Non-Standard Crystallography

Examples in 3- and 3+1 Dimensional Space

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Cover:
Top left: The departments Xcalibur3 Diffractometer
Top Right: The reconstructed hhlm layer of a cubically fourfold twinned Sn₄Sb₃ crystal
Bottom left: The $x_4$-x₃ plane electron density of the Sn and Sb atoms in the structure.
Bottom right: The final Sn₄Sb₃ structure after refinement.

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"A man is not idle because he is absorbed in thought. There is a visible labor and there is an invisible labor".

**Victor Hugo**

_French dramatist, novelist, & poet_.

_(1802 - 1885)_
Abstract

Crystallography today is by many seen as merely a tool for determining the structure of a material on the atomic level. It is expected that whatever comes out of the tool is the indisputable truth, a fact. This thesis is based on five publications illustrating that this is very far from the real world of materials research. The experiences drawn from the structural work in the papers are put together to illustrate when to be alert, and how to proceed with a structural investigation using non-standard crystallography. The focus is on interpreting the signs of additional order being present in a structure. The signs may be weak, such as extreme thermal vibration, or unit cell deformation. Or the signs can be strong, with superstructure reflections indicating the presence of either commensurate or incommensurate superstructures.
The thesis is based on the following publications:

I. "Solving Approximant Structures Using a 'Strong Reflections' Approach"
   J. Christensen, P. Oleynikov, S. Hovmöller, X. D. Zou

II. "The Sn\textsubscript{1-x}Sb\textsubscript{x}, x \sim 0.5, Solid Solution: the Relationship Between $\alpha$ and $\beta$"
    L. Norén, J. Christensen, S. Lidin, S. Schmid and R. L. Withers
    30th annual condensed matter and materials meeting. Wagga Wagga, Australia 2006. ISBN 1-920791-09-4

III. "The Samson phase, $\beta$-Mg\textsubscript{2}Al\textsubscript{3}, Revisited"

IV. "Vacancy Ordering Effects in AlB\textsubscript{2}-type ErGe\textsubscript{2-x} (0.4<x\leq0.5)."
    J. Christensen, S. Lidin, B. Malaman, G. Venturini
    Under revision by Acta. Cryst. B.

V. "The Origins of Superstructure Ordering and Incommensurability in Stuffed CoSn-type Phases"
    Fredrickson, D.C., Lidin, S., Venturini, G., Malaman, B., Christensen, J.
Publications outside this thesis:

"A new Approach for Solving Quasicrystal Structures"
X. D. Zou, J. Christensen, H. Zhang, P Oleynikov and S. Hovmöller
*Acta Cryst.* (2004). A60, s190

"Structure of Pseudodecagonal Al-Co-Ni Approximant PD4"
P. Oleynikov, L. Demchenko, J. Christensen, S. Hovmöller, T. Yokosawa, M. Döblinger, B. Grushko, X. D. Zou
*Philosophical Magazine, vol.86, No.3-5 /04 January 2006, 457-462*

"Strong Reflections in Quasicrystal Approximants"
J. Christensen
*Ph.Lic. Thesis 2004*
Preface

I have always taken great pleasure in working with and solving difficult problems. This is what initially led me to the field of crystallography. Together with my curiosity it is the key to the experiences I have gathered during my education. I always seek out crystallography-related problems both within my own projects, and within the projects of my colleagues. In this process I am often asked "How can you know that?" My intention with this thesis is to put together my experiences with certain kinds of problems that I have encountered during my Ph.D. education. The intended audience are people that have practical experience in crystallography but not necessarily the theoretical background. The thesis is not a textbook on the subject as many of these already exist. It is more an introduction to non-standard crystallography with the hope to make people aware of crystallography as a field still under development.
Introduction

During the last 30 years an impressive development of commercially available diffractometers has taken place. Especially the development of detector systems from film over point detector systems to the electronic area detectors, we have today, has had a great impact. This development has walked hand in hand with the development of electronic computing power. In all it has made what was once a technique reserved for the few, readily available for any researcher that would be in need of structural investigations. On top, in the last 15 years, there has been a development of software for structural determination from instruction file based Fortran programs to user-friendly windows based systems, or even fully automated systems. This has meant that there is no need for the user to have any background in mathematics or programming to determine a crystal structure. The result of the automatisation is that no theoretical background is needed either: X-ray crystallography is no more than a tool or black box; you enter a crystal and get back the structure.

Is this really true? Have we reached the end of crystallography as a research area - is there nothing more to learn?

For the majority of the crystal structures that are solved this is very near to the truth; otherwise there would be no market for the "black box" products. But what to do when the box fails to give an output, and how to evaluate the quality of an output, apart from looking at the refinement R-values? This thesis will present some of the situations where the black box is failing and some of the ways of handling the problem.
1. Methods for structure solution

When collecting diffraction data we only gain half of the information about the structure directly. It is well known that to solve a structure we must recreate the structure factor phases. Through time, many methods for solving the famous "phase problem" in crystallography have emerged. This chapter will shortly describe some methods that are useful when dealing with non-standard crystallography, and try to explain their strengths and weaknesses.

The crystallographic structure factor can be expressed using Equation 1-1 and the relation between measured intensities and the structure factor amplitude is given in Equation 1-2.

Equation 1-1 \[ F(\mathbf{H}) = \sum_{j=1}^{N} f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) = |F(\mathbf{H})| \exp[i\phi(\mathbf{H})] \]

Equation 1-2 \[ I(\mathbf{H}) \propto |F(\mathbf{H})|^2 \]

Among the early methods the Patterson function\(^1\)\(^2\) (Equation 1-3) stands out as a method still used today. The Patterson function is defined as the convolution of the electron density with itself; that is the autocorrelation function of the electron density distribution.

Equation 1-3 \[ P(u) = \frac{1}{V} \sum_{\mathbf{H}} |F(\mathbf{H})|^{2} \exp(-2\pi i \mathbf{H} \cdot \mathbf{u}) = \sum_j \sum_k P_{jk} [\mathbf{u} - (\mathbf{r}_j - \mathbf{r}_k)] \]

The peaks in a Patterson map correspond to the interatomic distances present in the structure. Mathematically, the Patterson function is only depending on the scattering intensity distribution, and can therefore be calculated directly from experimental data. The function does not rely on symmetry but the interpretation of the resulting map is greatly simplified by the occurrence of special positions for the heavy atoms. For simple structures with only a few atoms, this interatomic vector map provides a very good starting point for construction of structure models. A structure may also be regarded as simple in relation to the Patterson function if it contains only a few heavy atoms, as for example the sulphur atoms in a protein molecule. Macromolecular crys-
tallography is the area today where the Patterson function is used as a structure solution method. This is done in different disguises or incorporated into other methods. It is an essential part of ShelxD\(^3\) and Shelxpro\(^4\) where it is used for the initial assignment of "random" phases in MAD and SAD phasing routines. The Patterson function holds no assumption about atomicity or dimensionality, and is easily expanded to any dimension necessary to solve a modulated structure.

The most successful of all methods is the Direct Methods\(^5,6\)(incl. references). The method is model independent and only uses the information obtained from the diffraction experiment; diffraction intensities and symmetry. The use of symmetry reduces the calculation times significantly, something that was of great importance in the early days of computers and crystallography. Direct Methods are based on relationships among the structure factor phases induced by symmetry and by physical limits, e.g. the electron density of a real crystal cannot be negative. The most important formulas behind the procedure are: Sayres Equation\(^7\) (Equation 1-4). This may also be expressed as the famous triplet relation (Equation 1-5) stating that the most probable phase for a structure factor is given by the phase of the structure factors forming a vector triangle with the one for which we seek the phase. Karle and Hauptman\(^8\) were the first to put forward the Tangent Formula (Equation 1-6), which is a development of Sayres Equation and more suitable for computer programming. In this equation \(E_H\) is a normalized structure factor for reflection \(H\).

\[ F(H) = \frac{\theta(H)}{V} \sum_{H'} F(H')F(H-H') \]  
\[ \langle \phi(H) \rangle = \phi(H') + \phi(H-H') \]  
\[ \tan \phi(H) = \frac{\sum_{H'} [\kappa(H,H') \sin(\phi(H') + \phi(H-H'))]}{\sum_{H'} [\kappa(H,H') \cos(\phi(H') + \phi(H-H'))]} \]  
\[ \kappa(H,H') \propto |E(H)E(H')E(H-H')| \]

The introduction of Direct Methods into structure solution programs have made crystallography available to a broad audience, and has solved literally hundred of thousands of structures and it is the first choice for almost any structural investigation. However, it is well known that large numbers of
unique atoms tend to cause difficulties when applying standard Direct Methods programs\textsuperscript{9,10,11,12}. Furthermore pseudo-symmetries in a structure will cause some reflections to be systematically weaker or stronger. This may give rise to phase ambiguities\textsuperscript{13} or other problems\textsuperscript{14,15} when trying to solve the structure by Direct Methods.

Large quasicrystal approximants for example contains both a large number of unique atoms and several different kinds of pseudo symmetries, both rotational, translational and inversion centre related. This has been shown to cause difficulties when applying standard Direct Methods\textsuperscript{16,17}. To solve structures having pronounced sub-cells and pseudo-symmetry not compatible with 3D space groups, such as quasicrystal approximants, a method referred to as "Strong Reflections Approach" has been explored recently\textsuperscript{18,19,20,21,22}. The method takes advantage of the correlations caused by the pseudo-symmetries and the sub-cell. It is a well known phenomenon that the diffraction patterns and structures of certain approximants are related\textsuperscript{23,24}. This relation is based on the assumption that the element content of the structures are similar. The Strong Reflections Approach may be detached from any such assumptions about element content or for that matter the full symmetry of the diffraction data. The method simply relies on how Direct Methods are working; that a given geometric distribution (a given set of triplet relations) of intensity in reciprocal space will yield a specific phase solution, no matter what actual structure it arises from. Two structures do not need to be obviously related in direct space as long as they are similar in reciprocal space, for example being related by the same sub-cell or pseudo-symmetry. Even small variations in geometry will not affect the result as long as the intensity distribution is maintained. It is the same principles we use when solving a superstructure by first solving the basic structure from the main reflections, and then apply the assumption that the result will be unaffected by the addition of superstructure reflections.

A new method called Charge Flipping\textsuperscript{25,26,27} has recently been developed. Charge Flipping is a dual-space Fourier cycling method that is symmetry independent and independent of atomicity. As a result of the later, Charge Flipping will work in any dimensionality and is as such especially useful for modulated structures. Shortly described, the Charge Flipping routine works in the following way. First the unit cell (of any dimension) is overlaid with a grid. The electron density will be evaluated on the grid points only. An initial electron density is calculated using the observed structure factor amplitudes, $F_{ obs}$. For reflections not measured $F_{ obs}$ is set to zero. Random phases are then assigned, applying only Friedel pair relations.

\[
F_{ obs}^0(H) = \begin{cases} 
F_{ obs}(H) \exp \left[ i \varphi^{(0)}(H) \right] & \text{if } F_{ obs}(H) \text{ is known} \\
0 & \text{if } F_{ obs}(H) \text{ is not measured}
\end{cases}
\]
In the $n$th iteration cycle each grid point is evaluated, and the electron density from the previous cycle (n-1) is kept if the density is larger than a small positive threshold, $\delta$, and inverted if below the threshold, Equation 1-9. From this new electron density, new structure factor phases are calculated and combined with $F_{\text{obs}}$.

**Equation 1-9**

$$\rho_{CF,k}^{(n)} = \begin{cases} 
\rho_k^{(n-1)} & \text{if } \rho_k^{(n-1)} > \delta \\
-\rho_k^{(n-1)} & \text{if } \rho_k^{(n-1)} < \delta 
\end{cases}$$

The cycling continues until convergence is achieved and an overall positive electron density has emerged. Charge Flipping relies on the $F_{\text{obs}}$ being correctly determined and will not work for twinned crystals if the twinning is not recognized. The overlapping reflections can be separated if the twin law is known. Charge Flipping can then be applied to the corrected data. For a more detailed description additional reading may be found in the references 30a, 25 and 27.
2. Warning signs of incomplete solution

What remains after solving the phase problem is the structure model refinement. Apart from the cases where the refinement will not proceed to reasonable R-values, certain signs sometimes emerge indicating that the model used to describe the structure is not optimal or incorrect when it comes to the details. In this chapter some of these signs will be briefly presented with examples of their occurrence. The signs may be grouped into those relating to the model and those emerging directly from the data. It should be stressed here that models not taking these effects into account are not necessarily wrong; they may give a very useful and correct image of the overall average structure. For many purposes this kind of model is sufficient.

2.1. Extreme Thermal vibration, partial Occupation and/or Disorder.

This group of effects constitutes the weakest indications that a model is not optimal, and they are normally ignored as arising from bad crystal quality or poor data. We must also remember that a statistical distribution of atoms on a certain site in some situations is perfectly reasonable and possible. Many examples of these signs exist in the literature, and here we will use the AlB$_2$-type structures. A typical model found for this structure type is shown in Figure 2-1.

![Figure 2-1 The structure of NpSi$_{1.6}$ with 75% thermal ellipsoids indicated. Blue is Si atoms and gray is Np atoms.](image)
The NpSi\textsubscript{1.6} structure alone illustrates the issues of partial occupation and large thermal ellipsoids; The hexagonal planes are only 80 % occupied. The Si atom is modelled with an unusually high thermal vibration within the plane whereas the vibration out of the plane is similar to the vibration of the Np atoms. This structural picture is typically what is found for all the AlB\textsubscript{2}-type structures being deficient on the B site. AlB\textsubscript{2}-type forming elements found by a literature search are shown in Figure 2-2.

![Figure 2-2 An overview of the elements forming the AlB\textsubscript{2}-type structure. Elements coloured gray prefer the Al site and elements coloured blue prefer the B site.](image)

2.2. Unit cell deformation

One of the most subtle indications that something is not quite right, can be seen already at the data collection stage: Slight deformations of the unit cell away from what would seem like the correct crystal class. This sort of behaviour is often ascribed to physical effects associated with the data collection, such as instrument calibration. It may indeed be caused by crystal quality, alignment of the crystal and so on. Examples exist though were the observed deformation is a real effect even if the data appears to have the full point symmetry of the higher crystal class.

A typical case is deformation due to the introduction of vacancies. In the group of rare earth germanides and silicides with the ThSi\textsubscript{2}-type structure the vacancies are not visible as thermal vibrations mimicking the lattice relaxation but as partial order with lower occupancy on certain sites. The partial ordering results in cell deformations away from tetragonal geometry, and the orthorhombicity ratio \( \frac{(a-b)}{(a+b)} \) will depend on the occupancy\textsuperscript{29}. The result
is a large number of structures not being recognized as belonging to the ThSi$_2$-type structure.

2.3. Extinction conditions

In reciprocal space, a strong sign of erroneously chosen symmetry is the presence of violations of the extinction conditions. If these reflections are many or strong it is no problem to detect them. They may though be weak and hard to find, as in the case of $\beta$-Mg$_2$Al$_3$. In this example violations to the $d$-glide in the cubic space group $Fd\overline{3}m$ are found as indicated in Figure 2-3.

![Figure 2-3](image)

**Figure 2-3** hk0 Laue image reconstructed from room temperature data on $\beta$-Mg$_2$Al$_3$. The $d$-glide violations are marked with red circles.

Another sign, indicating that a change of space group may be appropriate is the presence of additional extinction conditions not exploited in the used space group. Such conditions may well show not to comply with any 3D space group symmetry.

2.4. Un-indexed reflections in 3D reciprocal space

A very obvious indication that a 3D model will not be sufficient is the occurrence of reflections that cannot be indexed using only three reciprocal space vectors. These reflections may lie along one of the principal 3D axes, in a plane defined by two principle axes, or in the general case all three 3D axes are needed to define the position. This kind of reflections will in the rest of the thesis be referred to as satellite reflections; an example is given in
Figure 2-4. To index the satellite reflections with integers, additional lattice vectors are needed. Each such vector is referred to as a modulation wave vector or q-vector, and adds an additional dimension to the unit cell. The q-vector is expressed in terms of the principal 3D lattice vectors, Equation 2-1. The parameters $\alpha$, $\beta$, and $\gamma$, are the q-vector’s component along each of the principal 3D lattice vectors and should not be confused with the unit cell angles.

\[ q = (\alpha a^* + \beta b^* + \gamma c^*) \]

In some cases more than one q-vector will be needed to index the entire diffraction pattern, and the vectors are then numbered $q_1, q_2, \ldots$. Each q-vector gives rise to an additional Miller index for all reflections. In the 3+1D case the additional index is labelled $m$. The value of $m$ determines what is called the order of a reflection. For $m=0$ the reflections are main- or basic reflections. For $m=\pm1$ the reflections are 1$^{\text{st}}$ order satellites, and for $m=\pm2$ the reflections are called 2$^{\text{nd}}$ order satellites and so on. All of this is illustrated in Figure 2-4 and further reading on the subject may be found in the references. 

![Figure 2-4 hhlm layer from a Sn$_{1.8}$Sb$_{1.5}$ compound with a rhombohedral unit cell in hexagonal setting. The use of the q-vector to index the satellite reflections is illustrated.](image)

The values of $\alpha$, $\beta$, and $\gamma$ are also important. If any of these are non-rational the modulation is incommensurate. If the values of all three parameters si-
multaneously are rational the modulation is \textit{metrically} commensurate, and reflections will overlap. The nature of this overlap is what determines whether the modulation is truly commensurate or not. If the overlap results in the sum of intensities, the structure is incommensurate, but if the overlap result is the sum of structure factors, the modulation is truly commensurate. This is schematically illustrated in Equation 2-2.

\begin{equation}
I_{\mathbf{s}+\mathbf{t}} = \begin{cases} F_s^2 + F_t^2 \iff \text{Incommensurate} \\ (F_s + F_t)^2 \iff \text{Commensurate} \end{cases}
\end{equation}

\section*{2.5. Diffuse scattering}

It is not always that additional scattering takes the form of Bragg reflections. In many cases the extra order in a crystal structure is only partial and the satellites will have the form of diffuse "blobs" or streaks. No standard method exists for dealing with diffuse scattering, but qualitative analysis is still possible. As the diffraction arises from an extra order that is not fully realized it will occur between the Bragg reflections, and therefore give information about the length scale of the ordering. It is then often possible to "guess" the ordering effect from the structure solution, as this will often show some of the other warning signs discussed here.

A different kind of diffuse scattering arises from strain at the grain boundaries in the crystal. This will normally occur near the Bragg reflections and may look like a smearing of the peaks. It is the result of a mechanical effect on the nanometre scale and it may help to perform annealing to relieve the strain.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-5.jpg}
\caption{Left: Two reconstructed Laue images (hexagonal setting) from Cu$_3$In$_2$. $h2l$ showing well ordered satellites and $h7l$ with diffuse satellites. Picture is courtesy of Shuying Piao. Right: The $Ikl$ (cubic setting) diffraction pattern of Sn$_4$Sb$_3$ showing cubic twinning, satellites and diffuse scattering.}
\end{figure}
2.6. Intergrowth structures

A special kind of situation occurs when a structure may be described as an intergrowth between two structure types. Nothing can be said to be wrong with a 3D structure solution, but it does not take advantage of the correlations that exist within each of the structure types present. To take a different approach using the symmetry in each of the structure types is first of all a question of parameter economics, especially of interest when using powder data. A second issue to add is the question of what is an elegant description; this is of course an individual taste. In the literature numerous examples of intergrowth structures are found\textsuperscript{31,32,33,34,35,36,37,38,39} but they are not always recognized as an intergrowth. A good and simple example can be found in the homologous series formed by the compounds USn\textsubscript{2}, U\textsubscript{3}Sn\textsubscript{7}, Ce\textsubscript{2}Sn\textsubscript{5},\textsuperscript{40,41,42} The structures are illustrated in Figure 2-6. We will return to this series in section 3.3.

![Figure 2-6](image-url)

**Figure 2-6** The homologous series a) USn\textsubscript{2}, b) U\textsubscript{3}Sn\textsubscript{7}, and c) Cs\textsubscript{2}Sn\textsubscript{5}. Blue indicate the Sn atom and gray is the rare earth atom.
3. Symmetry Reduction as a solution to the problems

The problems discussed in chapter 2 call for different approaches to arrive at a solution, but they all involve the reduction of symmetry in one way or another. Here we will present four approaches illustrated with examples.

3.1. Group-Subgroup relations

The simplest form of symmetry lowering is to remove certain symmetries by changing the space group. As a solution to the refinement problems discussed here, this is most appropriately done by following group-subgroup relations to eliminate unwanted symmetries that relate to, and may be the cause of the observed problem. The indication of a need for such a step may come either from direct space, in the form of disorder, for example an atom moving out of a mirror plane or from reciprocal space as unit cell deformations or violations to extinction conditions. A good example structure is the $\beta$-Mg$_2$Al$_3$ structure first solved by Samson$^{43}$ and now re-determined within the CMA-network$^{44}$. The background for studying this structure once more is presented in the introduction to paper III.

One of the crystals received from Michael Feuerbacher$^{44}$ is shown in Figure 3-1. Room temperature data were collected, giving a cubic unit cell and R-merge indicating cubic symmetry. The structure was refined in the space group $Fd\bar{3}m$ (no. 227 origin choice II, origin on 3m). This gave a disordered structure similar to that reported by Samson.

We then proceeded with a low temperature (100K) data collection, and this yielded the same result. On careful inspection of $hk0$-Laue images reconstructed from the data, we discovered some weak but sharp

Figure 3-1 One of the spherical crystals of $\beta$-Mg$_2$Al$_3$, cut from a large single crystal, and polished. All samples received were cut from the same single crystal.
Bragg peaks violating the $d$-glide extinction condition, Figure 3-3a. This lead us to explore the group-subgroup relations for $Fd\bar{3}m$. Following the diagram in Figure 3-2 we then tried the space group $F\bar{4}3m$ as this splits the partial occupied orbits in the structure. This had little effect on the R-values and still resulted in a disordered model. We then tested the space group $R\bar{3}m$ (in non-standard setting this is equivalent to $F\bar{1}3m$), this lead to a significant improvement of the R-values but a disordered and twinned model.

![Figure 3-2 Diagram of the group-subgroup relations connecting the space groups $Fd\bar{3}m$ (no. 227) and $R\bar{3}m$ (no. 160). The diagram is constructed using the program SUBGROUPGRAPH\textsuperscript{46}. No distinction is made between κ and τ type group-subgroup relations.](image)

We then compared the room temperature data with the 100K data and some prominent diffuse scattering could be seen around the most intense Bragg reflections, while weaker diffuse scattering was located between the Bragg reflections. For the room temperature data an example of the observed diffuse scattering is visible in Figure 3-3a. The intensity of the diffuse scattering did not decrease when lowering the temperature, this rule out thermal effects as the cause, leaving the possibility of grain boundary strain in the crystal.
To relieve the strain, the crystal was annealed at 180°C for 36 hours, and new data were collected showing a dramatic change in the diffuse scattering (Figure 3-4) and also in the number of $d$-glide violations, Figure 3-3b.

Figure 3-3 a) $hk\theta$ Laue image reconstructed from room temperature data on $\beta$-Mg$_2$Al$_3$. The $d$-glide violations are marked with red circles. b) $hk\theta$ Laue image reconstructed from room temperature data collected on the annealed crystal. The $d$-glide extinction condition is now clearly unfulfilled. Both images are in cubic setting.
The unit cell found for the new data is metrically cubic, but the data statistics for cubic symmetry was significantly worse than for the data before annealing. By comparing the data statistics for rhombohedral symmetry corresponding to each of the four cube diagonals, one direction stood out as a particularly good choice indicating that only one of the cubic 3-fold axes remains after annealing. The data were integrated and data statistics showed that the symmetry should be lowered even further to $R\bar{3}m$ (no. 160). Structure solution and refinement proceeded in this space group. The difficulties do not stop here though. During the initial steps of the structure refinement it became obvious that the cubic pseudo-symmetry is so strong that the Direct Methods solution was cubic. As a result, residuals appeared corresponding to a cubic twinning of the structure. It was necessary to let these enter into the refinement and eventually the atoms that break the cubic symmetry were located. Once this happened, the atoms in the ghost twins refined to zero occupancy and could be removed from the model. The appearance of these ghost twins are illustrated in Figure 3-5 for the location of one cluster. In the final refinements a twin matrix corresponding to cubic twinning was used. This resulted in the refined phase volumes 85% for the major component and 5% for each of the remaining twins.

An additional twist to the story is the poor elemental contrast between Mg and Al that only differ in one electron. The elemental distribution was resolved using two different approaches. One approach is to look at inter-atomic distances as Mg is larger than Al. The other approach is to set all atoms equal to Mg and refine positions and thermal displacement parameters. If the quality of the collected data is high, then the atoms having ex-
tremely small thermal parameters will be the Al sites. The two methods yielded the same elemental distribution and the same ambiguities.

Figure 3-5 The location of ghost atoms around one cluster centre, necessary to locate the inner shell (blue) of the cluster. The figures a) to d) are consecutive refinement cycles. In the final model no ghost atoms remain.

Inspection of the final structure shows that it is build from two different cluster arrangements each build up by three shells. These clusters are then ordered in a diamond network and the space between the clusters is filled by a network of Friauf polyhedra, Figure 3-6. This entire arrangement is cubic. The breaking of cubic symmetry happens within the clusters. The colour coding used in Figure 3-6 is also used in Figure 3-7.
Figure 3-6 a) The arrangement of clusters in a diamond network surrounded by Friauf polyhedra. b) The same arrangement viewed down the rhombohedral c-axis. c) The Mg centred Al build Friauf polyhedron filling the space between the clusters. The clusters in the diamond network are coloured according to the central atom. Ambiguous means that the element species was undetermined by the two methods used.

The shells building up the two clusters are shown in Figure 3-7. The overall point symmetry of the clusters is $3m$, and some very distinct features breaking the cubic $\overline{4}3m$ point symmetry are visible in both clusters. If we compare the second shell of the clusters, (b) and e) in Figure 3-7), we see that the shell in b) have a triangular feature of Mg atoms where the shell in e) has a three-star of Al and visa versa. In total b) has 3 triangles and one star whereas e) contains 1 triangle and 3 stars. Apart from this the two shells have point group symmetry $\overline{4}3m$. In the same way we can compare the shells shown in c) and f) of Figure 3-7. Again they differ only in the distribution of triangles and stars, and the remaining part of the shells follows the $\overline{4}3m$ point symmetry. The inner shells shown in Figure 3-7 a) and d) are given again in Figure 3-8 for a better representation of the symmetry. In total, 13 atoms out of the 80 unique atoms break the cubic symmetry.
Figure 3-7 The different shells building up the clusters. The colour coding is the same as in Figure 3-6. The different features breaking the cubic symmetry are discussed in the text.
Figure 3-8 The inner shell of the two clusters. They are clearly seen to have different symmetry.
3.2. Supercells

A group of structures where ordering in the form of supercells often occur is the host-guest type structures, where varying interactions between the guest and host leads to a variety of superstructures. As an example representing this kind of structures, we will take the superstructures to the NaMo$_4$O$_6$ structure$^{47}$ type shown in Figure 3-9.

![Figure 3-9 The structure of NaMo$_4$O$_6$ viewed along the $a$-axis and along the tetragonal $c$-axis. The unit cell is shown in green.](image)

<table>
<thead>
<tr>
<th>S.G.</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Mo1</td>
<td>0.1021(1)</td>
<td>0.3979(1)</td>
<td>1/2</td>
</tr>
<tr>
<td>$c$</td>
<td>Mo2</td>
<td>0.3556(1)</td>
<td>0.1444(1)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Na1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>0.2064(9)</td>
<td>0.2936(9)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>0.2407(8)</td>
<td>0.0451(9)</td>
<td>1/2</td>
</tr>
</tbody>
</table>

In the different members of this family, the element on the guest (Na) site is varied, with varying occupancy of the guest site and distortion of the host framework as a result$^{48,49,50,51}$. This is illustrated in Figure 3-10 showing the case of Pb. In this case superstructure reflections were detected corresponding to a four-fold supercell, and the structure refined as a superstructure$^{51}$. This example and a similar superstructure with a mixture of Ti and Mo on the guest position will be treated in detail in section 4.1 and it will be shown how a different treatment of the satellite reflections will result in an ordered model.
Figure 3-10 The structure of Pb$_{0.62}$Mo$_4$O$_6$ as found in the literature. Here viewed along the $a$-axis and along the tetragonal $c$-axis. The unit cell is shown in green.

Table 3-2 Structural parameters for Pb$_{0.62}$Mo$_4$O$_6$. All metal atoms were allowed anisotropic temperature parameters, but only $U_{eq}$ values are listed. The total number of parameters is 45, as the occupancies are fixed.

<table>
<thead>
<tr>
<th>S.G.</th>
<th>$P4/mnc$ (no.128)</th>
<th>Atom</th>
<th>Occ</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$($\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>9.615(1)</td>
<td>Pb1</td>
<td>0.75</td>
<td>0</td>
<td>0</td>
<td>0.3009(2)</td>
<td>0.0097(3)</td>
</tr>
<tr>
<td>$c$</td>
<td>11.362(3)</td>
<td>Pb2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0474(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb3</td>
<td>0.125</td>
<td>0</td>
<td>0</td>
<td>0.4458(10)</td>
<td>0.030(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb4</td>
<td>0.125</td>
<td>0</td>
<td>0</td>
<td>0.2474(10)</td>
<td>0.013(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo1</td>
<td>1</td>
<td>0.1435(2)</td>
<td>0.6435(2)</td>
<td>0.25</td>
<td>0.0076(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo2</td>
<td>1</td>
<td>0.1445(3)</td>
<td>0.6434(2)</td>
<td>0</td>
<td>0.0091(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo3</td>
<td>1</td>
<td>0.6024(1)</td>
<td>0.1015(1)</td>
<td>0.1250(1)</td>
<td>0.0043(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1</td>
<td>1</td>
<td>-0.2067(12)</td>
<td>0.7067(12)</td>
<td>0.75</td>
<td>0.008(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2</td>
<td>1</td>
<td>0.0415(11)</td>
<td>0.7627(11)</td>
<td>0.1237(9)</td>
<td>0.005(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O3</td>
<td>1</td>
<td>0.0413(12)</td>
<td>0.7597(12)</td>
<td>0.3750(9)</td>
<td>0.010(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O4</td>
<td>1</td>
<td>-0.2098(19)</td>
<td>0.7043(19)</td>
<td>0.5</td>
<td>0.010(3)</td>
</tr>
</tbody>
</table>
3.3. Commensurate

A different kind of superstructure is the intergrowth between two structure types. To get an overview of the whole structural variety of such a family it is convenient to make a superstructure model in higher dimensions covering all the existing structures. This will greatly reduce the number of parameters necessary to describe the structures. A model can be built using only the information already published. Here we will take as an example a very simple structure family; that of intergrowth between the CuAu- and Cu\textsubscript{3}Au structure types, exemplified with RE-Sn structures. The superstructure ordering in this family is different from the long range ordering in the Au-Cu system itself\textsuperscript{31,52,53}.

The RE-Sn compounds of interest exist in the range 66.67 at.% Sn to 75 at. % Sn, and shows composition driven long range ordering. The known commensurate members are given in Table 3-3 and their structures are shown in Figure 3-11.

Table 3-3 The known members of the intergrowth series between the CuAu- and Cu\textsubscript{3}Au structure types formed in the RE-Sn systems. Space group and unit cell parameters are given for comparison. The number of parameters refined in the published work are given where known and the theoretical minimum number corresponding to one common thermal parameter for all tin atoms and one for the rare earth atoms are given in parenthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>S.G.</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>#Parameters</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>USn\textsubscript{2}</td>
<td>Cmmm</td>
<td>4.4228(9)</td>
<td>15.451(3)</td>
<td>4.4683(9)</td>
<td>- (4)</td>
<td>40</td>
</tr>
<tr>
<td>U\textsubscript{3}Sn\textsubscript{7}</td>
<td>Cmmm</td>
<td>4.473(2)</td>
<td>24.59(1)</td>
<td>4.498(2)</td>
<td>- (6)</td>
<td>40</td>
</tr>
<tr>
<td>USn\textsubscript{33}</td>
<td>Pm\textbar{3}m</td>
<td>4.62</td>
<td>-</td>
<td>-</td>
<td>- (2)</td>
<td>42</td>
</tr>
<tr>
<td>Ce\textsubscript{3}Sn\textsubscript{7}</td>
<td>Cmmm</td>
<td>4.524(1)</td>
<td>25.742(11)</td>
<td>4.610(2)</td>
<td>10 (6)</td>
<td>41</td>
</tr>
<tr>
<td>Ce\textsubscript{2}Sn\textsubscript{5}</td>
<td>Cmmm</td>
<td>4.559(6)</td>
<td>35.01(4)</td>
<td>4.619(4)</td>
<td>14 (8)</td>
<td>41</td>
</tr>
<tr>
<td>CeSn\textsubscript{3}</td>
<td>Pm\textbar{3}m</td>
<td>4.721(2)</td>
<td>-</td>
<td>-</td>
<td>- (2)</td>
<td>41</td>
</tr>
</tbody>
</table>

To analyze the series we first have to locate the end members. The 1:3 compounds are the end of high tin content, but investigating the 1:2 compounds both in direct space (Figure 3-11) and in reciprocal space (hk0 layer Figure 3-12) it is seen also to be a superstructure. The real low tin content end member is the CuAu structure type.

We may now commence a symmetry analysis based on the known structures. The space group of the CuAu structure type is \textit{P4/mmm} (no.123) equivalent to \textit{C4/mmm} in a non-standard setting, and for the Cu\textsubscript{3}Au structure type the space group is \textit{Pm\bar{3}m} (no.221). The intermediate commensurate members listed in Table 3-3 all have the symmetry \textit{Cmmm} (no.65), and further does the modulation wave vector have the form \(q = \beta b^*\) as seen from Figure 3-12. In all, this requires us to lower the symmetry for the end members to orthorhombic. The highest allowed symmetry for the CuAu structure type is then \textit{Cmmm} and for the Cu\textsubscript{3}Au structure type it is \textit{Pmmm}.
Figure 3-11 From left to right, the published structures of Ce$_2$Sn$_5$, U$_3$Sn$_7$ and USn$_2$. Important to note is how the Sn atom at the interface moves out of the plane defined by the rare earth atom (sn2 in the superspace model).
The diffraction pattern from USn$_2$ shows that all reflections follow the condition $hklm: h+k+m=2n$, indicating a centring vector of $\frac{1}{2}\frac{1}{2}0\frac{1}{2}$ for the 3+1D superspace lattice. In total the information results in the superspace group $X\text{mmm}(0\beta0)000$ where $X$ represents the non-standard centring involving the fourth dimension.

Figure 3-12 The $hkl0$ layer calculated from the published USn$_2$ structure. The pattern shows superstructure reflection, and the USn$_2$ is thus not the low tin content end member. The published cell is shown in black and the new basic cell shown in green. For two reflections the satellite indexing and overlap is indicated.
The two end structure types are shown in Figure 3-13 and a calculated $hk0$ layer for each is shown in Figure 3-14. The Cu$_3$Au type corresponds to $\beta=0$ and the CuAu type corresponds to $\beta=1$.

Figure 3-13 Left: The CuAu structure type. Right: the Cu$_3$Au structure type. For both structures yellow indicate the gold sites and orange indicate the copper sites. Intergrowth ordering occurs along the b-axis.

Figure 3-14 a) The $hk0$ layer for the CuAu structure type. The standard cell is shown in black and the new basic cell is shown in green. b) The $hk0$ layer for the Cu$_3$Au structure type. The published cell is identical to the basic cell used in the superspace description, and is shown in green.
Comparing the length of the b-axis for the compositions in Table 3-3 with the length of the b-axis for the 1:3 compounds we find the value of $\beta$ for each compound. For USn$_2$ we can also see from Figure 3-12 that $\beta$ is $1/3$. From the literature$^{54}$ we find that the stoichiometry can be described by one single parameter, $n$. This may be used to describe the value of $\beta$ as well, as shown in Table 3-4.

Table 3-4 The connection between the observed structures and the parameter $n.$

<table>
<thead>
<tr>
<th>$n$</th>
<th>Formula (RE$<em>n$Sn$</em>{3n-2}$)</th>
<th>$\beta=1/(2n-1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>USn$_2$</td>
<td>1/3</td>
</tr>
<tr>
<td>3</td>
<td>U$_3$Sn$_7$</td>
<td>1/5</td>
</tr>
<tr>
<td>4</td>
<td>Ce$_2$Sn$_3$</td>
<td>1/7</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$\infty$</td>
<td>CeSn$_3$</td>
<td>0</td>
</tr>
</tbody>
</table>

Looking at the structures in Figure 3-13 it is seen that half of the atoms in the unit cell are always tin, while the other half will be a mixture of RE atoms and tin atoms with a ratio given by $n$. With this observation it is convenient to reformulate the stoichiometry expression: As half of the atoms can be expressed as 2n-1 the new expression for the composition is RE$_n$Sn$_{2n-1}$Sn$_{2n-1-n}$

To calculate the occupancy it is necessary to normalize to one atom, this is done by division by 2n-1, and the stoichiometry now reads

**Equation 3-1** \( \text{RE}_{n/(2n-1)}\text{Sn}_{1}\text{Sn}_{(n-1)/(2n-1)} \)

From the structures shown in Figure 3-11 it is seen that the tin atom in the boundary between the Cu$_3$Au-type blocks moves towards the neighbouring block. Now all the information is ready to put together the complete 3+1D superspace model. The parameters are given in Table 3-5.

Table 3-5 The structural parameters for the 3+1D structural description. The only parameters free to refine are the harmonic modulation wave on Sn2, (symmetry restricted to only affect the position along $x_2$) and thermal parameters on the atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>Occ.</th>
<th>Modulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>n/(2n-1)</td>
<td>crenel on occupancy $x_4^0=0$</td>
</tr>
<tr>
<td>Sn1</td>
<td>$1/2$</td>
<td>$1/2$</td>
<td>0</td>
<td>$(n-1)/(2n-1)$</td>
<td>crenel on occupancy $x_4^0=0$</td>
</tr>
<tr>
<td>Sn2</td>
<td>0</td>
<td>$1/2$</td>
<td>$1/2$</td>
<td>1</td>
<td>1 harmonic wave on $x_2$</td>
</tr>
</tbody>
</table>

The minimum number of parameters to refine is 2 thermal parameters and 1 harmonic wave parameter to account for the relaxation at the block interface, the rest is locked by symmetry or the composition. This should be compared
to the number of parameters mentioned in Table 3-3. A more reasonable number is 3 thermal parameters if all atoms are treated independently, but isotropic. Only the very symmetry restricted 1:3 end structure has less parameters.

For the observed structures \( n \) is an integer, but nothing in this description prevents \( n \) from taking on any value. This corresponds to the ratio of the \( q \)-vectors length becoming irrational with respect to the basic unit cell as described in section 2.4. When this happens, the structure is said to be incommensurately modulated. The superspace models used to describe intergrowth compounds are not restricted to the commensurate members; they describe all the intermediate compositions too. For the model we have just derived two theoretical incommensurate cases are illustrated in Figure 3-15. Whether or not these compounds exist is another question. The lack of information on these intermediate compounds may rely on that only the "best quality" crystals of a product were investigated, or that no syntheses have been attempted in the region. It may also be that specific intermediate stoichiometries are not favourable as is the case in the \( \text{AlB}_2 \)-type \( \text{ErGe}_{2-x} \) compounds discussed in paper IV. When passing through the incommensurate values the \( q \)-vector may change not only in length but also its direction to encompass a continuous change in composition. The family of intergrowth between the \( \text{ScFe}_6\text{Ga}_6 \) and \( \text{ScFe}_6\text{Ge}_6 \) structure types thoroughly described in paper V is an excellent example.
Figure 3-15 Two hypothetical incommensurate structures generated using the proposed model and values of $n = \pi$ and $n = \sqrt{5}$. The models does not show the relaxation at the block interface. For easy overview the empty octahedra formed by the Sn atoms are drawn to show the Cu$_3$Au structure type blocks.
3.4. Incommensurate

3.4.1. The structure of $\beta$-SnSb

Stoichiometry variation controlled by block interfaces is not a phenomenon limited to intergrowth compounds. In the Sn-Sb intermetallic system the $\beta$-SnSb compound has a large homogeneity range, best described as $\text{Sn}_{1-x}\text{Sb}_{1+x}$ ($-0.57 \leq x \leq 0.4$). Though the Sn-Sb system has been investigated several times many unsolved questions exist$^{55,56,57,58}$. Like with the $\beta'$-$\text{Mg}_2\text{Al}_3$ structure, the Sn-Sb compounds show little elemental contrast from the difference in electron count, and any ordering should be expected difficult to find. For this reason it is surprising that the $\beta$-SnSb shows satellite reflections as strong as the main reflections. Where does the contrast come from?

In the homogeneity range of $\beta$-SnSb four samples were produced. Two samples were synthesised by a Sn flux method and two were made by melting stoichiometric mixtures of the elements. Finally, the high temperature $\text{Sn}_3\text{Sb}_2$ compound was synthesised using a Sn flux. This compound decomposes into the most tin rich member of the $\beta$-SnSb. An overview of the samples can be found in Table 3-6. Upon extraction of the samples they showed obvious differences in appearance. The synthesis of $\text{Sn}_3\text{Sn}_2$ produced cubic crystals while the remaining samples were plate like. With increasing Sb content the plate like behaviour becomes less prominent and the samples gain a more glass like appearance. All the samples are brittle. The samples were studied with SEM and elemental analyses were performed with EDS. The SEM images are presented in Figure 3-16 and the EDS results are given in Table 3-6.

Table 3-6 Data on the synthesized samples. The two temperatures given are first for synthesis and the second for annealing. The temperature was lowered with the sample still in the furnace. All samples were quenched in water upon removal from the furnace.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Synthetic mixture</th>
<th>Temp. /°C</th>
<th>% Sn from EDS</th>
<th>% Sb from EDS</th>
<th>a</th>
<th>c</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMB504</td>
<td></td>
<td></td>
<td>57</td>
<td>44</td>
<td>4.338(3)</td>
<td>5.316(4)</td>
<td>1.285(2)</td>
</tr>
<tr>
<td>A41</td>
<td>Sn$_3$Sb$_2$</td>
<td>650/260</td>
<td>58</td>
<td>43</td>
<td>4.339(3)</td>
<td>5.312(9)</td>
<td>1.276(9)</td>
</tr>
<tr>
<td>A43</td>
<td>Sn$_3$Sb$_2$</td>
<td>650/350</td>
<td>53</td>
<td>45</td>
<td>4.326(2)</td>
<td>5.349(2)</td>
<td>1.311(2)</td>
</tr>
<tr>
<td>jc001</td>
<td>SnSb</td>
<td>650/400</td>
<td>43</td>
<td>56</td>
<td>4.330(2)</td>
<td>5.372(2)</td>
<td>1.356(2)</td>
</tr>
<tr>
<td>jc002</td>
<td>Sn$<em>9$Sb$</em>{11}$</td>
<td>650/420</td>
<td>40</td>
<td>59</td>
<td>4.329(9)</td>
<td>5.412(2)</td>
<td>1.371(8)</td>
</tr>
</tbody>
</table>
Figure 3-16 SEM images representing each of the samples synthesized. It is seen how the morphology changes from stacked plates to a more glass like appearance.
Figure 3-17 Reconstructed Laue images representing the collected x-ray diffraction data. For CMB504 the image shows the $Ikl$ layer using a cubic setting, the remaining images show the $hhlm$ layer in hexagonal setting. The images show that the length of the q-vector changes, and that the higher order satellites appear at high Sb content. The change from plate like to glass like appearance is seen as a decrease in the tendency to form powder rings.
From each sample a crystal was selected for single crystal x-ray diffraction. The collected data show a composition dependent q-vector (Figure 3-17) and that the superspace group is $\bar{R}3m(00\gamma)00$. The basic cell is very near metrically cubic (the rhombohedral angle is debated in the literature\textsuperscript{56,57}), with one atom at the origin. The satellites must result form elemental ordering on this site possibly combined with a relaxation of the lattice. The composition and the length of the q-vector must therefore be coupled, and from the EDS analysis the relation can be established. Unfortunately the EDS analysis also show that the samples are not homogeneous and to establish a more accurate relationship EDS analysis will have to be performed on the crystals used for the diffraction experiments. Analyzing the phase diagram, the samples CMB504 and A41 must have the same composition. Thus only the un-twinned sample is discussed from hereon.

When solving and refining the structures it emerges that Sn in two ways is a rather soft atom whereas Sb is hard. The tin have a higher thermal vibration and is modulated with a single harmonic function. The antimony on the other hand has a low vibration and is best described using a saw-tooth function. The thermal vibration smears out the electrons of the lighter tin atom and bunch together the electrons of the heavier antimony. This helps increase the x-ray diffraction contrast. How the appearance of the two atoms evolves in the density maps from the four compositions are shown in Figure 3-18. It shows how the total modulation becomes stiffer with increasing Sb content. This is also indicated in the data, with more 2\textsuperscript{nd} and 3\textsuperscript{rd} order satellites emerging for the samples with high Sb content.

We may now evaluate how the structure can cover such a large homogeneity range. From the refinements we see that the structure is build from slabs of SnSb arranged in the NaCl structure type. The slabs are stacked along the cube diagonal of the NaCl cell, resulting in an overall rhombohedral arrangement. The composition is controlled by the width of the slabs and by the composition of the interface between slabs. In the Sn rich samples the slabs are small, and Sn-Sn interfaces dominate. For the Sb rich samples the slabs are wider, and Sb-Sb interfaces are dominating. The four structures solved are presented in Figure 3-19.
Figure 3-18 The final electron density maps of Sn and Sb. Blue indicate Sb and red indicate Sn. From left to right the Sb content increases.
Figure 3-19 Representative parts of the refined structures showing their block behaviour. With increasing Sb content, the interfaces changes from pure Sn-Sn to mixed Sn-Sn and Sb-Sb interfaces, and finally pure Sb-Sb interfaces. At the same time the block size increases.
3.4.2. The AlB$_2$-type family of structures

We have in section 2.1 briefly introduced this structural family as an example of structures where certain atoms have extreme thermal vibration, in combination with deficient occupancy. We will in this section elaborate on the issue and show the cause of it, by investigation of structures found in the literature, together with the refinement of nine new structures against powder diffraction data. For clarity we reproduce below the structural image also shown in section 2.1.

**Figure 3-20** The structure of NpSi$_{1.6}$ with 75% thermal ellipsoids indicated$^{28}$. Blue is Si atoms and gray is Np atoms.

The apparent high thermal vibration found in these structures could be real or mimic static displacements. The image becomes much clearer when considering special variations of the AlB$_2$-type structure. The Y$_3$Ge$_5$ structure$^{60}$ is one such example, and the structure is shown in Figure 3-21, while the structural parameters are given in Table 3-7.

**Figure 3-21** The structure of Y$_3$Ge$_5$ with 75% probability thermal ellipsoids indicated. Only one hexagonal layer is shown for clarity. Blue indicate Ge and gray is Y.
Table 3-7 The structural parameters for Y₃Ge₅.

<table>
<thead>
<tr>
<th>S.G.</th>
<th>P-62c</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ</th>
<th>B (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.838(2)</td>
<td>Y1</td>
<td>0.328(5)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.62(8)</td>
</tr>
<tr>
<td>c</td>
<td>8.298(3)</td>
<td>Ge1</td>
<td>0.323(5)</td>
<td>0.390(3)</td>
<td>1/4</td>
<td>0.82(1)</td>
<td>0.62(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge2</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
<td>1</td>
<td>0.62(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge3</td>
<td>2/3</td>
<td>1/3</td>
<td>1/4</td>
<td>0.82</td>
<td>0.62(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge4</td>
<td>0.390(3)</td>
<td>0.323(5)</td>
<td>1/4</td>
<td>0.18(1)</td>
<td>0.62(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge5</td>
<td>1/3</td>
<td>2/3</td>
<td>1/4</td>
<td>0.18(1)</td>
<td>0.62(8)</td>
</tr>
</tbody>
</table>

For this structure the static disorder is no longer hidden in the thermal parameters, but refined as partially occupied sites. To get a better view of what is going on, we simply remove the less occupied atoms, as illustrated in Figure 3-22. This ordering of the structure is discussed in detail in the original paper⁶⁰ and is similar but not identical to the structure of Yb₃Ge₅ which has a different stacking of the layers along the c-axis⁶¹.

![Figure 3-22 One layer of the Y₃Ge₅ structure after removing the less occupied atoms. The stacking of layers is such that vacancies in one layer are between three-connected germanium atoms in the adjacent layers.](image)

When investigating rare earth germanide and -silicide systems, Venturini and Malaman⁶² discovered the presence of weak superstructure reflections, both in Weissenberg images⁶³ and in their powder diffractograms together with line splitting from distortion of the basic hexagonal cell. They indexed the patterns and put forward a structural hypothesis that was tested for one commensurate case, Tm₂Ge₅. This revealed the existence of a new group of structures with extended vacancy ordering in the parent AlB₂-type structure. It also showed the modulation wave vector to be directly coupled to the oc-
cupancy of the germanium or silicon, though the relation at that time was somewhat unclear.

To take on a rigorous full scale modulation approach to the problem, eight new samples were prepared in the Er-Ge system, ranging from Er$_{41}$Ge$_{59}$ to Er$_{39.25}$Ge$_{60.75}$ in steps of 0.25 at.% germanium in the synthesis mixture. The samples were arc melted and the products analyzed using x-ray powder diffraction.

The collected data confirmed the previous reported line splitting originating in the distortion of the hexagonal basic cell, and also the effect of composition on the modulation wave vector. Representative parts of the data are reproduced in Figure 3-24 showing the discussed line splitting. As a result of the distortion, the space group of the basic cell was determined as C2/m (no.12) according to the group - sub group relation P6/mmm - Cmmm - C2/m. Apart from the C-centring condition $h$kl0; $h+k=2n$ on the main reflections an additional condition applies to the satellite reflections. To illustrate this, Figure 3-23 shows the indexing of some observed and unobserved reflections. Similar analysis of all the measured data confirmed the condition $h$klm: $h+k+m=2n$, note that this condition includes the C-centring condition for the main reflections.

![Figure 3-23](image)

**Figure 3-23** Part of the diffractogram from ErGe$_{1.59423(18)}$ indicating observed and systematically extinct reflections, according to the condition $h+k+m=2n$. Forbidden reflections are marked as red. The impurities present are top row tick marks: Er$_2$O$_3$. Middle row tick marks: ErGe$_{1.83}$. 
Figure 3-24 Examples of observed line splitting and satellite positions depending on composition. The reflections 2200 and 0400 are split due to orthorhombic distortion and 1110 and \(\overline{1}110\) are split due to a monoclinic distortion. The impurities present are indicated with vertical lines. For clarity only diffractograms from 6 samples are shown.
Put in words, the condition states that first order satellites are only allowed for main reflections systematically absent due to the C-centring, whereas second order satellites are only allowed for main reflections allowed by the C-centring. It is the equivalent of a centring vector $\frac{1}{2} \frac{1}{2} 0 \frac{1}{2}$ of the 3+1D superspace lattice. The allowed superspace groups are then:

\[ X_2/m(\alpha \beta \gamma)0s \]
\[ X_2/m(\alpha \beta \gamma)00 \]

The group $X_2/m(\alpha \beta \gamma)0s$ fulfils the same extinction conditions as $X_2/m(\alpha \beta \gamma)00$ but in addition contains the extinction condition for the $s$-glide, \( h0lm: m=2n \). This later condition is strictly adhered to in all cases studied. This determines the superspace group to be $X_2/m(\alpha \beta \gamma)0s$.

To prepare a model suitable for refinement, the AlB\(_2\)-type parent structure is first transformed through the group-subgroup relation to $C2/m$ and from here lifted to the 3+1D superspace group $X_2/m (\alpha \beta \gamma) 0s$.

Table 3-8 The structural parameters of AlB\(_2\) transformed into 3+1D superspace.

<table>
<thead>
<tr>
<th>S.G.</th>
<th>( X_2/m (\alpha \beta \gamma) 0s )</th>
<th>Atom</th>
<th>Er</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>3.009</td>
<td>x1</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>( b )</td>
<td>5.2117</td>
<td>x2</td>
<td>0</td>
<td>0.1667</td>
</tr>
<tr>
<td>( c )</td>
<td>3.262</td>
<td>x3</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>( \beta )</td>
<td>90</td>
<td>Occ</td>
<td>1</td>
<td>crenel funct.</td>
</tr>
</tbody>
</table>

The function describing the Ge occupancy is called a crenel function\(^{64}\). The function is defined by a centre in the fourth dimension $x_4^0$ and a width $\Delta x_4$. A principal drawing is shown in Figure 3-25. In addition to this description of the occupancy, all atoms are allowed to move away from the ideal position by applying two sinusoidal modulation waves to each atom. This allows the structure to relax around the vacancies. The density maps after refinement are shown in Figure 3-26 for the Er atom, and in Figure 3-27 for the Ge atom. To obtain a 3D image of the real crystal we have to perform a 3D cut of 3+1D superspace. In the density maps such a cut will be represented by a line perpendicular to the $x_4$-axis. We can directly relate such a cut to the real structure by comparing the density maps in Figure 3-27 with the Ge layer in Figure 3-28.
Figure 3-25 Principal drawing of a crenel function. The interpretation of Δ₄ is shown.

Figure 3-26 The 3+1D electron density of Er.
Figure 3-27 Top: The $x_2$-$x_4$ density map of Ge. Each line corresponds to a sequence of atoms in the real crystal. Bottom: One layer of Ge atoms. Bands of atoms corresponding to specific cuts of the 3+1D density are highlighted in colour corresponding to the cuts shown in the $x_2$-$x_4$ map above. The band labelled "5" corresponds to the cut shown in the $x_1$-$x_4$ map in Figure 3-28.
Figure 3-28 Top: The $x_3$-$x_4$ density map of Ge. A cut in this map corresponds to the stacking of consecutive hexagonal layers of Ge. The example drawn shows that vacancies will not be stacked onto each other. Bottom: of $x_1$-$x_4$ density of Ge. A specific cut is shown with the same colour coding and number as in Figure 3-27.
Apart from pure AlB$_2$-type structures, slabs of this structure type may be incorporated into other structures; building intergrowth compounds, and simultaneously preserving the preference for vacancy ordering. An example of this is found in the YGe$_{1.82}$ structure$^{61}$ shown in Figure 3-29 with the structural parameters given in Table 3-9. In this case one network atom is disordered and partially occupied. By using the ordering information from the Y$_3$Ge$_5$ structure we can systematically remove 2/3 of these atoms. The result is again vacancy ordering as illustrated in Figure 3-30, this is discussed briefly in the original paper.

![Figure 3-29 The structure of YGe$_{1.82}$. Ytterbium atoms are gray and germanium atoms are blue; dark blue indicate planar square nets and light blue indicate AlB$_2$-type slabs.](image)

Table 3-9 Structural parameters for YGe$_{1.82}$.

<table>
<thead>
<tr>
<th>S.G.</th>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Y1</td>
<td>0.9402</td>
<td>1/4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>b</td>
<td>Y2</td>
<td>0.1725</td>
<td>1/4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>c</td>
<td>Ge1</td>
<td>0.3541</td>
<td>1/4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Ge2</td>
<td>0.5917</td>
<td>1/4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ge3</td>
<td>0.7486</td>
<td>1/4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ge4</td>
<td>0.5109</td>
<td>0.334</td>
<td>0.323</td>
<td></td>
</tr>
</tbody>
</table>


Apart from the vacancy ordering within the planes an interesting issue is the possible schemes for ordering the planes with respect to each other. The simplest way is: Adjacent planes are in phase, and planes separated by a square net are in phase. This situation is illustrated in Figure 3-31. In the literature it has been debated whether the structure is ordered or not, and what the true symmetry is. There is though a general agreement that it is impossible to choose between the suggested space groups $Cmcm$ (no.63) and $Cmc2_1$ (no.36) neither from refinement R-values$^{61,65}$ nor from investigation of high resolution neutron diffraction data giving information about the presence of a centre of symmetry$^{65}$. The standard is to go for the highest symmetry group, but arguments have been put forward regarding which model is the physically most reasonable$^{65}$. At a first glance it is true that a model in $Cmcm$ results in short Ge-Ge distances, but, as we have seen in Figure 3-30, this situation does not need to occur in the real crystal with the refined atomic occupancies.

The question is how big a difference in the diffraction data an ordering of the vacancies would result in. To illustrate how difficult it would be to detect any ordering, Figure 3-32 shows theoretical precession images calculated from the published disordered model and from the theoretical simple ordered model in Figure 3-31. Obviously one will need a perfect crystal with no domain disorder but also a reliable instrument giving a minimum of background noise to detect these subtle differences. Further more it is hard to imagine that the different ordering schemes are separated by large differences in energy so the hope for a perfect ordered crystal is small. Indeed investigations using a Weissenberg film camera did not reveal the presence of any super structure reflections$^{61}$. 

Figure 3-30 A zoom-in on the AlB$_2$-type slab in YGe$_{1.82}$ with a theoretical ordering of vacancies indicated.
Figure 3-31 The simplest form of vacancy ordering in YGe$_{1.82}$.

Figure 3-32 The theoretical precession image of the $0kl$ plane calculated from a) the disordered YGe$_{1.82}$ and b) the ordering scheme from Figure 3-31.
4. Approaching the Problem: Two textbook examples.

Apart from the situation where a diffraction pattern clearly is not indexable using only 3 vectors, it can be quite difficult to explain how to recognize that a structure is modulated. In this chapter we will go through two textbook examples, from the initial structure solution to the final full 3+1D model. The examples belong to the family of superstructures to the NaMo$_3$O$_6$ structure type discussed in section 3.2. For the purpose of being a teaching example we will treat them as being unknown samples.

Figure 4-1 Diffraction patterns from different structures encountered during the Ph.D. project. All except the germanate are modulated.
4.1. The structure of Pb$_{0.69}$Mo$_4$O$_6$

With today’s single crystal x-ray diffractometers, a structural analysis of an unknown sample can be almost completely automated. A crystal is selected and mounted for the experiment. A computer program then controls the collection of a small set of data in order to determine the unit cell. Afterwards an optimized data collection procedure is generated, and data are collected. Finally the data are integrated, and a space group determination is performed using the intensity statistics. The final step of solving and refining the structure can be automated as well, but is normally performed manually.

On investigation of the title compound, the data extraction, automatic peak search, indexing and space group determination resulted in the space group $P4/mbm$ (no.127) with $a=9.6112(3)$Å and $c=2.8411(1)$Å. Solving the structure using standard software produced the model shown in Figure 4-2. Expanding to a few unit cells along the c axis immediately shows that one atom residing inside a channel is disordered. This atom also turns out partially occupied.

![Figure 4-2](image)

Figure 4-2 The structure of Pb$_{0.69}$Mo$_4$O$_6$ viewed down the a-axis. The structure was solved from an automated data collection and integration.
As discussed in section 2.1 this kind of behaviour signals that one should investigate the possibility for vacancy ordering. First question arising now is whether the data contains information about such ordering; were all reflections integrated properly, or are some weak superstructure reflections missing. To investigate this, one could follow the data integration as it progresses, but software development now allows for the reconstruction of Laue images of any plane in reciprocal space, showing the indexing of any point. With this approach it is easy to see if non-integer indexed reflections are present. Reconstructions of the principal zone axes are shown in Figure 4-3.

Figure 4-3 The reconstructed Laue images of $0kl$, $h0l$, $hk0$ and $hhl$.

If additional reflections are found, the new unit cell can be derived from the old one, using the Laue images, and a new data integration can be performed. Using the new unit cell, the Laue images may be regenerated. From Figure 4-3 extra reflections are seen corresponding to a 4-fold superstructure along the c-axis. As extra reflections are only seen along the c-axis reconstructing the $0kl$ and $1kl$ will be almost indispensable when it comes to determine the systematic absence conditions and from them the space group symmetry. Laue images with the new cell are identical to those in Figure 4-3.
as the cell orientation is the same, only the indexing is changing. To determine the extinction conditions and thus the superspace group Figure 4-4 highlights the main and satellite reflections.

For the main reflections (yellow) in the 0klm layer it is seen that $k=2n$, and no conditions arise for these reflections from the 1klm layer, giving the condition 0kl0: $k=2n$. For the satellite reflections (red) extinctions are seen in both images, giving the condition hklm: $h+k+m=2n$. Finally, as the unit cell is metrically tetragonal, the hhlm layer should be investigated.

The extinctions from the hhl layer give the condition hhlm: $m=2n$. To summarise:

0kl0: $k=2n$

hklm: $h+k+m =2n$

hhlm: $m=2n$

This results in the 3+1D superspace group $P4/mbm \ (00\gamma)\ 00ss$

Figure 4-4 The reconstructed Laue images of the 0klm, 1klm and hhlm layers with the unit cell grid overlaid and allowed main- (yellow) and satellite- (red) reflections indicated. The reflection condition is seen to be 0kl0: $k=2n$ hklm: $h+k+m =2n$ and hhlm: $m=2n$. 
First the basic structure is solved using the main reflections \( hkl0 \). This approach results in a structure identical to the one obtained from the automated approach mentioned earlier. To make the structure useful for refinements in the 3+1D approach, the disordered lead atom is moved to it’s ideal position on the mirror plane, as in the parent NaMo\(_4\)O\(_6\) structure shown in Figure 3-9. The refinements now proceeds as follows; after initial refinement, an electron density map of the lead atom is generated, Figure 4-6a. The smearing of the density indicates that the atom position is a function of \( x_4 \), and is better treated with a modulation function. From here two "roads" are possible, we will describe them one at a time: The lead atoms occupancy may be described with a crenel functions as the density map indicates unique atoms along \( x_4 \). The starting values of the parameters may be extracted from the density map, giving \( x_4^0 = 0 \) and \( \Delta x_4 = 0.5 \). The crenel function is described in section 3.4.2. The electron density map after refinement is shown in Figure 4-6b. In this map the deepest hole of -45 electrons is between the Pb atoms. The map also indicates that a better description would be to use a saw tooth function to describe the positional modulation, again the initial parameter values can be extracted from the map. The centre is still \( x_4^0 = 0 \), the extension in \( x_4 \) is \( \Delta x_4 = 0.5 \) and the extension in \( x_3 \) is \( = 0.18 \). The saw tooth function is defined in Equation 4-1 and a principal drawing is given in Figure 4-5.

**Equation 4-1**  
\[
U = 2U^0 \frac{(x_4 - x_4^0)}{\Delta x_4}
\]

Figure 4-5 Principal drawing of a saw tooth function with indication of the parameters.
After refinement a much better description is obtained as shown in Figure 4-6c. Though the over all agreement looks good, the saw tooth function is off at the point of termination, this may be corrected by adding a harmonic function. From the refinement three discrete atomic positions appear in the density map in Figure 4-6d. Going back to the previous density map, a tendency for this is already visible. To complete the model a new atom is added and the occupancies of both atoms are described using a crenel function. The parameter values read from the density map are for the new atom Pb1: \((x_1, x_2, x_3) = (0, 0, -0.21), x_4^0 = 0.67 \) and \(\Delta x_4 = 0.3\). And for the original atom Pb: \(x_4^0 = 0\) and \(\Delta x_4 = 0.3\). The parameters are refined and finally the Pb atoms are allowed harmonic thermal parameters. The final density map is shown in Figure 4-6f.

As mentioned, a second refinement route exists. After refinement of the basic structure, the Pb atom is allowed to move in the \(x_3\)-\(x_4\) plane using a harmonic modulation wave. The resulting density map, Figure 4-6e, is strikingly similar to Figure 4-6d, and the procedure is the same as for that description, again arriving at the density map in Figure 4-6f.

As the q-vector is metrically commensurate to the c-axis, it should be tested how the model refines as a commensurate structure, and as a superstructure. Both these results yield worse refinement R-values, and the final result is the incommensurately modulated structure. The structural parameters after the final refinement are given in Table 4-1, Table 4-2 and Table 4-3. The R-values are given in Table 4-4. We can now compare with the structural model that has been published\(^46\) and for which the structural parameters were given in Table 3-2. The published superstructure model uses 45 parameters compared to the 22 parameters used in the 3+1D model we have just derived, and further more the present model is ordered compared to the 3D model.
Figure 4-6 The $x_3$-$x_4$ electron density map for the lead atom residing inside the tunnel formed by Mo$_4$O$_6$ clusters. The maps are calculated using $F_{obs}$ and the contours are for each 5 electrons. The blue line represents Pb and the red line represents O1 being the nearest neighbour forming the side of the tunnel. Each map represents the result after improvements to the model and the resulting R-value for satellite reflections are given. For clarity the lower cut-off is at 0 electrons. The models represented are: a) no modulation, all atoms isotropic. b) a crenel wave used to describe the occupancy of the lead atom. c) a saw-tooth function used to describe the lead atom. d) a harmonic wave added to the saw-tooth description. e) the lead atom described using only a harmonic wave. f) the lead atom is split into two atoms each described using a crenel wave. Only the two Pb sites are allowed harmonic thermal vibration parameters.
Table 4-1 The atomic parameters and uncertainties after final refinement.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Occ</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.5</td>
<td>0.4589(12)</td>
<td>0.2627(13)</td>
<td>0</td>
<td>0.006(2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.25</td>
<td>0.2099(15)</td>
<td>0.2902(15)</td>
<td>0</td>
<td>0.014(4)</td>
</tr>
<tr>
<td>Mo1</td>
<td>0.25</td>
<td>0.60193(17)</td>
<td>0.10193(17)</td>
<td>0.5</td>
<td>0.0041(4)</td>
</tr>
<tr>
<td>Mo2</td>
<td>0.25</td>
<td>0.3564(2)</td>
<td>0.1436(2)</td>
<td>0</td>
<td>0.0099(5)</td>
</tr>
<tr>
<td>Pb_a</td>
<td></td>
<td>0.0879(17)</td>
<td>0</td>
<td>0</td>
<td>0.0390(17)</td>
</tr>
<tr>
<td>Pb_b</td>
<td></td>
<td>0.1421(18)</td>
<td>0</td>
<td>-0.2042(10)</td>
<td>0.0132(7)</td>
</tr>
</tbody>
</table>

Table 4-2 The parameters for the crenel wave describing the occupancy of the guest atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$X_4^0$</th>
<th>$\Delta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb_a</td>
<td>0</td>
<td>0.390(5)</td>
</tr>
<tr>
<td>Pb_b</td>
<td>0.673(2)</td>
<td>0.368(4)</td>
</tr>
</tbody>
</table>

Table 4-3 Harmonic thermal parameters for the guest atoms. Note how Pb_a having more space in the structure is also moving more. This effect could be static disorder still not being treated in the model.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb_a</td>
<td>0.029(2)</td>
<td>0.029(2)</td>
<td>0.060(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pb_b</td>
<td>0.0123(12)</td>
<td>0.0123(12)</td>
<td>0.0151(13)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4-4 Final refinement R-values for the incommensurately modulated model.

<table>
<thead>
<tr>
<th></th>
<th># Observed</th>
<th>$R_{obs}$</th>
<th>#</th>
<th>$R_{all}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main reflections</td>
<td>143</td>
<td>7.75</td>
<td>189</td>
<td>8.59</td>
</tr>
<tr>
<td>1st order</td>
<td>99</td>
<td>6.99</td>
<td>296</td>
<td>17.07</td>
</tr>
<tr>
<td>2nd order</td>
<td>59</td>
<td>13.90</td>
<td>169</td>
<td>20.08</td>
</tr>
</tbody>
</table>
4.2. The structure of $(\text{Mo,Ti})_x\text{Mo}_4\text{O}_6$

A similar compound also being a variation on the NaMo$_4$O$_6$ structure type is the $(\text{Mo,Ti})_x\text{Mo}_4\text{O}_6$ with a mixture on the guest atom position. Following what we have just learned in section 4.1, we begin by investigating reciprocal space by means of the reconstructed Laue images shown in Figure 4-7.

![Laue images](image)

Figure 4-7 The Laue images for the principal axes of $(\text{Mo,Ti})_x\text{Mo}_4\text{O}_6$, together with the extinction conditions.

There are no indications of superstructure reflections or special extinction conditions so we proceed in 3D and determine the unit cell parameters $a=9.7962(2)\text{Å}$ $b=9.4497(1)\text{Å}$ $c=8.5815(1)\text{Å}$. The space group is determined from the extinction conditions listed in Figure 4-7 to $Pbam$ (no. 55). Solving the structure with Shelx97$^{66}$ using the winGX$^{67}$ interface results in the disordered structure shown in Figure 4-8.
Figure 4-8 The structure of (Mo,Ti)$_4$Mo$_6$O$_{16}$, solved in the 3D space group Pbam.

What went wrong?

To analyze this, we go back and investigate the data once more. By careful inspection of the $0kl$, $1kl$, $2kl$, and $3kl$ layers shown in Figure 4-9 it is seen that a 3-fold superstructure is present. The extinction conditions found earlier translates to

$h000$: $h=2n$
$0k00$: $k=2n$
$h0lm$: $h=2n$
$0klm$: $k=2n$

This results in the 3+1D superspace group $Pbam(00\gamma000$ and the unit cell parameters are now $a=9.7962(2)\text{Å}$ $b=9.4497(1)\text{Å}$ $c=2.8564(1)\text{Å}$
Figure 4-9 The reconstructed Laue images for $0 \geq h \geq 3$, indicating a 3-fold superstructure.

From here we follow the same procedure as in the previous section. After refinement of the basic structure, the electron density map of the troublesome atom is drawn (Figure 4-10a). The interpretation of the density map in Figure 4-10a is that the occupation should be described using a crenel wave with $x_4^0=0$ and $\Delta=0.6$ as the initial parameter values. After several refinement cycles where modulation functions are added to the remaining atoms the electron density for the Mo/Ti site is unchanged, and the remaining atoms show the electron density maps presented in Figure 4-11.
Figure 4-10 a) The electron density of the mixed Mo/Ti site after refinement of the basic model. b) The same position after refinement using a crenel wave.
Figure 4-11 The final density maps for a) and b) the Mo1 c) the Mo2.

Once again, as the q-vector is commensurate with the c-axis, the final 3+1D model is transformed to a 3D superstructure and refined. In contrast to the $\text{Pb}_{0.69}\text{Mo}_4\text{O}_6$ structure that gave worse R-values in a supercell description, we now obtain R-values that are similar to the modulated approach. This behaviour reminds us of the $\beta'$-$\text{Mg}_2\text{Al}_3$ structure where the cubic pseudo-symmetry is so strong that the initial Direct Methods solution is cubic. In the present example we cannot obtain the ordered supercell model using Direct Methods as tested in the beginning of this section. Instead we have to use a 3+1D superspace approach to phase all the superstructure reflections correctly, and then transform the solution back into 3D. The final parameter values for both models are presented in the tables below.
Table 4-5 The atomic parameters and uncertainties after final refinement of the 3+1D model.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Occ</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_{iso}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.5</td>
<td>0.31699(17)</td>
<td>0.23098(17)</td>
<td>0.5</td>
<td>0.0066(3)</td>
</tr>
<tr>
<td>O2</td>
<td>0.5</td>
<td>-0.24346(16)</td>
<td>0.02323(16)</td>
<td>0</td>
<td>0.0054(3)</td>
</tr>
<tr>
<td>O3</td>
<td>0.5</td>
<td>-0.43595(17)</td>
<td>0.25886(17)</td>
<td>0</td>
<td>0.0055(3)</td>
</tr>
<tr>
<td>Mo1</td>
<td>0.5</td>
<td>0.408387(17)</td>
<td>0.111053(18)</td>
<td>0</td>
<td>0.00416(5)</td>
</tr>
<tr>
<td>Mo2</td>
<td>0.5</td>
<td>-0.349354(18)</td>
<td>0.133017(18)</td>
<td>0.5</td>
<td>0.00434(5)</td>
</tr>
<tr>
<td>Mo3</td>
<td>0.780(3)</td>
<td>0</td>
<td>0</td>
<td>0.36686(8)</td>
<td>0.00712(6)</td>
</tr>
</tbody>
</table>

Table 4-6 The parameters for the crenel wave describing the occupancy of the guest atom, and the parameters describing the harmonic modulation of the framework atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X_{04}</th>
<th>Δ_{x4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo3</td>
<td>0.7900(2)</td>
<td>0.3095(10)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Zsin1</th>
<th>Xcos1</th>
<th>Ycos1</th>
<th>Zsin2</th>
<th>Xcos2</th>
<th>Ycos2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.0061(7)</td>
<td>-0.0002(2)</td>
<td>0.0043(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>-0.0004(8)</td>
<td>0.0105(2)</td>
<td>-0.0092(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>0.0024(7)</td>
<td>-0.0093(9)</td>
<td>0.0120(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo1</td>
<td>0.00381(10)</td>
<td>-0.00362(3)</td>
<td>0.00359(3)</td>
<td>0.0025(3)</td>
<td>0.00136(11)</td>
<td>0.00162(11)</td>
</tr>
<tr>
<td>Mo2</td>
<td>-0.04922(10)</td>
<td>-0.00018(4)</td>
<td>0.00061(4)</td>
<td>-0.02055(18)</td>
<td>-0.00007(10)</td>
<td>-0.00033(10)</td>
</tr>
</tbody>
</table>

Table 4-7 Harmonic thermal parameters for all atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{12}</th>
<th>U_{13}</th>
<th>U_{23}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.0070(6)</td>
<td>0.0081(6)</td>
<td>0.0049(6)</td>
<td>0.0038(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2</td>
<td>0.0041(6)</td>
<td>0.0063(6)</td>
<td>0.0058(6)</td>
<td>0.0005(4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O3</td>
<td>0.006086(6)</td>
<td>0.0046(6)</td>
<td>0.0058(6)</td>
<td>0.0038(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo1</td>
<td>0.00356(8)</td>
<td>0.00383(8)</td>
<td>0.0058(6)</td>
<td>0.00025(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo2</td>
<td>0.00377(8)</td>
<td>0.00409(7)</td>
<td>0.00516(9)</td>
<td>-0.00024(4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo3</td>
<td>0.00588(10)</td>
<td>0.00652(9)</td>
<td>0.00896(12)</td>
<td>-0.00052(6)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4-8 Final refinement R-values for the incommensurately modulated model containing 59 refined parameters

<table>
<thead>
<tr>
<th></th>
<th># Observed</th>
<th>R_{obs}</th>
<th># All</th>
<th>R_{all}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main reflections</td>
<td>820</td>
<td>1.67</td>
<td>895</td>
<td>1.84</td>
</tr>
<tr>
<td>1st order</td>
<td>1202</td>
<td>2.52</td>
<td>1562</td>
<td>3.39</td>
</tr>
</tbody>
</table>
Table 4-9 The atomic parameters and uncertainties after final refinement of the supercell model.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Occ</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_{iso}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1_a</td>
<td>1</td>
<td>0.31679(13)</td>
<td>0.23279(13)</td>
<td>0.16836(11)</td>
<td>0.0066(3)</td>
</tr>
<tr>
<td>O1_b</td>
<td>0.5</td>
<td>0.31715(17)</td>
<td>0.22710(17)</td>
<td>0.5</td>
<td>0.0068(4)</td>
</tr>
<tr>
<td>O2_a</td>
<td>0.5</td>
<td>-0.23358(17)</td>
<td>0.01530(16)</td>
<td>0</td>
<td>0.0058(4)</td>
</tr>
<tr>
<td>O2_b</td>
<td>1</td>
<td>-0.24812(14)</td>
<td>0.02761(13)</td>
<td>0.33320(12)</td>
<td>0.0061(3)</td>
</tr>
<tr>
<td>O3_a</td>
<td>0.5</td>
<td>-0.44391(16)</td>
<td>0.26973(17)</td>
<td>0</td>
<td>0.0061(4)</td>
</tr>
<tr>
<td>O3_b</td>
<td>1</td>
<td>-0.43123(13)</td>
<td>0.25300(14)</td>
<td>0.33381(11)</td>
<td>0.0063(3)</td>
</tr>
<tr>
<td>Mo1_a</td>
<td>0.5</td>
<td>0.404526(18)</td>
<td>0.115005(18)</td>
<td>0</td>
<td>0.00394(4)</td>
</tr>
<tr>
<td>Mo1_b</td>
<td>1</td>
<td>0.410309(14)</td>
<td>0.109075(15)</td>
<td>0.334609(13)</td>
<td>0.00422(4)</td>
</tr>
<tr>
<td>Mo2_a</td>
<td>1</td>
<td>-0.349405(14)</td>
<td>0.133371(14)</td>
<td>0.151482(16)</td>
<td>0.00418(4)</td>
</tr>
<tr>
<td>Mo2_b</td>
<td>0.5</td>
<td>-0.349183(19)</td>
<td>0.132358(19)</td>
<td>0.5</td>
<td>0.00496(5)</td>
</tr>
<tr>
<td>Mo3</td>
<td>0.7220(9)</td>
<td>0</td>
<td>0</td>
<td>0.788928(16)</td>
<td>0.00734(4)</td>
</tr>
</tbody>
</table>

Table 4-10 Harmonic thermal parameters for all atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{12}</th>
<th>U_{13}</th>
<th>U_{23}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1_a</td>
<td>0.0071(5)</td>
<td>0.0076(5)</td>
<td>0.0051(5)</td>
<td>0.0045(4)</td>
<td>0.0003(3)</td>
<td>-0.0002(3)</td>
</tr>
<tr>
<td>O1_b</td>
<td>0.0068(6)</td>
<td>0.0083(6)</td>
<td>0.0053(6)</td>
<td>0.0032(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2_a</td>
<td>0.0053(6)</td>
<td>0.0066(6)</td>
<td>0.0053(6)</td>
<td>-0.00013(48)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2_b</td>
<td>0.0059(5)</td>
<td>0.0072(5)</td>
<td>0.0052(5)</td>
<td>-0.0007(4)</td>
<td>0.00011(32)</td>
<td>-0.00021(31)</td>
</tr>
<tr>
<td>O3_a</td>
<td>0.0069(7)</td>
<td>0.0060(6)</td>
<td>0.0053(6)</td>
<td>-0.0003(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O3_b</td>
<td>0.0069(5)</td>
<td>0.0061(5)</td>
<td>0.0058(5)</td>
<td>-0.0004(4)</td>
<td>-0.0006(3)</td>
<td>0.00003(32)</td>
</tr>
<tr>
<td>Mo1_a</td>
<td>0.00356(8)</td>
<td>0.00374(7)</td>
<td>0.00453(7)</td>
<td>0.00041(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo1_b</td>
<td>0.00355(6)</td>
<td>0.00383(6)</td>
<td>0.00527(7)</td>
<td>0.00020(4)</td>
<td>-0.00015(3)</td>
<td>0.00024(3)</td>
</tr>
<tr>
<td>Mo2_a</td>
<td>0.00345(6)</td>
<td>0.00379(6)</td>
<td>0.00529(6)</td>
<td>-0.00025(4)</td>
<td>-0.00006(37)</td>
<td>0.00010(4)</td>
</tr>
<tr>
<td>Mo2_b</td>
<td>0.00433(8)</td>
<td>0.00455(7)</td>
<td>0.00599(8)</td>
<td>-0.00024(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo3</td>
<td>0.00616(6)</td>
<td>0.00684(6)</td>
<td>0.00902(7)</td>
<td>-0.00054(4)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4-11 Final refinement R-values for the supercell model containing 81 refined parameters.

<table>
<thead>
<tr>
<th></th>
<th># Observed</th>
<th>R_{obs}</th>
<th># All</th>
<th>R_{all}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main reflections</td>
<td>2022</td>
<td>1.55</td>
<td>2457</td>
<td>2.01</td>
</tr>
</tbody>
</table>
5. Conclusions

Through this thesis we have seen many examples on how the black box of standard crystallography breaks down. Some of the problems can be handled within 3D and some cannot. This also shows that even when we do get an output, it should always be evaluated critically. Crystallography is still far from being a finished book; some chapters are still in the writing and new ones are just emerging.

The observation of satellite reflections has led to the development of general crystallography in arbitrary dimensions, and structure determination of modulated phases and quasicrystals is still developing. An issue only touched briefly in this thesis is the observation of diffuse scattering. Diffuse scattering has been observed in electron microscopy for many decades, but quantification and more importantly refinement of a structural model using the information from the diffuse scattering is still lacking. The development of highly sensitive area detectors has the consequence that we now with x-rays see things that were not visible during the era of point detectors. As a consequence people from a different background than electron microscopy are beginning to observe diffuse scattering more regularly, and it is time to join forces on the issue.

To date there is no standard for quantitatively dealing with diffuse scattering at any step of a structure determination. This area of crystallography is now evolving, using a combination of complementary techniques, and the next decade we should expect to see the development of an even more general crystallography.

It is at the frontier that 'standard' no longer applies, and research begins.
Acknowledgements

First of all I would like to thank my supervisor Sven Lidin, for introducing me to higher dimensional crystallography and for being the link to a group of very interesting people working in this area.

Many people have contributed either directly or indirectly to the work presented in this thesis. I would like to acknowledge my collaborators who have provided the samples, without which there would be no thesis:

- Professor Holger Kleinke from University of Waterloo, Ontario, Canada, provided the samples for the Me$_x$Mo$_4$O$_6$ study.

- Professor Bernard Malaman and Dr. Gérard Venturini from Université Henri Poincaré, Nancy, France, provided the samples and powder diffraction data for the ErGe$_{2-x}$ study, and the study of ScFe$_6$Ge$_6$-ScFe$_6$Ga$_6$ intergrowth structures.

- The CMA network of Excellence, providing the β-Mg$_2$Al$_3$ sample. Especially the members with whom I have had fruitful discussions about not only the β’-Mg$_2$Al$_3$ structure but also the other samples I have studied, and on general aspects of materials research.

I would like to thank all of my colleagues at FOOS for providing an inspirational workplace. A special thanks to all of you who have asked questions relating to your own samples and projects, this has assisted in building the knowledge behind this thesis.

Finally I would like to thank my wife and daughters for being so supportive and understanding, when my research has led me to travel to meetings or to bring work home. My wife, Kirsten, is especially acknowledged for reading several drafts of the thesis and providing valuable comments on it.
"A Fourier series method for the determination of the components of interatomic distances in crystals"

"Systematic analysis of the Patterson function"

"Structure solution with SHELXD"

"SHELX for macromolecules"
Sheldrick, G.M.,
http://www.iucr.ac.uk/iucr-top/comm/ccom/School96/pdf/gs2.pdf

Several textbooks exist on the subject.

a. "Direct methods in crystallography"
   Woolfson, M.
   *Monographs on the physics and chemistry of materials.* 1961

b. "Direct phasing in crystallography"
   Giacovazzo, C.
   *IUCr Monographs on Crystallography no. 8*

"Direct methods - from birth to maturity"

"The squaring method: a new method for phase determination"
Sayre, D., *Acta Cryst.* **5** (1952) 60-65

"A theory of phase determination for the four types of non-centrosymmetric space groups 1P222, 2P22, 3P2, 3P2""Karle, J., Hauptman, H., *Acta Cryst.* **9** (1956) 635-651
"Direct phase determination in protein crystallography"
Kyriakidis, C.E., Ph.D. Theis (1993). Abstract available at:

"Crambin: a direct solution for a 400-atom structure"
Weeks, C.M., Hauptman, H.A., Smith, G.D., Blessing, R.H., Teeter, M.M.,

"The application of direct methods and Patterson interpretation to
high-resolution native protein data"

"Holographic analysis of diffraction structure factors"
Marchesini, S., Mannella, N., Fadle, C.S., van Hove, M.A., Bucher, J.J.,
Shuh, D.K., Fabris, L., Press, M.J., West, M.W., Stolte, W.C., Hussain, Z.,

"The problem with phase ambiguity in single crystal structure analysis"

"Kristallographische konsequenzen von pseudosymmetrie in kristall-
strukturen"

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"Three-dimensional reconstruction of the ν-AlCrFe phase by electron
crystallography"
(2003) 526-539

"The crystal structure of l-Al4Mn"

"Solving approximant structures using a strong reflections approach"
Christensen, J., Oleynikov, P., Hovmöller, S., Zou, XD., Ferroelectrics 305
(2004) 273-277

"Strong reflections in quasicrystal approximants"
Christensen, J., Licentiate Thesis 2004
"Structure model for the tau(mu) phase in Al-Cr-Si alloys deduced from the lambda phase by the strong-reflections approach"

"Structure relations in real and reciprocal space of hexagonal phases related to i-ZnMgRE quasicrystals"

"Structure determination of the hexagonal quasicrystal approximant mu'-(Al,Si)(4)Cr by the strong reflections approach"

"On the solution of the phase problem in quasiperiodic crystals"

"Approximants - the key to the structure of quasicrystals"

"Ab initio structure solution by charge flipping"

"Charge flipping at work: a case of pseudosymmetry"

"Ab initio determination of incommensurately modulated structures by charge flipping in superspace"

"Structural chemistry of the neptunium-silicon binary system"

"Neutron diffraction study of magnetic ordering in the system NdSi_x (1.67≤x≤2.00)"

Several texts on superspace crystallography exists, and are highly recommended reading for someone who wish to enter the field. The four main references are

a. "Incommensurate crystal structures"

Multiple authors. Z. Kristallogr. 219 (2004) 680-767

c. "Aperiodic crystals: from modulated phases to quasicrystals"
   Janssen, T., Chapuis, G., de Boissieu, M.
   *IUCr Monographs on Crystallography* no. 20

d. "Incommensurate crystallography"
   van Smaalen, S.
   *IUCr Monographs on Crystallography* no. 21

31 "Modulated structure of CuAu II (one-dimensional modulation)"

32 "Structure determination of a mixed-layer bismuth titanate, Bi$_2$Ti$_4$NbO$_{21}$, by super-high-resolution electron microscopy"

33 "Electron-microscopy study of crystal structures of mixed oxides in the system Rb$_2$O-Ta$_2$O$_5$, Rb$_2$O-Nb$_2$O$_5$ and K$_2$O-Ta$_2$O$_5$ with composition ratios near 1:3"
   "I. Stacking characteristics of MO$_6$ layers"
   "II. Various intergrowth phases and two-dimensional ordering of pentavalent ions"

34 Three papers on Direct Methods on incommensurate intergrowth structures
   a. "Direct methods for incommensurate intergrowth compounds. I. Determination of the modulation"

   b. "Direct methods for incommensurate intergrowth compounds. II. Determination of the modulation using only main reflections"

   c. "Direct methods for incommensurate intergrowth compounds. III. Solving the average structure in multidimensional space"

35 "Chalcogenide misfit layer compounds"
"Studies on Ba$_2$Nb$_{5-x}$Ti$_x$O$_9$ (0 ≤ x ≤ 1.75)"

"'Inverted twinning' in intergrowth tungsten bronzes"

"Structure refinements of the layered intergrowth phases Sb$_{x}$Sb$_{3-x}$xA$_{1-x}$TiO$_6$ (x=0, A = Ta, Nb) using synchrotron x-ray powder diffraction data"

"New HfFe$_6$Ge$_6$-ScFe$_6$Ga$_6$ intergrowth structures in ScFe$_6$Ga$_{6-x}$Ga$_x$ compounds (0.5 ≤ x ≤ 5.5)"
Venturini, G., J. Alloys Comp. 322 (2001) 190-197

"Neutron diffraction studies of the binary uranium stannides USn$_2$ and U$_3$Sn$_7"

"Structures of Ce$_2$Sn$_5$ and Ce$_3$Sn$_7$, Two superstructures of CeSn$_3"

"The structure of some metal compounds of uranium"

"The crystal structure of the phase β Mg$_2$Al$_3"
Samson, S., Acta Cryst. 19 (1965) 401-413

European Commissions Network of Excellence on Complex metal Alloys (ECNoE-CMA). For more information see https://www.cma-ecnoc.org/

Institut fyr Mikrostrukturforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany.

The program SUBGROUPGRAPH is available freely from the Bilbao Crystallographic Server http://www.cryst.ehu.es/ together with many other useful crystallography programs.

"Sodium tetramolybdenum hexaoxide (NaMo$_4$O$_6$). A metallic infinite-chain polymer derived by condensation of octahedral clusters"

"La$_{1.16}$Mo$_8$O$_{16}$: a Hollandite-related compound with an incommensurate modulated structure"
"Synthesis and characterization of a new modification of the quasi-low-dimensional compound Kmo$_4$O$_6$"

"Synthesis, characterization, and electronic structure of a new molybdenum bronze SnMo$_4$O$_6$"

"Pb$^{2+}$ Cation Ordering in Pb$_3$(Mo$_4$O$_6$)$_4$"

"Microdiffraction from anti-phase domain boundaries in Cu$_3$Au"

"The local domain configuration in partially ordered AuCu$_3$"

"Crystal chemistry and magnetism of neodymium stannides including compounds of the structural series RE$_n$Sn$_{3n-2}$"
Weitzer, F., Hiebl, K., Rogl, P., J. Solid state chem. 98 (1992) 291-300

"Constitution and thermodynamics of the antimony-tin system"

"A method for determination of the rhombohedral angle of SbSn"

"Old friends in a new light: "SnSb" revisited"

"Structural chemistry of the neptunium-silicon binary system"

"Hexagonal Y$_3$Ge$_5$ with a new AlB$_2$ derivative structure"

"The crystal structure of Yb$_3$Ge$_5$"

"Vacancy ordering in AlB$_2$-type RGe$_{2-x}$ compounds (R = Y, Nd, Sm, Gd - Lu)"

"Single crystal x-ray analysis of YGe$_x$ compounds (1<x<3)"
"On the use of crenel functions for occupancy modulated structures"

"Structure and magnetic ordering in the defect compound ErGe_{1.83}"

SHELX97

"WinGX suite for small-molecule single-crystal crystallography"