demonstrate the way in which neutron scattering is able to complement structure analysis by X-ray diffraction. In particular, neutron scattering techniques reveal their strong potential in probing details of structural arrangements involving hydrogen-containing species (such as water and hydroxyl groups) as well as determining hydrogen bonds, cation positions, and the location of adsorbed molecules. Frequently these techniques are successfully used for further refinement of X-ray diffraction data.

Chapter 3, written by *O. Terasaki*, is devoted to the use of the various kinds of electron microscopy in the investigation of zeolites and related porous solids. The author's contribution focuses on the potential of electron microscopy in studying crystallite morphologies as well as features of the fine structure, e.g., bulk and surface defects; details of the crystal surface (edges and kinks), and, as such, related to crystal growth; and modification of frameworks. Moreover, the valuable assistance of electron microscopy in solving new structures is illustrated by a number of examples.

Chapter 4 is contributed by *W. Depmeier*, and it concerns particular pheno-
mena of the structures of zeolites and related solids which are attracting more
and more interest. Such phenomena are, inter alia, phase transitions as well as
mechanisms of reduction in symmetry and volume as a consequence of tilting,
distortion of the whole framework or framework units, modulations of the
framework, and partial amorphization. These are demonstrated by a variety
of instructive examples, and their importance is pointed out in view of, for
example, catalytic, shape selective and separation properties of zeolite materials.

General problems of zeolite structures are dealt with in Chapter 5 which is
jointly authored by *W. M. Meier* and *C. Baerlocher*. It includes basic aspects of
zeolite crystallography such as topology, configuration, and conformation of
framework structures. Similarly, the idea of distinguishing zeolites on the basis
of framework densities is presented. The attempts at classification of zeolite
structure types are critically discussed. The authors then describe the inter-
esting concepts of structural characterization via loop configurations and coor-
dination sequences and also reconsider the long-standing question of whether
zeolite framework structures are predictable.

This volume concludes with Chapter 6, a review devoted to industrial synthe-
sis. Contributed by *A. Pfenninger* and entitled "Manufacture and Use of Zeolites
for Adsorption Processes", this chapter provides an extremely useful adjunct to
Volume 1 of this series. Important aspects of industrial synthesis are described
and, simultaneously, the characterization and use of zeolites for separation pro-
cesses are discussed. In these respects, Chapter 6 is something of an introduction
to matters which will be extensively dealt with in Volume 5 (Characterization II)
and Volume 7 (Sorption and Diffusion) of this series.

The originally planned final chapter on the role played by solid state NMR
spectroscopy in the elucidation of structural features of microporous and meso-
porous materials was unfortunately not available at the time of going to press.
However, given the importance of this topic, an appropriate treatment of this
area is intended to appear in Volume 4 (Characterization I).

Thus, Volume 2 presents an extended overview over most of the relevant tech-
niques currently employed for investigations into structural properties of
micro- and mesoporous materials and offers in its last contribution a valuable
addition to the topics treated in Volume 1. From this volume it becomes evident
that the various techniques for structure determination are, to a large extent,
complementary and that evaluation of the experimental data, on the other hand,
is profiting much from recent developments in theory and modeling. It is the
Editors' hope that Volume 2 of the series "Molecular Sieves – Science and
Technology" will provide the researchers in the field of zeolites and related
materials with the necessary awareness of the great potential in modern
methods for structure analysis.

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Contents

Zeolite Structure Determination from X-Ray Diffraction

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1
Introduction

Zeolites and related microporous materials are a class of materials with an ever widening range of compositions, structures and uses. Since the earliest days of zeolite science X-ray diffraction has been one of the basic and most useful tools for characterization.

Initially X-ray diffraction was used to answer simple questions such as: "have I made a new material?" or: "has the crystallization process gone to completion?" Now the questions encompass everything that a researcher might want to know about the structure of a material. Early attempts at determining crystal structures using X-ray diffraction were often unsuccessful because many of these early synthetic materials were available only as powder samples. Fortunately many of these first synthetic materials had natural counterparts with large single crystals, and data from these were used to determine the framework structures

of their synthetic counterparts. Today, the framework of a new material can be often determined from powder samples. In addition, single crystal techniques have improved considerably leading to increased accuracy in the bond angles and bond distances and to the ability to study crystals of much smaller size. It is now possible for a single crystal study to reveal details of the structure that show the interaction of a sorbed material with the framework or movement of cations within the framework and any ensuing distortions of the framework. Structural data from powder samples are beginning to reveal similar changes in the crystal structure with temperature, with sorbed materials and even under catalytic conditions. Even though the technique of X-ray powder diffraction has improved greatly since the early days of zeolite science, it is still more accurate to determine the crystal structure of a new material from single crystal data rather than from powder data.

Many of the advances in the structural information derived for zeolitic materials are a direct result of major improvements in powder and single crystal X-ray equipment available, in the development of new structure determination methods and in the use of new characterization tools including magic angle spinning NMR, neutron diffraction and electron microscopy, which are described in subsequent chapters. Two excellent review papers [1, 2] discuss the use of X-ray diffraction techniques to study zeolites and the problems encountered, and it is recommended that they be used in combination with this chapter.

The stages in determining the crystal structure of a material have been described as: (i) obtain a suitable sample, (ii) collect the data, (iii) determine a trial structure using *ab initio* methods, and (iv) refine the data.

However, with zeolites it is not as simple as the above infers since subtle changes in the zeolite framework can influence, to a greater or lesser extent, both the observed intensities and the symmetry. These subtle changes in the observed intensities and the symmetry can cause serious problems for crystallographers performing a zeolite structure analysis. The crystallographic problems include:

- Severe overlap of reflections in powder data leading to problems with the techniques used to decompose the peaks into individual reflections
- Incorrect determination of the space group especially when the true symmetry is masked by pseudo-symmetry
- The effect of framework flexibility on the structure analysis
- Disorder of the non-framework species and its effect on the structure solution
- Faulting within the framework
- Problems caused by isomorphous replacement of framework atoms
- The effects due to small crystal size and the limits on the crystal size that can be used

In order to help those in the zeolite community to better appreciate the beauty of an excellent crystallographic study while learning to evaluate the pitfalls that are present in an incorrect study, several structures, published in the last decade and that are examples of the problems listed above, will be reviewed.

2
Severe Overlap of Reflections in Powder Data

For a single crystal structure determination one crystal is chosen from the sample and it is assumed that the chosen crystal is both suitable for the study and typical of the bulk material. Often several crystals have to be evaluated before a "good" crystal for the study is found. In contrast, it is relatively easy to obtain a sample for a powder study and to use a synchrotron source to obtain the best data. Synchrotron X-ray data are high intensity and high resolution data and, as such, are far superior to in-house data. The improvements in the quality of the data obtained from the synchrotron have reduced the magnitude of the problems that plagued early attempts at structure determination. However, there is still only one dimensional intensity information in the powder pattern and it is not a trivial task to determine the correct three-dimensional unit cell dimensions especially if a few weak peaks from an unknown impurity phase are present.

A successful structure determination starts with a set of accurately determined peak positions. Unfortunately, this task is often left to the computer with disastrous results. With carefully deconvoluted data the currently used indexing programs [3, 4] often yield a number of equally probable answers. When combined with even partial unit cell information from electron diffraction, it is usually possible to reduce this number to one or two unit cell sets. If no other data are available then the wrong choice between two equally probable unit cells may prevent the structure from being accurately determined. Even when a unit cell is derived it may later prove to be "incorrect" (too highly symmetric) once the structure has been refined. Unfortunately, the only way to know that a chosen unit cell is correct is to solve the crystal structure.

Table 1 lists part of the data obtained from a new material. It was known from TEM/SEM studies that the synthesis product was impure and that the impurity was an offretite material based on observed d-spacings and a knowledge of the synthesis conditions. These offretite peaks were removed from the data before using the indexing programs. However, the best unit cell obtained did not index all the reflections suggesting that there might be three phases present in the sample which seemed unlikely. The final solution used several common reflections (such as that at $2\theta = 9.958°$) that came from both the offretite impurity and the new phase and indexed all 60 observed reflections, out to a d spacing of 3.04 Å. The only difference between the first and final unit cell solutions was the value for the c dimension. The number of un-indexed reflections now became zero (see Table 1). Thus it is very important to account for all observed peaks in a pattern even those assigned to other phases and to review even small differences between the observed and calculated 2θ values, in order to be sure that the calculated unit cell dimensions are reasonable.

In order to determine the crystal structure, the intensity of the exactly or partially overlapping reflections are usually separated by a number of simple techniques such as splitting them fifty-fifty. However, these structure determinations were often unsuccessful and more sophisticated methods were developed to partition the intensity of the overlapping reflections.

Table 1. A partial list of the observed and calculated 2θ values for a new phase with an offretite impurity[a]

2θ Values			Solution 1[b]	Final solution[c]
			h k l	h k l
Observed	Calculated	Difference		
2.402	2.396	0.007	1 0 0	1 0 0
4.142	4.150	0.008	1 1 0	1 1 0
4.784	4.792	0.009	2 0 0	2 0 0
6.606			1 0 0 (Off.)	1 0 0 (Off.)
6.338	6.341	0.003	2 1 0	2 1 0
7.189	7.191	0.002	3 0 0	3 0 0
8.302	8.305	0.003	2 2 0	2 2 0
9.595	9.593	−0.002	4 0 0	4 0 0
9.958	9.957	−0.001	0 0 1 (Off.)	0 0 1 (both)
10.244	10.243	−0.001	0 0 1	1 0 1
10.463	10.456	−0.007	3 2 0	3 2 0
10.793	10.791	−0.002	U	1 1 1
11.451			1 1 0 (Off.)	1 1 0 (Off.)
11.815	11.813	−0.002	U	2 1 1
12.002	11.999	−0.003	5 0 0	5 0 0
12.295	12.293	−0.002	U	3 0 1
12.478	12.471	−0.007	3 3 0	3 3 0
12.704	12.701	−0.003	4 2 0	4 2 0
12.980	12.980	0.000	U	2 2 1
13.369	13.367	−0.002	5 1 0	5 1 0
13.843	13.843	0.000	U	4 0 1

Off. indicates an offretite reflection and U an unindexed reflection
[a] Personal communication, Smith W, Bennett JM.
[b] Solution 1 had a = 36.147(3) and c = 7.329(1) Å.
[c] Final correct solution had a = 36.150(2) and c = 7.541(1) Å.

The use of Direct Methods in determining a weighting scheme for partitioning the intensities was developed by Jansen, Peschar and Schenk [5, 6]. The method was tested on a structure containing 22 atoms in the asymmetric unit cell; of the 527 observed reflections, 317 overlapped within half of the peak full width at half the peak maximum (FWHM) as determined in the fitting process [7]. Estermann et al. [8] described the structure determination of SAPO-40 (AFR)[1] using a different method for partitioning the intensities of the overlapping reflections. This Fast Iterative Patterson Squaring (FIPS) method indicated how to partition the intensity and only after this redistribution did an *ab initio* structure determination become possible.

Yet another method was applied to the structure determination of VPI-9 (VNI; [9]). This method uses a set of random starting phases for the intensities

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[1] The arrangement of the tetrahedral atoms in most of the zeolite structures is indicated by a three letter code. This code is independent of the composition of the zeolite, the space group and symmetry. A full list of all currently assigned codes can be found in the 'Atlas of Zeolite Structure Types' by W.M. Meier, D.H. Olson and Ch. Baerlocher, Fourth Revised Edition, published on behalf of the Structure Commission of the International Zeolite Association by Elsevier, London, Boston, 1996.

obtained from the powder pattern and is then combined with a topological search routine in the Fourier recycling procedure. With this method both chemical and structural information are incorporated into the partitioning procedure used for the powder diffraction profile. With seven crystallographically unique tetrahedral sites, VPI-9 is the most complex framework arrangement currently solved from powder diffraction without manual intervention.

Since one-dimensional intensity data from powders is resolved into three-dimensional intensity data for single crystals, the problem with obtaining individual intensity data is not present with single crystal data. Therefore, the determination of the unit cell and symmetry is less difficult. Using the correct unit cell dimensions the intensities of all the single crystal reflections can be measured without serious overlap in most cases.

The lack of individually measured reflections with powder data also has a detrimental effect on the structure determination and refinement procedure. In powder diffraction the ratio between the number of observations and the number of parameters to be refined is very often less than or equal to one. However, with single crystal data this ratio usually ranges from three to ten. This over abundance of data allows an incomplete, or even partly wrong starting model to be used to yield a successful solution and final refinement of the structure. A recent example, illustrating the difference between powder and single crystal data, is the structure determination of $GaPO_4(OH)_{0.25}$ (-CLO; [10]). Even with high-resolution synchrotron powder data, 552 of the first 617 reflections have exact 2θ overlaps. This extreme example of the overlap of the individual intensity data could not be overcome until a large single crystal became available for conventional analysis. Then 2776 independent reflections were measured and the refinement converged smoothly.

3
Incorrect Determination of the Space Group

Space groups are determined from a list of hkl reflections that are not observed. This is very difficult with powder data because of the occurrence of overlapping reflections. Without a space group no crystal structure solution can be completed. However, in many cases it is not necessary to determine the space group that will result from a successful structure refinement. It is often only necessary to determine the starting space group that defines the maximum symmetry of the topology (maximum topological symmetry). For example, it is not necessary to differentiate between the tetrahedral aluminum and phosphorus atoms in a microporous aluminophosphate material in order to determine the correct framework topology. Fortunately, there have been found to be only a small number of maximum topology space groups that are applicable; some of them are $C2/m$, $Cmcm$, $I4_1/amd$ and $P6_3/mmc$. Since the choice of unit cell dimensions will affect the systematic absences and ultimately the space group, this knowledge of applicable space groups can be helpful when choosing between two different, but equally possible, unit cells. However, it must be remembered that the space group chosen must account for all of the low hkl systematic absences.

There are many different techniques used by crystallographers to arrive at the starting topology of a new material. All techniques, except model building, require that the space group be correctly determined. However, this very important step of determining the starting topology is often not adequately reported, possibly because it is the most time consuming step of a powder structure determination. It is possible to spend months to years determining the correct topology which, when determined, can lead to spending only days to weeks on the final refinement. The powder pattern of the proposed topology can be simulated after refinement of the interatomic distances using a Distance Least Squares (DLS) refinement [11] procedure and can then be compared to the experimental pattern of the material. Even when there is a passable match between the observed and simulated powder patterns it does not mean that the proposed framework arrangement is correct. Probably, any partially incorrect topology can be refined with the Rietveld technique [12] to yield an apparently acceptable solution.

ZSM-18 (MEI; [13]) is the only aluminosilicate zeolite that has been reported to contain a three tetrahedral atom ring (a T_3-ring)[2]. However, similar framework structures, such as MAPSO–46 (AFS; [14]), CoAPO–50 (AFY; [14]) and beryllophosphate–H (BPH; [15]), do not support this novel arrangement. An examination of the reported framework topology shows that the three ring arrangements can be replaced by a vertical SiOSi unit with practically no change in the positions of the remainder of the framework atoms. Lowering the symmetry by removing the six-fold axes and changing to orthorhombic symmetry allows the framework to rotate off the original six-fold axis thereby reducing the vertical SiOSi bond angles of 180°, which are undesirable but observed in the proposed structure. Unfortunately, any DLS refinement of an orthorhombic arrangement always refines back to a pseudo six-fold axis. The final answer to the question of whether ZSM-18 contains three rings will require a complete structure determination using powder data and consideration of the possibility that the original space group used to determine the structure was incorrect.

A postulated framework arrangement based on a DLS refinement should always be treated with suspicion because very few DLS refinements use the full symmetry of the chosen space group since the only symmetry operations needed are those that generate bonds that lie across the asymmetric unit cell boundaries. In addition, there is always the possibility that the space group chosen is incorrect and that therefore the final structure is incorrect as well. Several correct structures have been refined in two or more space groups and illustrate that there are subtle changes in the framework topology depending on the choice of space group [16].

An example showing that the observed distortions of the framework are dependent on the choice of the space group is given by the refinement of SAPO-40 (AFR; [17, 18]). The ordering of aluminum and phosphorus in the structure required that the c-axis be doubled and the space group be changed from orthorhombic *Pmmm* to monoclinic *P112/n*. Subsequently, it was realized that

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[2] The standard method used to describe the number of atoms in a ring of a zeolite structure is to only count the tetrahedral (T) atoms. Thus a three ring opening would have three silicon atoms and the interconnecting three oxygen atoms for a total of six atoms.