STELLINGEN
behorende bij het proefschrift "Domain structures in (NH₄)₂ZnCl₄"
van G.J. de Bruin-Hordijk.

1. Bij 46⁰ C heeft (NH₄)₂ZnCl₄ geen kristallografische fase overgang.

2. Een onderzoek naar domein structuren dient vooraf te gaan aan experimenten
waarbij men een "devil's staircase" wil aantonen.

3. Experimenten met ultra zuivere kristallen, zoals gedaan door K. Hamano, worden
ernstig vervuild door het feit dat voor het doen van deze experimenten goud
elektroden opgedampt worden.
K. Hamano, "Effect of Purification on Dielectric Properties near the Commensurate-
Incommensurate Transition Point of Rb₂ZnCl₄", Phase Transitions, 1988, Vol. 11,
pp. 279-296.

4. Bij experimenten betreffende fase-overgangen in kristallen is het van belang te
melden in welke fase de kristallen gegroeid zijn.

5. De niet-lineaire optische meetmethode van Tweede-Harmonische-Generatie is een
weinig tijdrovende aanvulling op poederdiffractie metingen en dient in geval van
NaLiSO₄ uitgevoerd te worden alvorens Monte Carlo berekeningen gedaan
worden.
L. Karlsson, R.L. Mc Greevy, "Mechanisms of ionic conduction in LiSO₄ and

6. Het gebruik van veiligheidsbrillen wordt aanzienlijk bevorderd indien de
randapparatuur van hoogvermogen infra-rood lasers voorzien is van groene in
plaats van rode display's.

7. Bij klachten aan het kniegewricht dient eerst een MRI scan gedaan te worden en niet
een kijkoperatie.

8. Academische titels dienen bij voorkeur gebruikt te worden bij het
ondertekenen van brieven voor Amnesty International.

9. "Part-time werken" dient niet verward te worden met "werk half doen".
Domain structures in $(\text{NH}_4)_2\text{ZnCl}_4$
Domain structures in (NH₄)₂ZnCl₄

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op vrijdag 28 juni 1996 te 16.00 uur

door

Geertruida Johanna DE BRUIN-HORDIJK

natuurkundig doctorandus

geboren te Vlaardingen
Dit proefschrift is goedgekeurd door de promotor
Prof. dr. ir. F. Tuinstra

Samenstelling promotiecommissie:

Rector Magnificus, voorzitter
Prof. dr. ir. F. Tuinstra, TU Delft, promotor
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PK Publishers
Lorentzweg 1,
2628 CJ Delft

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Domain structures in (NH₄)₂ZnCl₄
de Bruin-Hordijk, Geertruida Johanna
Delft: PK Publishers
Thesis Technische Universiteit Delft-
With ref.-With summary in Dutch
ISBN 90-75698-05-4
Subject headings: domain structures/
ferroelasticity/ incommensurate crystals
This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).

aan mijn ouders
aan Hein
aan Oswald, Sanne en Margriet
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"What's in a domain ?"
CHAPTER 1. INTRODUCTION.

1.1. Twinning.

Studies of thermal, optical, electric and elastic properties are important in the research of (new) materials. Fundamental knowledge of the structure of solids is essential in order to understand the macroscopic properties.

The most striking form of solid material is undoubtedly the crystalline state. Up to the 19th century the external forms of crystals with the shiny flat surfaces, the straight edges and the bizarre optical refraction phenomena fascinated mankind. Until that time the macroscopic appearance of the crystal, the morphology, was the tool to obtain crystallographic information. The regularity of the appearance and of the external form disposed observers to the belief that crystals are formed by a regular repetition of identical blocks (fig. 1.1). One of the founders of the modern crystallography, R.J. Haüy, based the dimensions of "molecules" on strict quantitative relations between fundamental crystal forms$^{10,12}$.

In 1912 the first X-ray diffraction experiments delivered the proof of the ideas of Haüy. X-ray diffraction patterns of crystals showed spots at regular distance. We now know that the elementary building blocks are atoms or groups of atoms. Introducing translation symmetry in three dimensions, and adding mirror and rotation operators, one was able to classify crystals in 230 three dimensional crystallographic space groups.

The most evident observation of a crystalline aggregate not being a monocrystal was shown by the phenomenon of macroscopic twinning. It was already observed early in the history of physical sciences in naturally found minerals as for instance quartz and calcite. Though early scientists discovered regularities in the angular relationship between the members of twinned crystals (the so called twin laws), the classical science of crystallography almost entirely devoted its attention to those samples which were supposed to be single crystals.

Closer examination with a magnifying glass of for instance ice crystals, however, revealed a finer twinning of what at first glance would have been characterized as a single crystal. The advent of the polarizing microscope gave an even further restriction to what could be
Fig. 1.1. Relation of the external form of crystals to the form of the elementary building blocks. The building blocks are identical in (a) and (b), but different crystal faces are developed. (Haüy, from the atlas to the 1822 edition of his "Traité de cristallography")\textsuperscript{12}.

Fig. 1.2. a A pseudo-hexagonal triplet of (β-)K\textsubscript{2}SO\textsubscript{4}, clearly displaying the three orthorhombic domains.

b An aggregate of (β-)K\textsubscript{2}SO\textsubscript{4} showing mimicry, the deviation from the hexagonal symmetry is visible in the dimples on the pyramidal faces indicated by the dashed lines.

c A cross section showing the domains as well as the dimples\textsuperscript{11}. 

- 10 -
regarded as a single crystal and what clearly was a multi domain structure. Though the naked eye would characterize it being a single crystal, the colours of the differently oriented domains, sometimes only of the order of a few μm across, revealed the true nature of the crystalline aggregate.

At the end of the nineteenth century a favorite subject of academic discussion was the suggestion that all crystals of high symmetry in reality were multiple twins, in which the domain size was beyond the resolving power of the microscope.

The mentioned phenomena were related to the so called pseudo-symmetry. A crystal was said to have pseudo-symmetry if the deviation from a higher symmetry could hardly be observed. The interfacial angles sometimes happened to deviate only a few seconds of arc from those expected from a point group with higher symmetry; the same applied to the measured axial ratios. An aggregate of a few macroscopic twins clearly showed the effect of pseudosymmetry as illustrated for a triplet of potassium sulphate in figure 1.2a. In its stable room temperature phase the crystals are orthorhombic but pseudo-hexagonal; de ratio a/b of the crystal axes \( a \) and \( b \) is nearly \( \sqrt{3} \). If the structure is hexagonal the ratio \( a/b \) is exactly \( \sqrt{3} \).

However, in the nineteenth century there was a remarkable observation that pseudo-symmetrical crystals had a strong tendency to hide their true symmetry even further by multiply repeated twinning. As a result the external form of the aggregate can often imitate a higher symmetry.

This phenomenon, known as mimicry, could be shown for example by the mentioned potassium sulphate \( \text{K}_2\text{SO}_4 \). At a first glance many "crystals" of \( \text{K}_2\text{SO}_4 \) exhibit the full hexagonal bipyramidal habit as illustrated in figure 1.2b and accordingly would be classified as hexagonal. The angle between two adjacent "(110)" faces of the bipyramid happened to be 59°36' instead of 60° exactly; they actually belong to differently oriented orthorhombic members. Only a slight dimple in the pyramidal faces indicates the deviation of the hexagonal symmetry (fig. 1.2c).

When X-ray techniques became operational in the early decades of the twentieth century, for the majority of the dubious cases the true symmetry and structure could be determined with certainty.

Some twenty five years ago it became clear that there are solids possessing an X-ray diffraction pattern with sharp spots, showing perfect long-range order in three dimensions, but losing the translation symmetry in at least one direction.

In these materials a static perturbation of the basic structure was shown with a period incommensurate with the underlying lattice. The incommensurately modulated structures
were discovered.
The perturbation in modulated structures may be for example a variation in the
magnetization, the electrical polarization, the charge density, the chemical composition or the
atomic positions. All these solids belong to the class of modulated structures lacking three-
dimensional space group symmetry; on the other hand they possess a high degree of long
range order, they may be considered crystalline.
Blinck gives a list of the most representative examples of modulated crystals.

In this thesis only crystals with a one-dimensional displacive modulation are considered.
The difference between such an (incommensurately) modulated crystal and a conventional
crystal forces us to label the diffraction spots differently.
The diffraction condition for a conventional crystal is

\[ \mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]

- \( \mathbf{K} \) = diffraction vector
- \( \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* \) = reciprocal lattice vectors
- \( h, k, l \) = integers.

The diffraction condition for a one-dimensional modulated crystal is

\[ \mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q} \]

- \( m \) = integer
- \( \mathbf{q} \) = wave vector of the static perturbation = \( \gamma\mathbf{c}^* \).  

When \( \gamma \) is irrational the crystal is incommensurately modulated, when \( \gamma \) is rational the crystal
is commensurately modulated. In the latter case the crystal can be described as a
conventional crystal, with a multiple unit cell, a so-called superstructure. When the
modulation wave is a block function such a superstructure can be seen as a structure with
alternating domains which have regular spacing on a nanometer scale. The domain size is of
the order of the unit cell dimensions; we could speak of submicrotwinning or nanotwinning.
A nanotwinned "crystal" will behave as a single crystal for most of its physical properties
such as birefringence and dielectric or magnetic behaviour. Even the diffraction techniques
may fail to observe the true nature.
In an incommensurately modulated phase a crystal can develop lock-in phases, these are superstructures. The difference between an incommensurate structure and a superstructure with $\gamma = u/v$ ($u$, $v$ mutually prime integer) gets vaguer when $v$ increases and is lost in the limited instrumental resolution.

Within the incommensurate phase, close to the lock-in transition temperature, discommensurations may occur. Domains which have already the lock-in structure are separated by these discommensurations, small areas in which the phase of the modulation wave changes rapidly. In terms of multi-domain structures the discommensurations can be classified as domain walls. The whole structure now can be described as a multiple twin aggregate with a (periodic) domain wall structure.

A retrospective view of the history shows that in all the mentioned cases the differences between the various structures are quite subtle. A discrimination could hardly be based on even the most precise observations. The assignment of the term single crystal most of time was determined by the resolving power of the method of investigation. In many cases domain structures were the origin of problems in revealing the true structure.

1.2. Scope of the thesis.

The present work is an exploration of the border region between the single crystalline state and the multiple twin structures, incommensurate phases, and sequences of lock-in phases. For the investigations in this region we have chosen as a vehicle the compound $(\text{NH}_4)_2\text{ZnCl}_4$, which has many of the above-mentioned problems. Beyond that $(\text{NH}_4)_2\text{ZnCl}_4$ may be assumed to form a link between the classical $\text{A}_2\text{BX}_4$ substances such as $\text{K}_2\text{SeO}_4$, $\text{Rb}_2\text{ZnBr}_4$, $\text{Rb}_2\text{ZnCl}_4$ on the one hand and $[\text{N(CH}_3)_4]_2\text{ZnCl}_4$ and its isomorphs on the other hand.

Therefore in this thesis the phases and phase transitions of $(\text{NH}_4)_2\text{ZnCl}_4$ are discussed. To tackle the problems, different X-ray diffraction instruments are used: an X-ray topography set up, a photographic precession camera and two different four-circle diffractometers. Besides that, different optical methods with the polarizing microscope are used and the nonlinear optical method of second harmonic generation (SHG).
We also make extensive use of the results of the theoretical progress that has been made in the last decades. In chapter 2, sections 2.1 and 2.2, different aspects of the theory of ferroelasticity, as stated by Aizu, Sapriel and others, are reviewed. The theory is very helpful for the description of the domain structure of \((\text{NH}_4)_2\text{ZnCl}_4\) (§ 2.4) and for the manipulation experiments (§ 2.5). To illustrate the general applicability of the theory the same experiment is repeated on a completely other material: the zeolite H-ZSM-5 (§ 2.6).

Chapter 3 describes a method to visualize the domains: the technique of X-ray diffraction topography. After an introduction in section 3.1 the X-ray topographic method of Guinier-Tennevin is discussed in section 3.2. This topographic method is essential for experiments in the chapters 5, 6 and 7. Section 3.3 shows our topographic experimental setup.

Chapter 4 describes a model of the \(\text{A}_2\text{BX}_4\) crystal structures.

Chapter 5 describes a study of the thermal history of the ferroelastic domain structure of \((\text{NH}_4)_2\text{ZnCl}_4\) from room temperature up to the incommensurate phase. An attempt was made to detect the phase transition at 46° C by optical experiments, X-ray diffraction and X-ray topography.

The subject of chapter 6 is the phase transition of \((\text{NH}_4)_2\text{ZnCl}_4\) from the incommensurate phase to the lock-in phase at 91° C. The behaviour of the modulation vector in the incommensurate phase is measured. The intensity of special reflections is studied and an attempt is made to find a connection between the ferroelastic domains in the lock-in phase and the discommensurations of the incommensurate phase.

Chapter 7 describes the ferroelectric-ferroelastic domain structures in a low temperature phase of \((\text{NH}_4)_2\text{ZnCl}_4\) (-50° C — -100° C). Conflicting discussions about the modulation structure of this phase have been reported\(^{24,31}\). Therefore an accurate study of the positions of satellite reflections has been done with an X-ray diffractometer. Topographic experiments of the ferroic domains explain once more what has happened.

Chapter 8 shows some experiments with a precession camera of another low temperature phase of \((\text{NH}_4)_2\text{ZnCl}_4\) (-790° C and below).

Parts of the work of the chapters 2, 5, and 7 were published earlier\(^{5,6}\).
1.3. $\text{(NH}_4\text{)}_2\text{ZnCl}_4$.

1.3.1. Crystal growth and sample preparation.

From literature\textsuperscript{7,18,21} we know that $\text{(NH}_4\text{)}_2\text{ZnCl}_4$ can be grown from an aqueous solution of NH\textsubscript{4}Cl and ZnCl\textsubscript{2}. Laminar domains are reported in the a,c plane\textsuperscript{7,21} and the mechanical stability is low because of the easy perfect cleavage along the (100) plane\textsuperscript{21}.

For the experiments described in this thesis we grow transparant $\text{(NH}_4\text{)}_2\text{ZnCl}_4$ crystals at 40° C by slow evaporation (2-3 months) from an aqueous solution of NH\textsubscript{4}Cl and ZnCl\textsubscript{2}, in accordance with the phase diagram of Meerburg\textsuperscript{18}.

By repeated recrystallization and filtration of the saturated solution we obtain optically high quality crystals with dimensions up to 30 x 20 x 2 mm\textsuperscript{3}. Generally two types of crystals are obtained: crystals with preferential growth along the b-axis and crystal plates grown perpendicular to the a-axis. Crystals grown in this way show in polarized light laminar domains in the a,c plane at room temperature. The thickness of the domains varies from about 1 µm up to a few millimetres.

$\text{(NH}_4\text{)}_2\text{ZnCl}_4$ crystals are very hygroscopic.
Crystal plates, with thickness 0.5 - 0.8 mm and parallel to principal crystal planes, are flattened and polished on a wet soft tissue. During polishing we can control the crystal direction within 0.5° with a polarizing microscope in conoscopic view\textsuperscript{27}.
We enclosed crystal plates between microscope glass cover slips to use them for birefringence and X-ray topography experiments.
For the X-ray diffraction experiments crystals are ground to spheres of 0.3 mm diameter, and enclosed in thin-walled glass capillaries.

1.3.2. Structure and phase sequence.

The compound ammoniumtetrachlorozincate $\text{(NH}_4\text{)}_2\text{ZnCl}_4$ belongs to the large family of $A_2BX_4$ crystals having the distorted $\beta$-$K_2SO_4$ structure\textsuperscript{8}.

Hogervorst\textsuperscript{9} in his thesis gives a review of the whole class of $A_2BX_4$ crystals.
Most of the $A_2BX_4$ compounds have a normal high temperature phase, an incommensurate phase and a lock-in phase with a superstructure. In addition to the three mentioned phases $\text{(NH}_4\text{)}_2\text{ZnCl}_4$ has four other phases.
The structure of $\text{(NH}_4\text{)}_2\text{ZnCl}_4$ has been studied before by several authors (fig.1.3).
Phases of (NH₄)₂ZnCl₄

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<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Pcmn</td>
<td>The structure determination is done by Matsunaga¹⁵.</td>
</tr>
<tr>
<td></td>
<td>Z = 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hkl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>133 °C</td>
</tr>
<tr>
<td>II</td>
<td>Incommensurate hkl ± (1/4 + δ)</td>
<td>Sato²³ measured satellite 2 0 5/4 + δ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>91° C</td>
</tr>
<tr>
<td>III</td>
<td>P 1 21/c 1 Z = 16 hkl ± 1/4</td>
<td>Structure determination of Matsunaga¹⁵ resulted in space group P2₁cn. Deguchi⁷ measured a monoclinic angle and concluded P1 21/c 1.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46° C</td>
</tr>
<tr>
<td>IV</td>
<td>P1c1</td>
<td>Domains ⊥ c-or ⊥ a-axis in phase III and IV⁷,²¹. Structure determinations by van Koningsveld¹³ and Matsunaga¹⁵.</td>
</tr>
<tr>
<td></td>
<td>Z = 16 hkl ± 1/4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 50° C</td>
</tr>
<tr>
<td>V</td>
<td>P1</td>
<td>No structure determination. Weak ferroelectric phase²⁴. Satellite reflections at 1/4, 2/7 and 1/3²⁴,³¹. Ferroelastic domains in c-plate⁷, ²¹.</td>
</tr>
<tr>
<td></td>
<td>Z = 14 hkl ± ???</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 10° C</td>
</tr>
<tr>
<td>VI</td>
<td>P c 21 n Z = 12 hkl ± 1/3</td>
<td>Matsunaga¹⁵,¹⁶ has done a structure determination. The phase is ferroelectric³.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- 79° C</td>
</tr>
<tr>
<td>VII</td>
<td>triclinic</td>
<td>Raman spectra suggested that this phase is triclinic. A ferroelectric phase²,³ ???</td>
</tr>
</tbody>
</table>

fig. 1.3. The different phases of (NH₄)₂ZnCl₄.
In phase I, the high temperature phase above $133^\circ$ C, $(\text{NH}_4)_2\text{ZnCl}_4$ is orthorhombic with space group $\text{Pcmn}$. Matsunaga\textsuperscript{15} has done the structure refinement. Fig. 1.4. shows the unit cell with two mirror planes, perpendicular to the $b$-axis, at 1/4 and 3/4 of the $b$-axis. In these two mirror planes most of the atoms are found. A mirror plane in the $\text{ZnCl}_4^{2-}$ tetrahedron coincides with a crystallographic mirror plane. The nitrogen atoms are in the mirror planes. The hydrogen atoms have not been located.

Fig. 1.5a shows the projection along the $a$-axis of the normal high temperature phase. When the temperature is lowered each $\text{ZnCl}_4$ tetrahedron rotates around an axis nearly parallel to the $c$-axis. Below $133^\circ$ C the resulting phase, phase II, is incommensurately modulated. Sato\textsuperscript{23} has accurately measured the 2 0 5/4 +$\delta$ satellite: at $91^\circ$ C $\delta$ drops discontinuously to zero. The incommensurate phase locks-in to a fourfold superstructure, phase III. Matsunaga has done a structure refinement and assigned the space group $\text{P2}_1\text{cn}$ to it, but Deguchi has shown that this phase is monoclinic, he measured accurately the monoclinic angle $\beta$ (fig. 1.6), and supposed this phase to have space group $\text{P1}(2_1/c)1$, a subgroup of $\text{Pcmn}$. He has not performed a structure refinement. With a study of NMR spectra Micheli\textsuperscript{19} too supposed the space group to be $\text{P1}(2_1/c)1$.

The modulated structure is characterized approximately by a transverse phase modulation wave with the polarization vector parallel to the $b$-axis and with the wave vector $k$ equal to one quarter of the $c^*$-axis (fig. 1.5b).

The room temperature phase, phase IV, is a fourfold monoclinic superstructure with space group $\text{P1c1}$. Both van Koningsveld\textsuperscript{13} and Matsunaga\textsuperscript{15} have done a structure refinement. Van Koningsveld has taken into account that $(\text{NH}_4)_2\text{ZnCl}_4$ is always twinned, he did a twin refinement.

Literature data are contradictory in describing phase V, the phase of the superstructure between $-5^\circ$ C and $-10^\circ$ C$^{24,31}$. Satellite reflections at 1/4, 2/7 and 1/3 of the $c^*$ axis are reported. Deguchi\textsuperscript{7} has shown that this phase must be triclinic, not only angle $\beta \neq 90^\circ$, but in this phase angle $\gamma \neq 90^\circ$, too (fig. 1.7). Sato has shown that phase V is (weakly) ferroelectric. Deguchi concluded that the space group of phase V must be $\text{P1}$.

In phase VI, between $-10^\circ$ C and $-79^\circ$ C, $(\text{NH}_4)_2\text{ZnCl}_4$ has a threefold orthorhombic superstructure with space group $\text{Pc}2_1\text{bn}$. Matsunaga \textsuperscript{15,16} has done the structure refinement. The phase is ferroelectric\textsuperscript{3}.

Below $-79^\circ$ C, in phase VII, $(\text{NH}_4)_2\text{ZnCl}_4$ is suggested to be triclinic\textsuperscript{1}. The space group is unknown. Only Raman spectra of $(\text{NH}_4)_2\text{ZnCl}_4$ are reported and analyzed.

The phase transitions between the different phases of $(\text{NH}_4)_2\text{ZnCl}_4$ are observed with birefringence measurements, DTA measurements and measurements of the
permittivity\textsuperscript{20,21,22,24,29,30}. Raman and Brillouin scattering experiments and measurements of NMR spectra have been performed, too\textsuperscript{14,25,26,28}. The phase transition III-IV at 46° C is only detected with measurements of the dielectric constant $\varepsilon_0$ with specially prepared crystals\textsuperscript{20}.

Domains have been observed in the phases III, IV and V\textsuperscript{7,20,21}. In paragraph 2.4 the domain structures of (NH$_4$)$_2$ZnCl$_4$ are described in more detail.

\begin{align*}
\text{Pcmn} & \quad \text{(Matsunaga/March 1982)} \\
a &= 12.745 \, \text{Å} \\
 b &= 7.275 \, \text{Å} \\
 c &= 9.295 \, \text{Å}
\end{align*}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure14.png}
\caption{Occupation of the mirror planes in a unit cell of (NH$_4$)$_2$ZnCl$_4$ in phase I}
\end{figure}

- 18 -
fig. 1.5. Phase I and III of (NH₄)₂ZnCl₄ (Matsunaga¹⁵).
fig. 1.6. Temperature dependence of $\Delta \beta (= \beta - 90^\circ)$ of (NH$_4$)$_2$ZnCl$_4$ (Deguchi$^7$).

Fig. 1.7. Temperature dependence of $\Delta \gamma (= \gamma - 90^\circ)$ of (NH$_4$)$_2$ZnCl$_4$ (Deguchi$^7$).
References.


[27] Intern report. (Studentenverslag over polijsten van kristallen).


CHAPTER 2. DOMAIN STRUCTURES OF FERROELASTIC CRYSTALS.

2.1. Introduction.

If a crystal undergoes a (nearly) second order phase transition which lowers the point group symmetry, the lower symmetry phase is called a ferroic phase and the crystal is said to be ferroic.

The most familiar examples of ferroic crystals are ferroelectric and ferromagnetic crystals. The mechanical analogue of these are the ferroelastic crystals. The phase transition to a ferroelastic phase is accompanied by a lattice distortion with respect to the high temperature phase. This can be described as a strain, a second rank tensor.

At a phase transition to a ferroic phase there is loss of one or more symmetry elements. In this lower symmetry phase it is possible to get two or more energetically equivalent configurations having the same crystal structure but differing in orientation. These configurations are called orientation states, twin components or (twin) domains; they are related by (one of the) lost symmetry elements.

It is possible that two orientation states are ferroelectric as well as ferroelastic, or not only ferroelastic but also ferromagnetic, and so on. Aizu\textsuperscript{1,2,3} gives all the possible combinations for different phase transitions.

Ferroelectrics, ferromagnetics and ferroelastics are called primary ferroics. When in a crystal two orientation states do not differ with respect to quantities of the lowest rank of the ferroic concerned, but differ in components of tensor properties of higher ranks then this crystal is called a secondary ferroic. Wadhawan\textsuperscript{10} and Salje\textsuperscript{8} have discussed that in detail.

In the next paragraph some features and definitions of primary ferroelasticity are summarized, especially those aspects which are essential for the experiments in the sections 2.5 and 2.6.

2.2. Ferroelasticity.

An exact definition of ferroelasticity, given by Aizu \textsuperscript{1,2,3}, is as follows: "A crystal is said to be ferroelastic when it has two or more orientation states in the absence of mechanical stress, and can be shifted from one to another of these states by a mechanical
stress. Any of the two states \((S_1 \text{ and } S_2)\) are identical (or enantiomorphous) in crystal structure and different with respect to the mechanical strain tensor at null mechanical stress".

\(S_1\) and \(S_2\) must be able to change into each other only through a slight movement of the atoms. They may be regarded as a slight modification of a certain nonferroelastic ideal crystal structure, the prototype phase or paraphase. This is not always the next higher-symmetry phase, the prototype phase is the one with the highest conceivable crystallographic symmetry from which the given ferroelastic phase can result by a slight distortion.

A point-symmetry operation which can map orientation state \(S_1\) of a ferroelastic crystal onto orientation state \(S_2\) is called an "F-operation" from \(S_1\) to \(S_2\).

A set of representative F-operations on \(S_1\) is a set of F-operations which, carried out on \(S_1\), give all the possible orientation states of the ferroelastic crystal. The point group of the prototype should include all the F-operations from all to all of the orientation states of the ferroelastic crystal and should not include any other symmetry operation.

Each species of ferroelasticity is represented by a symbol that contains the letter "F" at its center, the prototypic point group on the left of "F" and the ferroelastic point group on the right of "F".

For example: the species mmmF2/m means that there is a phase transition from the (orthorhombic) point group symmetry mmm to the (monoclinic) point group 2/m.

The reduction of symmetry from mmm to for example 2/m can occur in two energetically equivalent ways giving the two orientation states \(S_1\) and \(S_2\) (fig. 2.1). \(S_1\) and \(S_2\) can be mapped onto each other by the mirror operations \(m_x\) and \(m_z\). That are the mirror operations, which are present in the prototypic point group mmm, but which are lost in the point group of the ferroelastic phase 2/m.

Aizu has shown that all possible orientation states of a ferroelastic phase can be found by taking the point group operations of the prototypic phase which are lost at the phase transition, and let them work on one orientation state.

The number of orientation states equals the order of the prototypic point group divided by the order of the ferroelastic point group. In the example mmmF2/m the order of the point group mmm is 8, the order of the point group 2/m is 4, so the number of orientation states is 2 \((S_1 \text{ and } S_2)\).

To see if a crystal phase is really ferroelastic one must determine the strain tensor in the different orientation states. When all the orientation states have a different strain tensor with respect to the same axes the crystal is said to be fully ferroelastic; when some orientation
The phase transition mmmF2/m\(\gamma\) can occur in two energetically equivalent ways giving the orientation states \(S_1\) and \(S_2\).

states have different strain tensors and others have not, the crystal is said to be partially ferroelastic.

Further it is important to know that a ferroelastic crystal, derived from a prototype belonging to a centrosymmetric point group, must be centrosymmetric\(^1,2,3\). The reason is as follows. Supposing the ferroelastic crystal is noncentrosymmetric, all orientation states can be divided into pairs such that states belonging to the same pair are changed to each other by the inversion. Since every second-rank polar tensor is unchanged by the inversion, states belonging to the same pair should be equal in mechanical strain.

As an illustration of the theory we further work out the species mmmF2/m.

Let \(S_1\) be an orientation state in the monoclinic phase.

The symmetric strain tensor with respect to the prototype is

\[
T_1 = \begin{pmatrix} p & 0 & s \\ 0 & q & 0 \\ s & 0 & r \end{pmatrix}
\]

(when the \(b\)-axis is unique)
Orientation state $S_2$ can be found by applying mirror operation $m_x$ to $S_1$. 
$T_2$, the strain tensor in $S_2$, can be found by the transformation of the strain tensor $T_1$ from orientation state $S_1$ to orientation state $S_2$.

$$T_2 = m_x T_1 m_x^{-1}$$

$m_x^{-1}$ is the inverse operation of $m_x$.

$$T_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p & 0 & s \\ 0 & q & 0 \\ s & 0 & r \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} p & 0 & -s \\ 0 & q & 0 \\ -s & 0 & r \end{pmatrix}$$

The strain tensors $T_1$ and $T_2$ are different, so the monoclinic phase is (fully) ferroelastic.

The most important measure for the "degree" of ferromagnetism and ferroelectricity is the spontaneous magnetization and spontaneous polarization. These state parameters are zero in the paraphase and unequal to zero in the ferroic phase. A state parameter of ferroelasticity is defined analogously\(^1\),\(^2\),\(^3\). The strain tensor is not a proper state parameter, because this tensor is not zero in the paraphase. The "degree of ferroelasticity" is measured by the spontaneous strain. This state parameter is obtained from the strain tensor. The spontaneous strain tensor is defined as

$$S_1 = T_1 \cdot \frac{1}{t} \sum_{l=1}^{t} T_1$$

$t = \text{number of orientation states.}$

and the spontaneous strain as

$$S^2 = \sum_{j=1}^{3} \sum_{k=1}^{3} S_{ikj}^2$$

In the example of the species mmmF2/m the spontaneous strain tensor is

$$S = \begin{pmatrix} 0 & 0 & s \\ 0 & 0 & 0 \\ s & 0 & 0 \end{pmatrix}$$
and the spontaneous strain is \( S^2 = 2 \, s^2 \).
The trace of the spontaneous strain tensor is equal to zero, that means that the strain occurs without change in the volume of the prototype.

2.3. Domain walls.

Orientation states or domains in a ferroic crystal are separated from one another by surfaces called domain walls. A study of the various domain walls can provide valuable information for characterizing the crystal structure. Domain structures of ferroics also determine their macroscopic properties, and therefore have an important bearing on their applications. Sapriel\(^9\) has determined a criterion to predict the orientation of domain walls.

Even when no external stress is applied to the crystal, there is a finite internal strain because two adjacent domains are locally stressed in order to join along the wall. The determination of the direction of the domain wall is based on the condition that the spontaneous strains of two adjacent domains (\( S_1 \) and \( S_2 \)) must be identical in the boundary.

Sapriel's formulation leads to the following equation for the orientation of (permissible) domain walls:

\[
(S_{ij}(S_1) - S_{ij}(S_2)) \, x_i \, x_j = 0
\]  

\( x_i \) \(( i = 1,2,3 \)\) denotes the coordinates of a point on the domain wall. \( S_{ij} \) are elements of the spontaneous strain tensor.
The physically acceptable solutions are two mutually perpendicular planar walls, fullfilling the condition

\[
\det \left| S_{ij}(S_1) - S_{ij}(S_2) \right| = 0
\]  

These permissible domain walls can be of two types.
First, the W-walls: crystallographically prominent planes of fixed indices. The orientation of a W-wall does not change with temperature.
The other type of permissible walls are called W'-walls. The orientation of a W'-wall is determined by the components of the spontaneous strain tensor, and thus varies with temperature.
Fig. 2.2a. Interaction between a W wall and a W' wall. At the junction, the walls bend to each other with a rounding of the tip. Lattice planes are highly distorted close to the junction\(^8\).

Fig. 2.2b. Lattice distortion around two twin walls of the one type (e.g. W, shown as vertical) interacting with a wall of the second type (e.g. W', shown as horizontal)\(^8\).
Sometimes, symmetry considerations are sufficient to obtain the directions of the domain walls. Then domain wall orientations correspond to those symmetry operations which are lost at the phase transition. For example in the case of the species mmmF2/m, the possible directions of the domain walls are the directions of the lost mirror planes m_x and m_z. But, in general, to obtain the complete set of domains it is necessary to solve systematically equation (2.2). Chapter 7 shows an example.

Domain orientations predicted by equation (2.2) represent an idealization. In real crystals one may have to take into account not only the elastic energy, but also the electrostatic energy (if the crystal is ferroelectric too) or the interfacial energy of the domain wall. Furthermore equation (2.2) describes the orientation of the domain walls in terms of the lattice planes of the prototype phase, but in the ferroelastic phase the spontaneous strain changes the orientation of these lattice planes, small rigid body rotations of the domains must be incorporated to achieve physical contact between the domains.

Furthermore, there is the effect of the inter-wall interactions. Salje distinguish three interactions:

a. The wall intersection (fig. 2.2).
b. The interaction between a right angle domain and a planar domain wall (fig. 2.3) and
c. The formation of needle twins (fig. 2.4).

The general condition for all these interactions is that the shape of the domain walls will change until the wall energy reaches a minimum. Lattice planes can be highly distorted to reach this minimum.

2.4. Domain structures in (NH₄)₂ZnCl₄.

In the phases III, IV and V of (NH₄)₂ZnCl₄ (fig. 1.3) domains are observed by Deguchi and Mel'nikova. Between -10° C and 70° C, in phase III, IV and V, they observed with a polarizing microscope laminar domains in the a,c plane with domain walls perpendicular to the c-axis. The monoclinic angle β varies between these temperatures, ∆β (= β - 90°) is about 0.02° at room temperature and 0.08° in phase V (fig. 1.6).

The nature of the ferroic domain structure has been subject to controversy. An uniaxial compression, up to failure of the crystal, and a static electric field, up to 20 kV/cm, left the twin boundaries unchanged.

In phase V another type of domains is reported: laminar domains in the a,b plane with domain walls perpendicular to the a- or the b-axis. The angle difference ∆γ (= γ - 90°) of
Fig. 2.3. The forces acting on a non-intersecting wall (right hand side) close to a junction between two twin walls. The non-intersecting wall is bent into an s-shaped wiggle.$^8$

Fig. 2.4. Wall configuration during the formation of a needle twin. The two junctions with the distance $r$ attract each other thereby bending the walls between the domains A and B.$^8$
one of the triclinic angles $\gamma$ is about 0.2° (fig. 1.7). The walls of this domain pattern were found to be easily moved by application of an external stress, so the domains are ferroelastic. In chapter 7 the domain pattern of phase V will be discussed in detail. In this chapter the character of the domain pattern of phase III and IV will be discussed and investigated.

With a polarizing microscope we observed the domain structure at room temperature. In accordance with the literature domains with domain walls oriented perpendicular to the c-axis were observed. Occasionally however, we also observed domain walls perpendicular to the a-axis. In both cases the width of the domains vary between 1μm and 4 mm. The domain structure is conserved up till 70° C, despite the phase transitions at 46° C. We observed no change of the domain pattern at 46° C.

We made the assumption that the domains, although optically not visible, are present up till the phase transition at 91° C (see chapter 5 for details). Then the theory of Aizu indicates that when phase I of (NH₄)₂ZnCl₄ (space group Pcmn) is the prototype phase of phase III (space group P1(21/c)1), phase III must be a ferroelastic phase and the domain walls will be perpendicular to the a-axis or the c-axis (see the species mmmF2/m in § 2.3). This was in excellent agreement with our observations of the domain walls. To prove the ferroelastic character of the domain structure experiments to manipulate the domains with a mechanical stress were set up.

2.5. Manipulation experiments.

In paragraph 2.2 it was shown that the spontaneous strain tensor was unequal to zero for the tensor elements 13 and 31. This indicates that the deformation during the orthorhombic-monoclinic phase transition is a shear deformation. The transformation of one of the monoclinic orientations into the other can be induced by a pure shear stress $\sigma_{13}$, which is difficult to apply. However, a uniaxial compressive stress $\sigma$ along the direction 45° inclined to the a and the c crystallographic axes, transforms into the required stress $\sigma_{13}$ superimposed on a uniform two dimensional compressive stress $\sigma_{11} = \sigma_{33}$. So, in order to manipulate the domains by a mechanical stress, the uniaxial stress must be exerted in the [101] direction.

To that goal the crystals were polished to thin plates (0.6 - 0.8 mm) perpendicular to the b-axis, with two sides making an angle of 45° with respect to the domain walls. The crystal was placed in a squeezer (fig. 2.5). One arm of the squeezer was fixed, the other one was controlled by a spring force gauge. In this way the uniaxial mechanical stress could be
exerted in the [101] direction.
With this setup the behaviour of the domain walls could be followed under a polarizing microscope.

The photographs 2.1 and 2.2 show that (NH₄)₂ZnCl₄ is indeed ferroelastic. The minimal compressive pressure needed to shift the domain walls at room temperature is about 50 N/cm².

A number of crystals, each containing only two domains of millimetre size, were heated above 91°C. After cooling to room temperature the crystals invariably were multitwinned with the domain walls about one µm apart. The volumes of the two orientations were equal or nearly so.

When a multitwinned crystal was clamped in the [101] direction between tweezers and heated above 91°C, the crystal, after cooling to room temperature, showed a large one-domain region.

These experiments show that the ferroelastic domain structure of (NH₄)₂ZnCl₄ is created and can be changed at (about) 91°C. The ferroelasticity of the domain structure is conserved by cooling to room temperature.

The theory of Aizu does not require that the prototype phase, phase I in (NH₄)₂ZnCl₄, directly transforms into the ferroelastic phase, here phase III. We have omitted, however, to mention in this description that the intermediate phase in (NH₄)₂ZnCl₄ is an incommensurate phase. In Chapter 6 we will pay attention to this subject.
Photos 2.1 and 2.2 show the ferroelastic character of the domains of \((\text{NH}_4)_2\text{ZnCl}_4\) at room temperature. Photo 2.1. shows the a,c plane of a two domain crystal before applying the stress. Photo 2.2 shows the same crystal during the stress.
photo 2.3. The laminar domain structure in the b,c plane of H-ZSM-5.
2.6. The zeolite H-ZSM-5.

The zeolite H-ZSM-5 shows an orthorhombic to monoclinic phase transition at about 67°C. The orthorhombic space group is Pnma, the monoclinic space group is P(21/n)11. The theory of Aizu predicts that the monoclinic phase might be ferroelastic and belongs to the species mmmF2/m.

Van Koningsveld5 shows that H-ZSM-5 is ferroelastic: application of a uniaxial mechanical stress during the orthorhombic to monoclinic phase transition changes the population of the monoclinic twin domains. Changes in the X-ray intensities of 25 reflections, measured with a CAD-4 diffractometer, indicate a change in the volume fraction of the smaller twin mate from 0.5 before to 0.06 after applying the stress.

With a polarizing microscope we did a direct observation of the moving domain walls of H-ZSM-5 in the same way as for (NH4)2ZnCl4. At room temperature we observed laminar domains in the b,c plane with domain walls perpendicular to the b-axis (photo 2.3). That is in good agreement with the theory of Sapriel9 which predicts domain walls perpendicular to the b-or the c-axis for the species mmmF2/m.

The width of the domains is about 1 μm. Not all the crystals show domains in the b,c plane. In that case the width of the domains is very probably below 0.5 μm, that is below the resolving power of the microscope.

The spontaneous strain tensor for H-ZSM-5 has the form

\[
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & s \\
0 & s & 0
\end{pmatrix}
\]

(a-axis unique)

At room temperature we applied a uniaxial mechanical stress in the [011] direction.

Because of the small dimensions of the crystal (150-200 μm), the squeezer of fig. 2.5 could not be used. One edge of the crystal was fixed with glue, the opposite edge in the [011] direction was pressed with a microscope glass cover slip. The results are presented in the photographs 2.4 a and b. Photograph 2.4a is taken before applying the stress, photograph 2.4b is taken during the stress. The upper part of the crystal (photograph 2.4b) shows that a large single domain region is created; the lower part of the photograph shows that as well, but the applied stress is at the limit of the mechanical strength of the crystal. Some cracks are visible in the lower part of the crystal. From this direct observation the conclusion can be drawn that H-ZSM-5 is ferroelastic at room temperature.
Photo 2.4. Domains of H-ZSM-5 before (a) and during (b) the stress.
References

CHAPTER 3. X-RAY DIFFRACTION TOPOGRAPHY.

3.1. Introduction.

All crystals are imperfect. It is only the degree of imperfection that counts. Single crystals of silicon and germanium grown for the electronic industry are among the most perfect crystals known. Minerals and laboratory grown crystals of inorganic chemical compounds invariably suffer from dislocations, vacancies, interstitials, mosaic-spread and domain structures. With the advent of X-ray diffraction techniques in 1912 crystal structure analyses have revealed the arrangement of the atoms in the unit cell of the ideal crystal. In addition to this type of analysis special techniques have been developed in order to study the presence, the nature and the extent of the defects.

X-ray diffraction topography is such a valuable method to study the perfection of a crystal. It is an aid in crystal growth studies. One can control the quality of a crystal. The presence of defects in a single crystal can be detected.

X-ray diffraction topography has been proved to be powerful too in the study of domain structures\(^6,10,11,12\). In all of the different methods of X-ray topography, the domain structure is imaged in the diffraction pattern because each domain diffracts separately in a slightly different direction caused by the spread in the orientation of the domains.

When a monochromatic X-ray beam with wavelength \(\lambda\) diffracts at a perfect crystal with a set of lattice planes, spaced \(d\), the Bragg relation can be applied

\[
2d \sin \theta = (n) \lambda
\]

\[\theta = \text{diffraction angle}\]

\[n = \text{integer}\]

When the set of lattice planes varies locally around a defect, or owing to differences in domain orientations, there are differences in intensity and/or orientation in the diffracted beam, showing an image of the defect or an image of the domain structure.

For domain structures the following holds: in all of the domains the crystal structure is the same and thus so is the interplanary distance \(d\). To satisfy the Bragg condition the only remaining variables are the diffraction angle \(\theta\) and the wavelength \(\lambda\).
During the last fifty years different methods of X-ray diffraction topography have been developed with monochromatic as well as polychromatic X-ray beams.\textsuperscript{3,4,8,12} Fig. 3.1 shows the principle.

Textbooks of crystallography and X-ray diffraction topography give a summary with the (dis)advantages of the different methods\textsuperscript{7,14,15}. We have selected the method of Guinier-Tennevin\textsuperscript{8} to study the domain structures of (NH\textsubscript{4})\textsubscript{2}ZnCl\textsubscript{4} in the phases III, IV and V (see chapter 5, 6, 7). The apparatus needed for this method is exceedingly simple, one can do it with standard laboratory equipment. We shall discuss the method in detail in the next section.

Our first motive to start with X-ray diffraction topography was the lack in optical information about the domain structure of (NH\textsubscript{4})\textsubscript{2}ZnCl\textsubscript{4} between 70° C and 91° C (see chapter 2 and 5).

---

**Fig. 3.1.a.** Orientation contrast from a monochromatic ideally collimated X-ray beam. Diffraction occurs only from one region.

**b.** Orientation contrast from a polychromatic X-ray beam. The differing directions of the beams from the two regions leads to contrast at the boundary if the plate-specimen distance is sufficiently large.\textsuperscript{15}
3.2. The Guinier-Tennevin method.

In 1949 Guinier and Tennevin developed a method to produce an image of a relatively large area of a single crystal with help of white radiation from a fine-focus X-ray tube. For them it was a way to get information about the degree of perfection of certain crystals, but we shall use this method to study domain structures. For a long time the topography method of Guinier-Tennevin has been little used because of long exposure times. Since the use of synchrotron radiation this topographic method has become popular. It needs only a few seconds to make a topograph. To visualize a domain structure a standard X-ray tube can be used, because a long exposure time is not a problem for static domains.

Figure 3.2 shows the schematic representation of the Guinier-Tennevin method. A polychromatic X-ray beam with small angular divergence, emitted by a point source S at about 1 m distance, is incident on a crystal. A photographic film is placed only a few cm behind the crystal. By means of a screen QQ placed in front of the crystal the exposed region is limited to a few mm². Such an X-ray diffraction setup looks like an arrangement for a Laue transmission diffraction recording but differs in two ways of it:

a. There is a long source-sample distance.

b. The width of the X-ray beam is a few millimetres instead of a few tenths of millimetres.

Due to this arrangement a wide nearly parallel X-ray beam diffracts at the crystal and the photographic film shows large "Laue spots" of some millimetres. If the exposed region of the crystal consists of subunits with slightly different angular orientation each unit will form its own image. The large "Laue spots" show nonuniform intensity distribution, which is an image of the exposed region of the crystal.

The "Laue spots" of a Guinier-Tennevin topograph of a crystal with a laminar domain structure show that each domain makes its own image which has a gap or an overlap with the images of other domains (Photo 3.1). A stepwise explanation of this phenomenon is given in figure 3.3a,b,c.

When a wide X-ray beam diffracts at a set of planes which are directed perpendicular to the crystal laminate the reflection image is a point image (fig.3.3a). When a wide X-ray beam diffracts at a set of planes which are not perpendicular to the crystal laminate the
Fig. 3.2. Schematic representation of the topographic method of Guinier and Tennevin.
S: point source of X-rays.
PP': crystal slab.
QQ': screen limiting the exposed region to a few mm width.
F: photographic film.

Photo 3.1. A two-domain crystal of (NH₄)₂ZnCl₄ at room temperature with the domain wall perpendicular to the c-axis.
reflection image is a parabolic image (fig. 3.3b).
In figure 3.3c a wide X-ray beam diffracts at a two-domain crystal. The parabolic images of a set of planes of each domain is given. \( n_1 \) is the unit vector normal to a set of reflecting planes of domain 1, \( n_2 \) is the unit vector normal to a set of reflecting planes of domain 2. AC and BD are the images of domain 1 resp. 2 in one "Laue spot", AB is the gap between these two images.
To get a good image of the domain structure the film-sample distance must be small in relation to the source-sample distance. The photographic film must be far away from the parabolic images (fig.3.3c). When the divergence of the X-ray beam is small, the parabolic images are far away from the photographic film too.

We look further to this topographic method and calculate the gap or overlap in a "Laue spot" to know the resolution of the topographic method.
A polychromatic (approximately parallel) X-ray beam diffracts at a crystal with a laminar domain structure. Fig. 3.3d. shows the situation for a two domain crystal. Suppose the crystal is infinitesimally thin. Let \( 2\delta \) be the (small) angle difference between the directions of the crystal lattices of the two domains, \( s \) the distance between the X-ray source and the sample and \( L \) the distance between the sample and the photographic film. The film is placed parallel to the surface of the crystal. In the middle of the domain wall the origin \( O \) of an axes system \( a, b, c \) is chosen.
In domain 1 is a set of planes \( W_1 \) and in domain 2 is an equivalent set of planes \( W_2 \).
We look especially to these sets of planes at the border of domain 1 and 2. Let \( n_1 \) be the normal of the set of planes in domain 1, let \( n_2 \) be the normal of the equivalent set of planes in domain 2. For the sake of convenience we suppose the ideal situation that the middle of the X-ray beam hits the domain wall at \( O \).
\( OB_1 \) is the reflection ray of plane \( W_1 \) of domain 1, \( OB_2 \) is the reflection ray of plane \( W_2 \) of domain 2. To know the limit for the measurement conditions the gap (or overlap) \( \Delta \) of a "Laue spot" on the photographic film is calculated.
The angle between \( n_1 \) and the surface of the crystal sample is \( \Phi \), between \( n_2 \) and the surface of the crystal sample \( \Phi + 2\delta \).
The gap
\[
\Delta = AB = BO' - AO' = L \left[ \tan (2\Phi + 4\delta) - \tan 2\Phi \right] =
\]
\[
= -L \left[ \frac{\sin 4\delta}{\cos (2\Phi + 4\delta) \cdot \cos 2\Phi} \right]
\]
\[.....(3.2)\]
Fig. 3.3. Figure a and b are a help to understand figure c.

a. When a wide X-ray beam diffracts at a set of planes which are directed perpendicular to the crystal laminate the reflection image is a point image.

b. When a wide X-ray beam diffracts at a set of planes directed not perpendicular to the crystal laminate the reflection image is a parabolic image.

c. A wide X-ray beam diffracts at a two-domain crystal. The parabolic image of a set of planes of each domain is given. 
   \( n_1 \) is vector normal to a set of reflecting planes of domain 1, 
   \( n_2 \) is vector normal to a set of reflecting planes of domain 2. 
   AC and BD are the images of domain 1 resp. 2 in one "Laue spot", AB is the gap between these two images.

d. Part of c.
If $\delta$ is small the gap is

$$\Delta \equiv -4L \delta / \cos^2 2\Phi. \,$$

$\Delta$ must have the dimension of some grains of the photographic film.
If $\delta$ is very small only special sets of planes show orientation contrast in their Laue spots.
Suppose each grain of a photographic film is about 40 $\mu$m and $\Delta = 2$ grains is the limit that can be observed. If $\Phi$ is small $\Delta \equiv -4L \delta$. When $L = 4.10^{-2}$ m the lowest limit of $\delta$ that can be observed is $\delta = 5.10^{-4}$ rad $\equiv 0.03^\circ$. When a grain is 4$\mu$m, the lowest limit of $\delta$ equals 0.003$^\circ$.

When a crystal is not infinitesimally thin the intensity distribution in the "Laue spots" is more complex (fig. 3.4). The front and the back of the crystal give different images.

We saw that when the angle difference between the directions of the crystal lattices of two domains is small not all the "Laue spots" show orientation contrast. A certain domain structure manifests itself best for specific planes and thus for specific hkl reflections, as one can realize in another way too:
Suppose an orthorhombic/monoclinic phase transition of a crystal in which the symmetry of the structure is lowered, two mirror planes and/or two twofold rotation axes of the orthorhombic phase disappear and (possibly) one of the angles $\alpha$, $\beta$, $\gamma \neq 90^\circ$. In the case $\beta \neq 90^\circ$ there are two possibilities to get laminar domains, with W domain walls (fig. 3.5):
The change in the crystal structure happens in the original a,c plane of the orthorhombic phase with
a) Change of the direction of the a-axis or
b) Change of the direction of the c-axis.
Figure 3.6. "translates" the two possibilities into the reciprocal space.
It is clear that laminar domains perpendicular to the a-axis manifest themselves best for hkl reflections with l large, laminar domains perpendicular to the c-axis manifest themselves best for hkl reflections with h large.
The description for $\alpha \neq 90^\circ$ or $\gamma \neq 90^\circ$ is equivalent.
Therefore a certain domain structure manifests itself more prominent in specific hkl reflections.
Fig. 3.4. When the crystal is not infinitesimally thin the topograph is more complex. The back and front of the crystal give different images on the photographic film.
Fig. 3.5. The transition in the crystal structure at an orthorhombic/monoclinic phase transition happens in the \( a, c \) plane when \( \beta \neq 90^\circ \).
fig. 3.6. A laminar domain structure manifests itself more prominent in specific hkl reflections:
laminar domains perpendicular to the a-axis: l large if $\beta \neq 90^\circ$.
    k large if $\gamma \neq 90^\circ$.
laminar domains perpendicular to the b-axis: l large if $\alpha \neq 90^\circ$.
    h large if $\gamma \neq 90^\circ$.
laminar domains perpendicular to the c-axis: h large if $\beta \neq 90^\circ$.
    k large if $\alpha \neq 90^\circ$. 

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Fig. 3.7. The experimental setup.
3.3. The experimental setup.

Fig. 3.7 shows the experimental setup. An X-ray beam is incident on a crystal. A Mo X-ray tube with a point-focus of 0.4 x 0.4 mm\(^2\) is at a distance of about 2 m of the crystal. A pipe is placed between point-focus and crystal to protect the experimenter. The beam is collimated at the end of the pipe through an aperture of 3 mm diameter. Because of the large source-sample distance and the collimation of the X-ray beam an approximately parallel beam reaches the crystal. The X-ray beam is directed along a prominent crystallographic axis.

The crystal is oriented with a precession camera. Subsequently a Laue recording is made with the same camera by choosing the precession angle 0°. Then it is possible to orient the crystal within 0.3° with respect to the crystallographic plane. After that the whole precession camera with the crystal is placed behind the pipe of the topography setup. A collimator of 0.3 mm is placed in the aperture of 3 mm and again a Laue recording is made to check the orientation of the crystal. The orientation of the crystal is adjusted again until it gives the same symmetric Laue recording as the first one. Then the collimator is removed and the topographs can be made with the aperture of 3 mm diameter.

The distance between the photographic film and the sample was for the experiments of (NH\(_4\))\(_2\)ZnCl\(_4\) crystals between 4 and 6 cm. In general one can say that the diameter of the X-ray beam and the film-sample distance must be optimized in such a way that the individual "Laue spots" do not overlap each other too much. Mostly the photographic film was placed perpendicular to the incident X-ray beam, but it was possible to set the film with an angle \(\neq 90°\) with respect to the beam. Then for special reflections the diffracted beam is perpendicular to the film. Oblique incidence to the film broadens the image unless films with thin emulsions and small grains are used. The film is often held in a cassette that can be evacuated to "pull" the film to the front of the cassette; this helps to keep the film flat.

The crystal could be heated or cooled by blowing a warm air current or cold nitrogen vapour over it. The temperature was checked by a thin Cr-Al thermocouple at about 1 millimetre distance of the crystal.

This experimental setup is used for the topographs of domain structures of (NH\(_4\))\(_2\)ZnCl\(_4\) which will be discussed in the chapters 5, 6 and 7.
References.

CHAPTER 4. THE MODEL STRUCTURE.

4.1. Introduction.

After the advent of X-ray structure analysis in the early decades of the present century the atomic structures of all of the simple ionic compounds became available. The structures were found to fulfill simple sphere packing rules with which the differences between structures of for instance NaCl and CsCl could be explained satisfactorily. An extensive system of rules was generated which could be applied provided that reliable ionic radii could be attributed to each type of ion, regardless of the compound under investigation. It was, however, soon discovered that successful application was possible only if the ionic radii were made to depend on the number of direct neighbours in the structure: the radii depend on the coordination number. With some more subtle refinements the developed methods were quite successful.

In many compounds, however, some of the constituent atoms formed rigid complex ions, the structure of which did not vary from compound to compound. For instance in the structures of the sulfates the complex $\text{SO}_4^{2-}$-ion always appears as a barely distorted regular tetrahedron. Though formally the sphere packing rules still could be applied, the rigid complex ions on the other hand gave rise to distortions of the structure which could not effectively be explained by simple arguments. For the compounds containing complex ions a classification was generated in which these complex ions were used as structural entities. Since these ions have generally no spherical symmetry small rotations of these ions may reduce the ionic energy of the crystal. In other words the non isotropic symmetry of the potential of the complex ions can result in a lowering of the electrostatic energy merely by slight rotations of the ions.

The mentioned classification of complex ionic structures has as a starting point a series of structural families each of which is named after a prototype of which all other members can be generated by slight structural distortions. This prototype is called the aristotype, its derivatives are called hetotypes. Quite often the structural distortions result in a multiplication of the unit cell size of the aristotype. The multiplication factor can either be a rational number resulting in a superstructure or it can be an irrational (temperature dependent) number in which case the structure is incommensurately
modulated. The well known rich polymorphy of the perovskite family\textsuperscript{1}, structures which are derivatives of the perovskite aristotype found in ideal form in SrTiO\textsubscript{3}, is an example of the above reasoning.

As mentioned in chapter 1 the structures of (NH\textsubscript{4})\textsubscript{2}ZnCl\textsubscript{4}, treated in the present work, belong to the β-K\textsubscript{2}SO\textsubscript{4}-family tree. Many structures of compounds with the chemical formula A\textsubscript{2}BX\textsubscript{4}, in which the A- and B-ions are positively and the X-ions are negatively charged, can be regarded as slight distortions or hettotypes of the β-K\textsubscript{2}SO\textsubscript{4} aristotype. Even if, as in the present work, the A-ions themselves are compound ions they can be classified in the β-K\textsubscript{2}SO\textsubscript{4}-family.

The aristotype β-K\textsubscript{2}SO\textsubscript{4} crystallizes in an orthorhombic pseudohexagonal structure\textsuperscript{3}. The lengths of the crystallographic axes are a = 10.071(4) Å, b = 5.763(2) Å, c = 7.476 Å; a/b = 1.74753, only slightly larger than \sqrt{3} = 1.73205.

The spacegroup is Pcmn or in full P 2\textsubscript{1}/c 2\textsubscript{1}/m 2\textsubscript{1}/m. In figure 4.1 the (glide-) mirrorplanes are given, showing the relation which they induce between the four tetrahedra in the primitive unit cell. The c, m and n mirrorplanes can act as the generators of the spacegroup, the twofold screw axes are then induced by these generators.

![Diagram](image)

**Fig. 4.1** The (glide) mirror planes of the aristotype β-K\textsubscript{2}SO\textsubscript{4} according to space group Pcmn. \(\sigma = K^+\) ion, \(\Delta = SO_4^{2-}\) ion
4.2. The model structure.

Hogervorst\textsuperscript{2} has made an analysis of all of the reported A\textsubscript{2}BX\textsubscript{4} compounds having the distorted β-K\textsubscript{2}SO\textsubscript{4} structure. In all of these structures layers of tetrahedra normal to the e-axis can be distinguished. In each of the layers the distortions are such that the tetrahedra are rotated about the e-axis all in the same sense (fig. 4.2). The modulation wave can be characterized by the amplitudes of the rotations in the subsequent layers and by its wavelength. The wavelength of the modulation can either be a rational multiple of the e-axis of the prototype or an irrational multiple resulting in a commensurate or an incommensurate phase respectively.

Hogervorst has performed model calculations which also indicate that the rotations of tetrahedra within a layer preferably are in the same sense.

Using this result as a stereochemical starting point we will compare the possible distortions changing continuously the modulation wave vector from e*/4 to e*/2.

For the sake of convenience we suppose that the function which shows the rotational amplitudes of subsequent layers is a block function.

In a string of tetrahedra, stretching out in the e-direction, the tetrahedra are either rotated in positive sense or in negative sense about the e-axis, through angles with the same magnitude. This has been experimentally observed in all of these A\textsubscript{2}BX\textsubscript{4} structures. Projected on the a,b plane four of these strings can be observed separately. They are contained in the projection of the unit cell. As depicted in figure 4.3 we will call them I, II, III and IV. In the prototype, in which the amplitude of the modulation is zero, the ions in the string are related by the symmetry operations c, m, n and the three 2\textsubscript{1}-screw axes.

The assumption that all tetrahedra within one layer rotate in the same sense relates the strings I and IV and also the strings II and III; their modulations are in phase.

If each of these strings has its own modulation function the strings would be structurally unrelated and no symmetry element related to those of the aristotype Pcmn would be present. Such a structure would principally be triclinic.

We now will analyse to what extent the original spacegroup elements of Pcmn can have effect on the distorted structures.

We examine each symmetry element separately keeping in mind that:

a. There are three possibilities to get a superstructure with \( q = \gamma e^* \):

\[ \gamma = \text{odd/odd, even/odd or odd/even}. \]
Fig. 4.2. One layer of tetrahedra (the tetrahedra II and III) normal to c.
Of each tetrahedron three X atoms are shown which are connected to
each other by solid lines to form a triangle\textsuperscript{2}.

Fig. 4.3. Four strings of tetrahedra, stretching out in the c-direction, can be
observed separately.
b. In one string of the superstructure successive tetrahedra are coming from successive unit cells of the prototype.

c. In one layer normal to $c$ the rotations of tetrahedra must be in the same sense.

A. The first symmetry element that attracts attention is the mirror plane perpendicular to $b$ (m. m.). All of the symmetry operations of Pcmn transfer one string to another except this mirror plane perpendicular to $b$. This symmetry element mirrors each tetrahedron of a string to itself and can therefore not be present in the modulated structure. It can, however, be transferred into a c-glide plane with the same orientation and position in the superstructures. It then leaves the space group of the average structure unaffected. The modified symmetry element c-glide does not relate different strings among each other. It reverses within a string periodically the sense of the rotation of the tetrahedra about the $c$-axis.

The amplitudes of the rotations of successive tetrahedra in a single string are related by the glide operation. Since the related tetrahedra are translationally equivalent in the prototype the shift must be an integer multiple of the original $c$-axis. The modulation wavelength $\lambda$ must be an even number times $c$, that is $1/\lambda = q = \gamma c^*$, thus $\gamma =$ odd/even (1/2, 1/4, 1/6, 1/8, 3/8, etc.)

B. The c-glide plane perpendicular to the a-axis (c . .) induces a relation between the string pair I and II (and also the string pair III and IV). Due to its orientation it reverses the sign of the rotations of the tetrahedra about the $c$-axis. The glide must be an odd number times $c/2$. The modulation wavelength $\lambda$ must be an odd number times $c$ and can not be an odd multiple of $c/2$. Thus $1/\lambda = q = (2m + 1)/(2n + 1)c^*$, thus $\gamma =$ odd/odd. (1/3, 1/5, 3/5, 1/7, 3/7, etc.)

C. The n-glide plane perpendicular to the c-axis does not reverse the sense of the rotations, it reverses the orientation of the direction of the tetrahedra. It links string I and IV and simultaneously string II and III. Since within each layer of tetrahedra these strings must have the same sense of rotation, the mirror plane must be located within a layer. The number of layers in half a wavelength thus must be odd. Now since the distance between adjacent layers is $c/2$, the wavelength must be an odd multiple of the $c$-axis.

The denominator in $\gamma$ must be odd, $\gamma = n/\alpha$ (1/3, 1/5, 2/5, 1/7, 2/7, etc.), $n =$ integer.
Fig. 4.4. Schematic representation of the modulation wave and the "directions" of the tetrahedra of three space groups.
D. The $2_1$-axis parallel to the a-axis ($2_1$ . .) causes string I to coincide with string IV (and II in III). This operation reverses the sign of the rotations. In order to map an ion of string I onto an ion of string IV, the twofold screw axis must be located within a layer. Then, however, the rotations of half of the tetrahedra within the layer would have opposite sense, and that is not in agreement with our starting point: all tetrahedra in one layer have the same sense of rotation. A $2_1$-axis parallel to the a-axis is not compatible with the existence of any of our superstructures.

E. The $2_1$-axis parallel to the b-axis ( . $2_1$ .) links string I to string III (and II to IV). This symmetry operation interchanges adjacent layers and reverses the sign of rotations. The distance of adjacent layers is $c/2$. If between the next layers also a $2_1$-axis is present the c-axis of the "modulated" structure would be the same as the one of the prototype. In the case that the next $2_1$-axis occurs at a distance c, the c'-axis will be $2c$ etc. This symmetry operation thus does not impose any restriction on the parameter $\gamma$. (It only says that its denominator should be an integer).

F. The $2_1$-axis parallel to the c-axis ( . . $2_1$) links string I and string II (and string III and string IV). This symmetry operation does not reverse the sense of the rotation of the tetrahedra. It must have a shift of an odd number times $c/2$ and the shortest translation it induces thus must be an odd number times c. The denominator in $\gamma$ must be odd. $\gamma = n/o$ (1/3, 1/5, 2/5, 1/7, 2/7, etc.)

4.3. Conclusion.

With help of our model we can predict that the space group of a modulated structure with wave vector $\mathbf{q} = 1/4 \mathbf{c}^*$ is maximally P1 $2_1/c$ 1, with wavevector $\mathbf{q} = 1/3 \mathbf{c}^*$ is P1 $2_1$ n and with $\mathbf{q} = 2/7 \mathbf{c}^*$ is P1 1 $2_1/n$. The actual symmetry of structures can be lower than the ones predicted here.

Fig. 4.4 shows schematically the modulation wave and the "directions" of the tetrahedra of these three space groups.
References.


CHAPTER 5. THERMAL BEHAVIOUR OF THE FERROELASTIC DOMAIN
STRUCTURE OF (NH₄)₂ZnCl₄ IN RELATION TO THE EXISTENCE OF A PHASE
TRANSITION AT T = 46°C.

5.1. Introduction.

In the literature it is well-known that (NH₄)₂ZnCl₄ exhibits a number of phase transitions that, from a crystallographic point of view, involve the translation period of the structure along the c-axis. Between -5°C and 91°C the crystals have a superstructure with a fourfold c-axis with respect to lattice of the prototype phase (fig. 1.3). Above 91°C the superstructure is incommensurate with a modulation vector \( \mathbf{q} = (1/4 + \delta) \mathbf{c}^* \). The high temperature phase, above 133°C, is orthorhombic with space group Pcmn. Below -5°C another three phases were reported. At each of these phase transitions the modulation vector \( \mathbf{q} \) changes. Solely on the basis of the occurrence of a peak in the dielectric constant \( \varepsilon_T \), however, another phase transition was reported\(^3,7\) to occur at 46°C. The corresponding space groups were suggested to be P1(21/c)1 above, and P1c1 below 46°C. Only the latter was confirmed by X-ray structure determinations\(^1,2,4\).

Between -5°C and 70°C a domain structure was reported\(^1,5\) with laminar domains. The results of experiments described in chapter 2 lead to conclude that the nature of the ferroic domain structure of the phases III and IV is ferroelastic, i.e. the domain walls can be moved by applying a uniaxial mechanical stress. The domain walls are preferentially oriented perpendicular to the c-axis, but occasionally we also observed domain walls perpendicular to the a-axis. We were not able to observe domains between 70°C and 91°C by means of a polarizing microscope, which is in agreement with literature\(^1\).

Deguchi\(^1\) measured the temperature dependence of \( \Delta \beta \), the deviation of the monoclinic angle \( \beta \) from 90°, with an X-ray double-crystal spectrometer. Fig 1.6 shows that the angular difference \( \Delta \beta \) is about 0.01° at room temperature.

In this chapter we will first use the twin factor to demonstrate that domains are present up to 91°C (§ 5.2). Then we will discuss the thermal behaviour of the domain structure using X-ray diffractometry (§ 5.2) and X-ray topography (§ 5.3) techniques. In order to trace the phase transition at 46°C, optical birefringence measurements were carried out (§ 5.4) and some (0,k,0) reflections with k= odd were carefully scanned with a diffractometer (§ 5.5). Finally, the consequences of the results for the phase transition at 46°C will be discussed in § 5.6.
Fig. 5.1  The Q-parameter for some selected reflections as a function of the temperature.
5.2. The twin factor.

In chapter 2 it was established that it is not possible to observe domains in (NH₄)₂ZnCl₄ crystals between 70°C and 91°C by means of a polarizing microscope, because the optical light intensity differences between the two domain directions are too small. In order to determine whether domains do exist up to 91°C we will consider the twin factor \( \alpha \), which is defined as the volume fraction of the smaller twin mate. The room temperature phase of (NH₄)₂ZnCl₄ is pseudo-orthorhombic, i.e. monoclinic with a monoclinic angle of 89.99°. The resolving power of a standard X-ray diffractometer cannot reveal a splitting up of reflections as a result of the twinning of such a crystal. Therefore the twin factor cannot be determined from the separate intensities of corresponding reflections from each of the twin mates.

Van Koningsveld² proposed a method to determine the twin factor of a twinned monoclinic, pseudo-orthorhombic crystal. He noted that in the case of orthorhombic symmetry each general reflection \((h,k,l)\) is representative for a group of eight symmetry related reflections \(\pm(h,\pm k,\pm l)\) that all have the same intensity. In the case of monoclinic symmetry this group can be divided into two subgroups of four reflections with equal intensities per subgroup. With the \(b\)-axis as the monoclinic axis, subgroup \(1\) with average intensity \(I_1\) contains \((h, k, l), (h, -k, l), (h, k, -l)\) and \((h, -k, -l)\), whereas subgroup \(2\) with average intensity \(I_2\) contains the other four combinations of indices.

From the intensities of the two subgroups a parameter \(Q\) can be defined:

\[
Q_{hkl} = \frac{|I_1 - I_2|}{I_1 + I_2} \tag{5.1}
\]

For an untwinned monoclinic single crystal \(I_1\) has a value \(J_1\) and \(I_2\) is \(J_2\).

For a twinned crystal with twin factor \(\alpha\):

\[
I_1 = (1 - \alpha)J_1 + \alpha J_2 \quad \text{and} \quad I_2 = \alpha J_1 + (1 - \alpha)J_2 \tag{5.2}
\]

With (5.2) equation (5.1) can be rewritten into:

\[
Q_{hkl} = (1 - 2\alpha) \cdot \frac{|J_1 - J_2|}{(J_1 + J_2)} \tag{5.3}
\]

So there is a linear relationship between the parameter \(Q\) and the twin factor \(\alpha\) and the ideal intensities \(J_1\) and \(J_2\). When \(Q = 0\), either \(\alpha = 1/2\) or \(J_1 = J_2\), or both.
Fig. 5.2  The intensities of the reflections (3,1,7) and (\(\overline{3},1,7\)) at different temperatures.
With equation (5.1) \( Q_{\text{ijkl}} \) can be determined experimentally for different reflections and for different crystals at a certain temperature \( T_1 \). When the twin factor \( \alpha \) of one crystal is determined with a (twin) structure refinement for this temperature \( T_1 \), the intensities \( J_1 \) and \( J_2 \) of different reflections can be calculated for that temperature. Then, with the help of equation (5.3), the twin factor \( \alpha \) of each crystal is known for that temperature. Van Koningsveld\(^2\) followed this method using his room temperature data.

With a Nonius CAD-4 X-ray diffractometer we measured the Q-parameter as a function of the temperature for five selected reflections of one crystal. For each set of symmetry related reflections within each subgroup the intensities were equal within experimental error, and differed significantly from those of the corresponding subgroup. The chosen reflections were all satellite reflections because the differences between the various phases of \((\text{NH}_4)_2 \text{ZnCl}_4\) predominantly involve changes of the modulation function. Therefore it can be expected that the differences between the orthorhombic and the monoclinic phases of \((\text{NH}_4)_2 \text{ZnCl}_4\) are best expressed in the intensities of the satellite reflections.

Fig. 5.1 shows the parameter \( Q \) for the five selected general reflections as a function of the temperature. The crystal used has a twin factor \( \alpha < 0.1 \) at room temperature, which was determined by applying the measurements of Van Koningsveld\(^2\). \( Q \) decreases on heating and gradually approaches 0 towards \( T = 91^\circ \text{C} \), which implies that the crystal symmetry is monoclinic. The domains are still present up to that temperature. Fig. 5.2a-e illustrate how the intensities of the two subgroups of general reflection \((3,1,7)\) converge at higher temperatures. At \( 91^\circ \text{C} \) the intensities of the eight reflections become practically equal, resulting in \( I_1 = I_2 \).

After cooling down to room temperature \( Q = 0 \), which implies that the twin factor \( \alpha = 50\% \). Repeated heating above \( 91^\circ \text{C} \) and then cooling down again to room temperature always gives \( Q = 0 \). This is in good agreement with the microscope observation that the crystal shows \( \mu \text{m} \) domains in a fifty-fifty ratio at room temperature after having been heated above \( 91^\circ \text{C} \).

Fig. 5.2f shows the intensities of the reflections \((3,1,7)\) and \((\ 3,1,7)\) at room temperature after the crystal passed the phase transition at \( 91^\circ \text{C} \) three times. With help of the measurements of van Koningsveld\(^2\) we know that now the twin factor \( \alpha = 0.45 \) at room temperature. Figure 5.2f is the experimental proof that the Q-parameter is directly related to the twin factor.

For \( Q = 0 \) at \( 91^\circ \text{C} \) there remain two possibilities:

a. The twin factor \( \alpha \) is 50\%, i.e. the domain pattern has changed such that the intensities \( I_1 \) and \( I_2 \) of the two subgroups approach each other.
Photo 5.1. A Guinier-Tennevin topograph of a two-domain crystal of (NH$_4$)$_2$ZnCl$_4$ at room temperature.
b. The domain pattern does not change, but both domains approach the orthorhombic structure, in which the eight intensities of the reflections \((\pm h, \pm k, \pm l)\) all become symmetrically related and therefore \(I_1 = I_2\).

From the polarizing microscope observations we know option b is correct up to 70°C. In order to discriminate between these two possibilities between 70°C and 91°C other experiments are necessary.

5.3. X-ray diffraction topography.

In chapter 3 a simple method to visualize the domain structure was described, i.e. the technique of X-ray diffraction topography of Guinier-Tennevin. This technique involves making a Laue photograph of a crystal using a wide parallel polychromatic X-ray beam, which causes intensity variations within all Laue spots due to the differences in the orientations of the domains.

In § 3.2 a model calculation showed that it is possible to see contrast differences in "Laue spots" for crystal planes of different domains having an angular difference in orientation as small as about 0.01°.

At room temperature the monoclinic angle of \((\text{NH}_4)_2\text{ZnCl}_4\) is 89.99°, implying that it is possible to see contrast differences in some "Laue spots".

In order to investigate the domain structure of \((\text{NH}_4)_2\text{ZnCl}_4\) up to 91°C we made X-ray topographs of different crystals. We started by making a normal Laue photograph of the \(a, c\) plane of \((\text{NH}_4)_2\text{ZnCl}_4\) at room temperature, i.e. with the incident X-ray beam directed along the \(b\)-axis. Subsequently, an X-ray topograph was taken using the method of Guinier-Tennevin.

Photograph 5.1 shows the topograph of the crystal at room temperature. This picture shows a two-domain crystal with domain widths that were optically observed under a microscope to be 2 millimetres. The laminar domains are perpendicular to the \(c\)-axis.

An X-ray beam with a width of 3 mm was used, whereas the photographic film was placed at a distance of 40 mm behind the sample and normal to the direction of the X-ray beam. The distance between the focus of the X-ray tube and the crystal was 2 m. All the "Laue spots" show intensity variations. Each spot shows the diffraction image of domain 1, the diffraction image of domain 2 and the overlap of these images (fig. 5.3).
A topograph at 50°C shows the same pattern in the "Laue spots", but the intensity variations within the spots are smaller and the pattern cannot be observed in all the spots. At 84°C orientation contrast could also be observed in the "Laue spots", but it was necessary to place the film at an angle of 25° with respect to the beam to get a better resolution in some "Laue spots" (see chapter 3).

The domain structure is not affected if the temperature is raised beyond 46°C. The crystals are definitely monoclinic up to 91°C. Orientation contrast in the "Laue spots" can be observed even slightly above the phase transition to the incommensurate phase (see chapter 6).

Fig. 5.3. In each "Laue spot" of photograph 5.1 the domain pattern is observed.
5.4. Optical birefringence.

In an anisotropic medium the relation between the dielectric displacement $D$ and the electric field $E$ is a tensor relation

$$D = \varepsilon_0 \varepsilon_r E$$

$\varepsilon_0$ = permittivity for vacuum
$\varepsilon_r$ = relative permittivity

A representation of this tensor relation can be given by the quadratic equation

$$\frac{x^2}{\varepsilon_{rx}} + \frac{y^2}{\varepsilon_{ry}} + \frac{z^2}{\varepsilon_{rz}} = 1$$

With $\varepsilon_{ri} = n_i^2$

the tensor representation gives the so-called optical indicatrix:

$$\frac{x^2}{n_x^2} + \frac{y^2}{n_y^2} + \frac{z^2}{n_z^2} = 1$$

$n_i$ = principal refractive index.

When light enters an anisotropic medium, in general there are two refracted light waves propagating the medium with different velocities and different, mutually perpendicular, vibration directions. With the help of the indicatrix the two refractive indices and vibration directions for these two plane polarized waves can be constructed.

For our optical experiments crystal plates of $(\text{NH}_4)_2\text{ZnCl}_4$ with faces parallel to the principal axes were flattened and polished on a wet soft tissue. When a plane light wave falls normally upon such a crystal plate, the light wave is split up in two waves with different velocities and different perpendicular vibration directions. Behind the crystal plate the phase difference $\delta$ between the two waves is given by

$$\delta = \frac{2\pi}{\lambda} (n'' - n'). \ t$$

(5.4)

$\lambda$ = wavelength of the light
$t$ = thickness of the crystal plate
$n''$ and $n'$ are the refractive indices of both waves.
Δn = n" - n' is defined as the birefringence.
The difference in the optical path length, the retardation R, is

\[ R = \Delta n \cdot t = (n" - n') \cdot t = \frac{\lambda \cdot \delta}{2\pi} \]  

(5.5)

The symmetry of the optical indicatrix must contain the symmetry elements of the crystal system. Therefore a change in the crystal symmetry can give a change in the refractive indices. Birefringence measurements as a function of the temperature can supply information about the phase transitions in (transparent) crystals.

Fig. 5.4 The principle of the indirect method.

Fig. 5.5 The principle of the Sénarmont method.
To visualize the phase transitions of \((\text{NH}_4)_2\text{ZnCl}_4\) we used two methods to determine the birefringence, an indirect method and the compensation method of Sénarmont.

Figure 5.4 shows the principle of the indirect method. A crystal plate is placed between a polarizer and a crossed analyser. The crystal plate is placed in such a way that the two vibration directions of the two waves in the crystal make an angle of 45° with the transparent direction of the polarizer and the analyser. Behind the analyser the intensity \(I\) of the light wave is given by:

\[
I = A^2 \sin^2 \left( \frac{\delta}{2} \right) \quad \text{with} \quad A = \text{amplitude.}
\]

With equation (5.5)

\[
I = A^2 \sin^2 \left( \frac{2\pi R}{\lambda} \right)
\]

(5.6)

I has a maximum for \(R = n\lambda/2\) and a minimum for \(R = n\lambda\), where \(n\) is an integer. Measurements of \(I\) give (indirect) information on the retardation \(R\), and thus on the birefringence. The maxima and minima of the intensity \(I\) can be traced very accurately. The accuracy of this method is determined by the accuracy of the temperature (0.1° C).

Figure 5.5 shows the principle of the Sénarmont compensation method. The difference with the above indirect method is that between crystal and analyser a compensator, a quarter-wave plate, is placed, which introduces a phase difference of \(\pi/2\) (a quarter of a cycle). Behind this \(\lambda/4\) plate the light is again plane polarized. When the transparent direction of the analyser makes an angle \(\phi\) with respect to the original transparent direction of the analyser in figure 5.4, the intensity behind the analyser is

\[
I = A^2 \sin^2 \left( \frac{\delta + \phi}{2} \right)
\]

(5.7)

The intensity \(I\) has a minimum for \(\pm \phi = -\delta/2 + m\pi\)

With equation 5.5 the retardation at such a minimum is

\[
R = \pm (\phi, \lambda/\pi) + m\lambda
\]

(5.8)
The angle $\phi$ at minimum intensity $I$ can be determined by rotation of the analyser. This renders $R$ and thus the birefringence. The accuracy of this measurement method is determined by the accuracy of the measurement of $\phi$ (10°) and the stabilization of the temperature.

With the above two methods optical birefringence experiments were performed in the temperature range between room temperature and 130°C. The measurements were carried out with a crystal in a thermal cell attached to a polarizing microscope in orthoscopic view ($\lambda = 546$ nm). The temperature could be controlled to within 0.1°C.

Fig. 5.6 Birefringence measurements of an a-plane of (NH$_4$)$_2$ZnCl$_4$ with the Sénarmont compensation method.
First the Sénarmont compensator method was used. At each temperature the minimum intensity $I$ and the corresponding angle $\phi$ were determined. This $\phi$ was related to the retardation according to equation 5.8. Figure 5.6 shows the result of measurements of an $a$-plate of (NH$_4$)$_2$ZnCl$_4$. A change in the retardation is indicative of a change in the birefringence. A change caused by the expansion of the crystal is more than $10^5$ times smaller than a change caused by the birefringence. All temperature runs show a continuous increase of the birefringence without any indication of a phase transition around 46°C. This is in contrast with prior results by Mel'nikova$^5$, who reported a slight discontinuity in $\Delta n$ near $T=47^\circ$C.

Subsequently the indirect, but more accurate, oscillation method was used. An (NH$_4$)$_2$ZnCl$_4$ crystal plate perpendicular to the $a$-axis was placed between the crossed polarizers. The transmitted light intensity behind the analyser is proportional to the retardation of the crystal, i.e. proportional to $\Delta n$ times the thickness of the crystal (see equation 5.6). The temperature was changed with a rate of 5°C/min. The light intensity transmitted by the analyser is plotted in fig. 5.7a. The successive minima and maxima of this plot, and thus the information on the retardation, are shown in fig. 5.7b. Again, there is no indication of a phase transition at 46°C. Only the slope of the graph changes somewhat over the whole range.

The same experiment was carried out with a $b$-plate, rendering the same conclusion, i.e. no indication of a phase transition (fig. 5.8 a and b). Repeated heating and cooling runs always gave the same results.

Fig 5.9 shows measurements of a $c$-plate. There are too few oscillations in this direction to plot the successive minima and maxima. No indication of a phase transition at 46°C was found, but another interesting phenomenon was observed. This $c$-plate, a very thin crystal with laminar domains perpendicular to the $c$-axis, was forced several times through the phase transition at 91°C. After four cycles the light intensity differences had clearly decreased. This observation can be attributed to the domain structure. Assuming that after four cycles the distribution of the two different types of domains has moved towards a fifty-fifty ratio, then the birefringence of one domain is mainly compensated for by another domain.
Fig. 5.7  Birefringence experiment of a a-plate of (NH₄)₂ZnCl₄ using the indirect method.

a. The light intensity behind the analyser.
b. The successive minima and maxima of figure 5.7a yield the retardation R.
Fig. 5.8  Birefringence experiment of a b-plate of (NH$_4$)$_2$ZnCl$_4$ using the indirect method.

a. The light intensity behind the analyser.

b. The successive minima and maxima of fig. 5.8a yield the retardation $R$. 

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Fig. 5.9  Birefringence experiments of a c-plate of \((\text{NH}_4)_2\text{ZnCl}_4\) with the indirect method.

a. First experiment.
b. Experiment with the same crystal after 3 temperature cycles from room temperature to 130°C.
5.5. The phase transition at 46°C.

The experiments of chapter 2 (§ 2.5) and of the preceding sections (§ 5.2 and § 5.3) show no change in the domain structure between room temperature and 91°C. The domain structure could only be changed by applying a mechanical stress, or by a heat treatment above 91°C. Also our birefringence experiments did not show any indication of a phase transition at 46°C (§ 5.4).

Matsunaga\(^3\) as well as Müller\(^7\) observed a peak in the dielectric constant \(\varepsilon_B\) at 46°C, which was attributed to a phase transition. The peak in the dielectric constant is clearly present but only in specially prepared crystals. Only crystals that were kept in the incommensurate phase for several hours showed the peak in the dielectric constant \(\varepsilon_B\). The dielectric constants \(\varepsilon_A\) and \(\varepsilon_C\) did not show a peak at 46°C.

In the literature\(^1\) the phase above 46°C was thought to have an additional twofold screw axis parallel to the \(b\)-axis with respect to the room temperature phase. Matsunaga\(^4\) performed a structural study and suggested the space group of phase III to be \(P2_1\text{cn}\) but Deguchi\(^1\) showed that phase III is monoclinic and supposed phase III has space group \(P1(2_1/c)\), but he did not perform a structural study. Matsunaga\(^4\) as well as Van Koningsveld\(^2\) executed a structural refinement of the room temperature phase IV in space group \(P1c1\).

In order to verify the hypothesis that the difference between the space groups of phase III and phase IV is the \(2_1\)-axis parallel to the \(b\)-axis, we carefully scanned some \((0,k,0)\) reflections with \(k=\text{odd}\) as a function of the temperature. The absence of such reflections can suggest that a \(2_1\)-axis is present.

A (nearly) single domain crystallite was mounted on a CAD-4 diffractometer. Scans through the position of the odd \((0,k,0)\) reflections were made at the lowest possible scan speed and the maximum power of the CAD-4 diffractometer. The measurement time for every scan was 10 minutes. Each \((0,k,0)\) reflection was scanned 20 times but Bragg peaks could not be distinguished (fig.5.10a). Since Müller\(^7\) reported the peak in the dielectric constant to be present only after a prolonged heat treatment above 91°C, we tried to reproduce his sample preparation procedure. For more than 18 hours the crystal was heated at about 115°C. After that, rather weak but sharp Bragg reflections were observed at the \((0,1,0)\), \((0,\,\overline{1},0)\), \((0,3,0)\) and \((0,\,\overline{3},0)\) positions in the entire temperature range between room temperature and 91°C (fig.5.10b and 5.11).
The intensities, though weak, all change continuously with the temperature. At 48°C the intensity of the (0,3,0) reflection is practically 0 (fig. 5.12). To make sure that the intensities were not due to an indirect reflection (Umweganregung) the crystal was rotated around the reflection vector of the (0,1,0) reflection, the intensity of which was found to remain constant.

Fig. 5.10 ω-2θ scans at room temperature with a CAD-4 diffractometer. Scans of the (0,3,0) reflection before heating (a) and after heating (b) into the incommensurate phase.
Fig. 5.11  The (0,1,0) and (0,3,0) reflections as a function of the temperature. At 93°C the (0,3,0) reflection was too weak to be measured.
Fig. 5.12  Integrated intensities of the (0,k,0) reflections as a function of the temperature. Each point is the average from 18 scans.
5.6. Discussion.

As was outlined in chapter 4, the structural model for modulated A$_2$BX$_4$ type crystals predicts that the highest possible space group symmetry for modulated crystals with $q = (1/4)\, e^*$ is that of P1(2$_1$/c)1. The actual symmetry of a structure can only be lower than this one. In the analysis of chapter 4 we saw that the $e$-glide plane is merely a symmetry element that transforms a string into itself. In contrast, the 2$_1$-axis relates string I to III (and II to IV). If the phase relation between these pairs of strings is disturbed for any reason, the 2$_1$-axis is absent, but the e-glide can still be present.

Between -5°C and 91°C (NH$_4$)$_2$ZnCl$_4$ has a modulated structure with $q = (1/4)e^*$.

Within this temperature range an additional phase transition at T= 46°C was proposed. The corresponding space groups were suggested to be P1(2$_1$/c)1 above, and P1c1 below 46°C (fig. 1.3). The latter corresponds with the one adopted in full X-ray crystal structure determinations$^{2,4}$

From our measurements we must conclude that there is no phase transition at 46°C. Both the Q-parameter and the topographic photographs show that domains are present up to 91°C and that the domain structure is not affected when the temperature passes 46°C. Moreover, also optical birefringence measurements did not show any indication of a phase transition at 46°C.

There is no doubt about the crystals being monoclinic in the entire temperature range between room temperature and 91°C, since there is no indication to suspect a change in crystal class. This only leaves the possibility of a transition between the point groups m and 2/m. Only a change to orthorhombic symmetry eliminates the domain structure and the ferroelastic behaviour.

In order to discriminate between the point groups m and 2/m, Second Harmonic Generation experiments were carried out. No SHG signal could be detected at room temperature. A comparable A$_2$BX$_4$ type crystal with an acentric point group 2mm at room temperature, K$_2$ZnCl$_4$, gave a well detectable SHG signal with the same setup. This suggests that (NH$_4$)$_2$ZnCl$_4$ has a crystal structure with space group P1(2$_1$/c)1, although this is not in agreement with the structure determinations in the literature$^{2,4}$.

In order to interpret the thermal behaviour of the (0,k,0) reflections (§ 5.5) and the domain structure (§ 2.5) we will return to the model structure of chapter 4. At the phase transition of 91°C the order parameter is presumably rather the modulation wave than the monoclinic angle, since in the monoclinic phase the latter deviates only slightly from 90°.
Fig. 5.13  The two possible domain structures. The two domains meet at a domain wall which coincides with the plane of an n-glide operation of the aristotype.
As shown in fig. 5.13, with our model structure the two possible phase relations between the strings of tetrahedra result in two possible domain structures. In the arrangement on the right the two domains meet at a domain wall which coincides with the plane of an n-glide operation of the aristotype.

In terms of the stepwise modulation wave the domain wall is merely the occurrence of one wavelength $\lambda = 3c$ in one of the strings (I in this example). In other words, if there is an error in the rotation sequence of the tetrahedra in one of the independent strings of tetrahedra, the fact that the rotations of the strings I and IV are correlated causes a plane defect in the structure, namely is the domain wall. The cell dimensions do not change essentially when passing a domain wall. The phase of the modulation wave, however, changes abruptly. The supposition that the strings I and IV are linked by stereochemical forces makes the domain wall contain complete layers perpendicular to the c-axis. The domain walls will preferably show up perpendicular to c. Fig. 5.13 shows that the domain wall breaks the symmetry of the $2_1$-axis, if present.

We concluded that there is no phase transition between room temperature and 91°C. The phases III + IV must have the monoclinic symmetry P1(21/c)1. The thermal behaviour of the domains and the odd (0,k,0) reflections learns that in a multidomain crystal the domain walls break the $2_1$-symmetry, with the result that the crystal only shows an apparent P1c1 symmetry. This is in agreement with the literature. In the X-ray structure analysis of Matsunaga, data were collected from a crystal that was first kept for 18 hours at 140°C. As we now know, such a crystal must have been multiply twinned, giving the (0,k,0) reflections with k= odd a weak but nonvanishing intensity. For this reason Matsunaga proposed the space group P1c1 in favour of P1(21/c)1. The intensities of the odd (0,k,0) reflections in the structure determination of Van Koningsveld were all below the significance level.

Some objections can be made about the above conclusions. Not only the (0,k,0) reflections are important in the discussion. Van Koningsveld performed a twin structure refinement and the space group P1c1 gave a (significantly) better fit than the space group P1(21/c)1. Furthermore, he described pseudo inversion centers in the structure, and that may well be the reason that the Second Harmonic Generation signal cannot be detected. Moreover, at least one other phase of (NH$_4$)$_2$ZnCl$_4$, phase V, also exhibits ferroelastic domains and is ferroelectric, and therefore has an acentric point group. To obtain such new ferroelastic domains in phase V, phase IV must also have an acentric point group. This would also make P1c1 a better space group candidate for the phases III and IV.
The appearance of the intensities of the odd (0,k,0) reflections are only marginal, these reflections may also originate from the domain walls themselves.

We make the conclusion that P1c1 is a better space group for the phases III and IV then space group IV.

However, there still remains a problem. The domains of phase III were explained on the basis of Aizu’s theory from the phase transition mmm2/m. This seems to contradict our conclusion that phases III and IV adopt point group m instead of 2/m. However, the description of Aizu’s theory does not require the prototype phase to transform directly into the ferroelastic phase. So far we have neglected the fact that (NH₄)₂ZnCl₄ exhibits an intermediate incommensurate phase in between. This phenomenon will be dealt with in chapter 6.

References.
CHAPTER 6. THE PHASE TRANSITION AT 910°C AND THE INCOMMENSURATE PHASE.

6.1. Introduction.

Many of the \( A_2BX_4 \) crystals have an incommensurate phase between the normal high temperature phase and a prominent superstructure phase. At a temperature \( T_1 \) the normal high temperature phase loses its stability and a static periodic perturbation of the structure appears which is incommensurate with the underlying crystal lattice, the translation symmetry in at least one direction is broken. In this incommensurate phase the extra periodicity in the structure is the origin of additional reflections in the diffraction pattern, satellite reflections at distances \( \pm mq \) from the basic lattice reflections, with \( m = \text{integer} \).

\[ q = \text{wave vector of the static perturbation}. \]

The amplitude of this modulation wave is the order parameter of the phase transition. Just below \( T_1 \) the modulation is well-described by a sinusoidal wave function. In this (so-called) harmonic region the wave vector is approximately constant. At lower temperatures the wave vector changes and the modulation function is no longer purely sinusoidal but contains higher harmonics.

In this lower temperature part of the incommensurate phase the structure may be described as consisting of nearly commensurate domains (where the structure will approximately be that of the underlying low-temperature superstructure phase) separated by domain walls. These domain walls are called discommensurations, intervals where the phase of the modulation wave changes rapidly. These discommensurations are equidistant. If \( b \) is the separation of the discommensurations, then the modulation wave vector \( q = q_0 + l/b \), \( q_0 \) is the wave vector of the low temperature superstructure phase.

With decreasing temperature the distance between the discommensurations grows and at the lock-in temperature \( T_1 \) the wavevector reaches the commensurate value \( q_0 \) of the superstructure.

In a number of incommensurate crystals the modulation wavevector changes continuously, with others the variation is discontinuous: small steps with commensurate wavevectors are separated by intervals with truly incommensurate modulations. This stepwise behaviour of the modulation wavevector as function of the temperature is called a "devil's staircase".
\((\text{NH}_4)_2\text{ZnCl}_4\) is one of the \(A_2\text{BX}_4\)-compounds which have a normal, paraelastic, high temperature phase separated from a ferroelastic lock-in phase by an incommensurate phase. (fig. 1.3).

The purpose of this chapter is to study the incommensurate phase of \((\text{NH}_4)_2\text{ZnCl}_4\), in particular the phase transition at \(T_1\) between the incommensurate phase and the commensurate lock-in phase.

Because \((\text{NH}_4)_2\text{ZnCl}_4\) crystals are grown at 40° C, that is below the lock-in temperature \(T_1 = 91°\ C\), it is a study of the phase transition in the direction from the ferroelastic phase towards the incommensurate phase, and not vice versa. From the preceding chapters it is known that the state of the samples, particularly the domain structure, is different for the first temperature cycle from room temperature into the incommensurate phase and for the following ones.

In § 6.2 birefringence measurements are described to characterize the phase transition at \(T_1\). Subsequently, § 6.3 shows the behaviour of the modulation vector of \((\text{NH}_4)_2\text{ZnCl}_4\). It is compared with the modulation vector of other \(A_2\text{BX}_4\) crystals.

In §6.4 and § 6.5 an attempt is made to find a connection between the ferroelastic domains of the lock-in phase and the discommensurations of the incommensurate phase. X-ray diffraction topography experiments are done and special reflections are measured with X-ray diffraction during the phase transition at \(T_1\).

In §6.6 the consequences are discussed.

6.2. Birefringence.

In the chapters 2 and 5 the ferroelasticity of the domains of \((\text{NH}_4)_2\text{ZnCl}_4\) in phase III and IV were explained with Aizu’s theory from the phase transition \text{mmm}F2/m. The directions of the domain walls perpendicular to the \(a\)-axis and the \(c\)-axis also could be explained with this theory.

After the discussion in § 5.6 there is a problem: until 91° C the crystal structure of \((\text{NH}_4)_2\text{ZnCl}_4\) in phase III and IV must have point group \(m\), and not \(2/m\). Aizu’s theory holds for (nearly) second order phase transitions.

If the transition at \(T = 91°\ C\) is such a second order phase transition then there are two questions. First: is \(T = 91°\ C\) the transition temperature to the ferroelastic phase, and second: where is the point group \(2/m\) gone?
Spontaneous strain is a second-rank tensor property. Its onset at a ferroelastic phase transition can be expected to be accompanied by the onset of, or changes in, other second-rank tensor properties like the birefringence tensor. So birefringence measurements are an excellent tool to characterize a phase transition to a ferroelastic phase.

With the same apparatus as in § 5.4 birefringence measurements have been performed. Fig. 6.1 shows measurements with a Sénarmont compensator. With increasing temperature the birefringence increases.

Kinks in the curve are an indication for a second order phase transition. The retardation changes, and so does the birefringence. At a phase transition where the point group symmetry of a crystal changes the optical indicatrix changes too.

At the temperatures $T = 89^\circ C$ and $T = 95^\circ C$ of figure 6.1 there seem to be small kinks in the curve, however, within experimental accuracy there is not an indication of a phase transition.

For comparison, fig. 6.2 shows the same experiment, done with the same apparatus, with (TMA)$_2$ZnCl$_4$. Here the phase transition from the incommensurate phase to the superstructure is more clear than with (NH$_4$)$_2$ZnCl$_4$. Between the incommensurate phase and the ferroelastic phase (TMA)$_2$ZnCl$_4$ has a ferroelectric phase$^7$.

Birefringence measurements of (NH$_4$)$_2$ZnCl$_4$ with the very accurate oscillation method are shown in fig. 5.7 and fig. 5.8. At about $T = 91^\circ C$ there is a very small kink in the optical retardation indicating that the phase transition at $T = 91^\circ C$ is of second order. Mel'nikova$^8$ did not observe this phase transition with birefringence experiments.

In contrast to (NH$_4$)$_2$ZnCl$_4$ other comparable ferroelastic $A_2BX_4$ compounds, namely Cs$_2$HgBr$_4$, [N(CH$_3$)$_3$]$_2$MnCl$_4$ and [N(CH$_3$)$_3$]$_2$CuCl$_4$, show more pronounced kinks at the birefringence measurements of the incommensurate-ferroelastic phase transition$^{1,5,13,14}$. 
Fig. 6.1. Birefringence measurements of an a-plate of (NH₄)₂ZnCl₄ with the Sénarmont compensation method.
Fig. 6.2. The same experiment as in fig. 6.1, done with the same apparatus, with a e-plate of (TMA)$_2$ZnCl$_4$. Here the phase transition from the incommensurate phase to the superstructure is more clear than with (NH$_4$)$_2$ZnCl$_4$. 

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Fig. 6.3.

The modulation vector $q$ as a function of the temperature for a virgin sample of $(NH_4)ZnCl_4$ (heating curve).
6.3. The behaviour of the modulation vector.

For (NH₄)₂ZnCl₄ satellite reflections appeared in the vicinity of the fundamental reflections of the normal high temperature phase below 133°C. Between 133°C and 91°C these satellite reflections are located at incommensurate positions. The wave vector, characterizing the modulated structure, is deduced from the distances of the satellite positions in the reciprocal space. The positions of the satellites are given by the scattering vectors

\[ \mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q} \]

\( \mathbf{q} = \) modulation wavevector

\( m = \) integer, indicates the order of the satellite.

With a Hilger & Watts diffractometer the positions of 22 satellite reflections were determined at different temperatures, between room temperature and 133°C. At every temperature the modulation wave vector \( \mathbf{q} \) has been calculated from the position of the 22 satellite reflections. Together with the 22 satellite reflections 22 main reflections were refined.

(NH₄)₂ZnCl₄ is characterized by a wave vector very close to 1/4 \( \mathbf{c}^* \). The positions of the satellites show that the wavevector is slightly larger than 1/4 \( \mathbf{c}^* \).

Fig. 6.3 shows the temperature dependence of the wave vector \( \mathbf{q} \) from room temperature up to the normal high temperature phase. The sample was heated by a hot air furnace, the temperature was controlled within 0.1°C.

Fig. 6.3 is a curve of the \( \mathbf{q} \)-vector from a virginal sample. The sample was never before heated into the incommensurate phase. The \( Q_{317} \)-parameter, related to the twin factor (§ 5.2), was 0.42 for this sample at room temperature. With help of the measurements of van Koningsveld we know \( \alpha = 0.32 \) for this sample at room temperature.

The curve shows steps and one can think of a devil's staircase.

Fig. 6.4 shows a heating and a cooling run from samples which were heated to within the incommensurate phase before. The curve of the \( \mathbf{q} \)-vector is more smooth, there is no devil's staircase, and the phase transition is second order.

Sato¹² was the first one who showed that (NH₄)₂ZnCl₄ has an incommensurate structure characterized by the \( (hkl \pm (1/4 + \delta)) \) satellite reflections. He showed the temperature dependence of the \( \delta \)-value, his measurements concerned data from a single satellite reflection only.
Fig. 6.4. The modulation vector $\mathbf{q}$ as function of the temperature. A heating (○) and a cooling (●) run from samples which were heated into the incommensurate phase before.
Fig. 6.5.  The length of the crystal axis \( a \) as function of the temperature. The \( b \)- and \( c \)-axis show the same irregular behaviour.
It is unclear whether or not he refined the satellite reflection together with main reflections. At 91° C δ drops discontinuously to zero, which differs from our measurements.

In generally, virginal samples show irregular behaviour of the q-vector. Many times at about 91° C there were measurements with chaotic results, the lengths of the crystal axes show irregular behaviour (fig. 6.5), and sometimes the crystal axes, calculated from 22 main reflections, do not fit with the crystal axes calculated from the 22 satellite reflections. Further heating of the sample stabilizes the crystal and at higher temperature the q-vector and crystal axes again could be calculated very well. Very probably the measurement of the q-vector around 91° C are disturbed by pinning of discommensurations by impurities and defects.

Deuterated (TMA)$_2$ZnCl$_4$ and (N(CH$_3$)$_4$)$_2$FeCl$_4$ are A$_2$BX$_4$ crystals comparable with (NH$_4$)$_2$ZnCl$_4$ with an incommensurate-ferroelastic phase transition. The modulation vectors of these samples show devil's staircases. In these measurements no attention is paid to presence of domain structures and pinning of discommensurations.

![Photo 6.1](image)

T = 20° C  T = 93° C

Photo 6.1. Intensity contrast in "Laue spots" of a topograph of (NH$_4$)$_2$ZnCl$_4$ at room temperature and at T = 93° C.
6.4. The discommensuration region\textsuperscript{4}.

In the lower part of the incommensurate phase the displacive modulation function is no longer a sequence of purely sinusoidal functions but contains higher harmonics. The structure consists of nearly commensurate domains (the structure of which is approximately that of the low temperature phase) and domain walls in between. In these domain walls, the so-called discommensurations, the phase of the modulation wave changes rapidly. The formation of discommensurations is limited by their repulsive interaction. When the density of discommensurations is high the discommensurations are equally spaced. Near the lock-in transition the density of discommensurations is smaller and the pinning of the discommensurations to the lattice becomes important. Besides this intrinsic mechanism of pinning forces there is another mechanism: the pinning of the discommensurations by impurities and defects. The intrinsic pinning has disappeared below the lock-in phase transition, the impurity pinning is present below T\textsubscript{1}.

Ribet\textsuperscript{10}, with his experiments of [N(CD\textsubscript{3})\textsubscript{4}]\textsubscript{2}ZnCl\textsubscript{4}, observed contrast differences in Lang X-ray topographs which correspond to the discommensurations. Just above T\textsubscript{1} he estimated the distance between the discommensurations to be of the order of few \textmu m.

Our X-ray topography experiments as described in § 5.3 are continued above T\textsubscript{1}. Photograph 6.1 shows a multitwinned crystal above T\textsubscript{1}. This daylight film, with small grains, shows contrast differences in the "Laue spots". It is hard to say if this photograph demonstrates the presence of new domain walls, the discommensurations. It is possible that we only observe some domain walls, already present in the commensurate phase and now present in the incommensurate phase by pinning by impurities.

Saint-Gregoire\textsuperscript{11} shows photographs and topographs of domains and discommensurations during phase transitions for [N(CD\textsubscript{3})\textsubscript{4}]\textsubscript{2}ZnCl\textsubscript{4} and [N(CH\textsubscript{3})\textsubscript{4}]\textsubscript{2}CuCl\textsubscript{4}.
Fig. 6.6. The intensities of the reflections (0,2,3) and (0,2,5) at $T = 86.5^\circ C$ and $T = 93^\circ C$ measured with a $\omega/2\theta$ scan.
6.5. Special reflections at the lock-in phase transition.

All A$_2$BX$_4$ crystals with a modulation wave parallel to the c-axis can be described in the incommensurate phase by one of the two non-equivalent 4-dimensional space groups\(^2\): Pcmn (00$\bar{1}$) (s s 1 1) or Pcmn (00$\bar{1}$) (1 1 1). The first one has as a consequence that satellite reflections such as (0, 2, 1, 1) and (0, 2, 1, 1) are present, the second one that satellite reflections as (0, 2, 2, 1) and (0, 2, 2, 1) are present\(^15\). During the phase transition from the commensurate to the incommensurate phase at T$_1$ these reflections (hereafter designated as (0,2,3), (0,2,5), (0,2,7) and (0,2,9)) are measured with a CAD-4 diffractometer. The intensity of these reflections are measured with $\omega/2\theta$ scans. The figures 6.6 and 6.7 demonstrate that (NH$_4$)$_2$ZnCl$_4$ has Pcmn (00$\bar{1}$) (s s 1) as 4-dimensional space group. Figure 6.6 shows the intensities of the reflections (0,2,3) and (0,2,5) just above and below T$_1$ = 91$^\circ$ C. The (0,2,7) and (0,2,9) reflections are zero at these temperatures.

Figure 6.7 shows profiles of the reflections (0,2,3), (0,2,5), (0,2,7) and (0,2,9) at four different temperatures. The profiles are made by varying the value of l of each (h,k,l) reflection. A $\omega/2\theta$ scan is made for every value of l. The tilt of the contour with respect to the c-axis is a consequence of diffractometer geometry and scan mode.

During the phase transition at T$_1$ together with the (0,2,3) and (0,2,5) reflections the (0,1,0) and (0,3,0) reflections are measured. As we know from chapter 5 the presence of these reflections coincides with the presence of the many domain walls in the monoclinic structure of the commensurate phase.

The (0, 1, 0) and (0, $\bar{1}$, 0) reflections are present in the incommensurate phase until 94$^\circ$ C (fig.5.11). Globally the intensity of the (0,1,0) reflection is one order of magnitude smaller then the intensity of the (0,2,3) reflection.

The (0,3,0) and (0, $\bar{3}$, 0) reflections have already disappeared at 91$^\circ$ C.

At 93$^\circ$ C it is clear that the satellites (0,2,3) and (0,2,5) are not at a distance of 1/4 c* of a main reflection any more. The (0,2,3) satellite reflection is wider as result of chaotic states in the lowest part of the incommensurate phase.

There must be more than one modulation wave just above T$_1$ in the incommensurate phase. At T = 93$^\circ$ C the maxima of the satellite reflections are at the positions (h,k,l) = (0,2,3,14) and (0,2,5,20), at T = 94$^\circ$ C the maxima are at (h,k,l) = (0,2,2,94) and (0, 2,4,94.)

The crystal lattice is refined at every temperature with 25 main reflections. During the measurements of profiles three main control reflections are measured too.

Izumi\(^3\) describes more than one modulation wave in Rb$_2$ZnBr$_4$ just above T$_1$.

The above measurements are measurements of a crystal that never had been in the incommensurate phase before.
Fig. 6.7. Profiles of the reflections $(0,2,3), (0,2,5), (0,2,7)$ and $(0,2,9)$ at four different temperatures.
6.6 Discussion.

The measurements of the \( q \)-vector (§6.3) and the special reflections (§6.5) show that just above the lock-in phase transition at \( T_1 \) the incommensurate phase has measurements with problematical results. The \( q \)-vector shows steps that look like a devil's staircase and satellite reflections and main reflections cannot be refined in one lattice. Repeated cycles through the phase transition at \( T_1 \) make the steps disappear. The special reflections \((0,2,3)\) and \((0,\overline{1},0)\) do not appear in a commensurate place any more, but more then one modulation wave is needed to explain the place of these satellite reflections.

The X-ray topographs show contrast differences and the \((0,1,0)\) and \((0,\overline{1},0)\) reflections are present above \( T_1 \), so domain walls are present in the incommensurate phase.

All these measurements show that the lower part of the incommensurate phase, the discommensuration region, is different from the upper part, the harmonic region. In the discommensuration region the discommensurations cause the problems. They can be pinned by impurities and defects, which causes the difference between a first temperature cycle into the incommensurate phase and subsequent temperature cycles (fig. 6.3 and 6.4).

The measurements of the special reflections of § 6.5 should be repeated with crystals stabilized in the incommensurate phase to see if more modulation waves are needed to explain the place of the satellites in the discommensuration region. The picture that emerges from our few experiments is: the (intrinsic and extrinsic) pinning of the discommensurations is the origin of the observation that more then one modulation wave is necessary to explain the place of the satellites. It explains too that sometimes the lattices of the main reflections and the satellite reflections cannot be refined together.

When the above measurements are confirmed by repeated experiments it is clear that the harmonic region and the discommensuration region of the incommensurate phase are different phases. In the latter case, domain walls are visible and the \((0,1,0)\) reflection is present. The crystal structure of the discommensuration region shows monoclinic symmetry. The phase transition to the ferroelastic phase must begin in the discommensuration region and not at \( T_1 = 91^\circ \text{C} \). It is an academic discussion to ask where it begins.
Somewhere, in the structure of some discommensurations, or possibly in the structure of a domain between the discommensurations, there must appear a structure with point group 2/m. However, the instrumental resolution of our X-ray detection apparatus cannot discriminate between the crystal structure of a discommensuration and of a domain.

References.

CHAPTER 7. \((\text{NH}_4)_2\text{ZnCl}_4\) IN ITS PHASE V.

7.1. Introduction.

Between -5° C and -10° C \((\text{NH}_4)_2\text{ZnCl}_4\) has a phase with an unspecified superstructure (fig 1.3).
Contradictory observations have been reported about the superstructure of this phase V, where simultaneously satellite reflections were observed with q-vectors of \((1/4)e^*, (2/7)e^*\) and \((1/3)e^*\) \(^7,8\).
In addition to the discussion in the literature about the satellites, there was a discrepancy concerning the phase transition temperatures.

Deguchi\(^1\) made an extensive study of the phase V.
He reported that a crystal plate cut perpendicular to the c-axis, a c-plate, of \((\text{NH}_4)_2\text{ZnCl}_4\) in phase V has laminar ferroelastic domains with domain walls perpendicular to the a-axis or the b-axis. The domain walls were reportedly induced by the phase transition IV \(\rightarrow\) V.
The domains in a b-plate with domain walls perpendicular to the c-axis, present in phase III and IV, persist until -10° C.
Deguchi measured that the angle \(\gamma\) deviates from 90° (fig. 1.7) and concluded phase V is triclinic. Sato measured that phase V exhibits (weak) ferroelectric activity\(^7\). The space group P1 should uniquely be assigned to phase V.

The purpose of this chapter is to clarify phase V, as an intermediate phase between phase IV and phase VI.
The following experiments have been done:
Birefringence experiments have been carried out to establish the order and transition temperatures of the phase transitions IV \(\rightarrow\) V and V \(\rightarrow\) VI (§ 7.2).
The behaviour of satellite reflections as a function of the temperature is studied with X-ray diffraction techniques (§ 7.3).
A study of the domain structure as a function of the temperature is performed with X-ray diffraction topography (§ 7.4).
Use is made of our structure model of chapter 4 and of Aizu's theory about ferroelasticity for the discussion in § 7.5.
Fig. 7.1. Birefringence measurements, with the indirect oscillation method, of an a-plate of (NH₄)₂ZnCl₄. The intensity I is proportional with Δn.t (see chapter 5).
7.2. Optical birefringence.

Optical birefringence measurements as a function of the temperature are performed to get information about the order and transition temperatures of the phase transitions $\text{IV} \rightarrow \text{V}$ and $\text{V} \rightarrow \text{VI}$

The temperature dependence of the birefringence ($\Delta n$) of (NH$_4$)$_2$ZnCl$_4$ has been studied by the indirect oscillation method as described in § 5.4.

The crystal is placed between the crossed polarizers. The transmitted light intensity $I$ passing the analyser is proportional to the retardation $R$ of the crystal, i.e. proportional to the birefringence $\Delta n \times$ the thickness $t$ of the crystal.

The measurements have been carried out with a polarizing microscope in orthoscopic view ($\lambda = 546$ nm). A temperature cell, stable to within $\pm 0.1^\circ$ C, was available for heating and cooling of the sample. The temperature was changed with a rate of $4^\circ$ C/min.

The intensity $I$ of an (NH$_4$)$_2$ZnCl$_4$ crystal plate, cut perpendicular to the a-axis, is plotted in fig 7.1 as a function of the temperature.

During a heating and cooling cycle hysteresis is observed indicating that the phase transitions are of first order. During the cooling run the phase transition temperatures are $-2^\circ$ C and $-10^\circ$ C. During the heating run the phase transitions temperatures are $-4^\circ$ C and $4^\circ$ C.

Repeated experiments with the same crystal and different heating rates always gave the same plot.

The phase transitions $\text{IV} \rightarrow \text{V}$ and $\text{V} \rightarrow \text{VI}$ show jumps in the values of the intensity $I$, but the hysteresis is reproducible and the crystal is unbroken. So the phase transitions are nearly of second order.

Repeated birefringence experiments show that phase $\text{V}$ is stable in a temperature region only $8^\circ$ C wide. The hysteresis of about $5^\circ$ C at the phase transitions $\text{IV} \rightarrow \text{V}$ and $\text{V} \rightarrow \text{VI}$ explains the discrepancy in the phase transition temperatures in the literature.
Fig. 7.2. The profiles of the (1,3,2) main reflection and the (1, 3, 2, 1) satellite reflection at room temperature. The distance between the main reflection and the satellite reflection is (1/4) \( c^* \). The scan plane is (3, 1, 0).

Fig. 7.3. The same experiment as in fig. 7.2, but now in phase V. There are 3 satellite reflections at (1/4) \( c^* \), (2/7) \( c^* \) and at (1/3) \( c^* \) distance of the main reflections, respectively.

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7.3. X-ray diffraction of the satellites.

With a Nonius CAD-4 diffractometer (Mo Kα radiation) the satellite reflections were examined in detail.
In order to study the exact position of the satellites the profiles of (h,k,l) main reflections and their satellite reflections were measured. We make ω/2θ scans of (h,k,l) reflections with h,k constant and l increasing with steps of 0.01 × l.

Fig. 7.2 shows the profile of the (1, 3, 2, 1) satellite reflection at room temperature together with the (1, 3, 2) main reflection at a distance of (1/4)c*. The tilt of the contour with respect to the c-axis is a consequence of diffractometer geometry and scan mode. The contours of the satellite and the main reflections have the same form.

When the crystal enters phase V for the first time the crystal shows three more or less separate satellite reflections, at a distance of (1/4) c*, (2/7) c* and about (1/3) c* from the (1, 3, 2) main reflection (fig. 7.3). At a temperature three degrees lower the crystal only shows satellite reflections at (1/4)c* and (1/3)c*.
However, a crystal that passed several times through the phase transitions IV → V and V → VI shows satellite reflections at (2/7) c* only (fig 7.4).

In order to obtain an overview of the satellite reflections of phase V we make X-ray photographs with an X-ray precession camera. Before we make the photographs the crystal has passed several times the phase transitions IV → V and V → VI.
Photograph 7.1 (a,..., f) represents the precession photographs of the b*,c* plane and its first and second level of an (NH4)2ZnCl4 crystal at room temperature and at T = 0°C in phase V. Only the b*,c* plane shows second and third order satellite reflections.
Fig. 7.4. Main reflection (1,3,2) and satellite reflection (1,3,2, -\bar{1}) in the phases IV, V and VI. The crystal has passed the phase transitions several times.
b. phase V.

Photo 7.1 a,b. X-ray photographs of the $b^*,c^*$ plane of (NH$_4$)$_2$ZnCl$_4$ in phase IV and phase V made with a precession camera.
c. phase IV.

d. phase V.

Photo 7.1.c,d. Precession photographs of the first level in phase IV and phase V.
Photo 7.1.e,f. Precession photographs of the second level in phase IV and V.
7.4. X-ray diffraction topography.

It is conceivable that the behaviour of the satellite reflections in phase V is due to the complex domain structure in this phase.
So X-ray diffraction topography experiments are performed according the method of Guinier-Tennevin to observe the domain structures in phase V.

Deguchi\(^1\) reported that a c-plate of \((\text{NH}_4)_2\text{ZnCl}_4\) in phase V has laminar ferroelastic domains with domain walls perpendicular to the a-axis or the b-axis.
The domains in a b-plate with domain walls perpendicular to the c-axis, present in phase III and IV, persist until -10° C.
Deguchi measured that the angles \(\beta\) and \(\gamma\) deviate from 90° (fig. 1.6 and 1.7)

To distinguish the two ferroelastic domain species we shall call them \(\gamma\)- or \(\beta\)-domains, because the two domain species are the consequences of deviation from 90° of angle \(\gamma\) or angle \(\beta\) respectively. The ferroelastic \(\beta\)-domains have domain walls perpendicular to the a- or the c-axis. These are the domains which have been discussed extensively in the chapters 2 and 5.

A 3 mm wide polychromatic X-ray beam has been used for the Guinier-Tennevin method.
In the present experiments the optimum film-sample distance was between 40 mm and 60 mm.
All the topographs in this chapter are recorded with the X-ray beam along the pseudo-hexagonal c-axis.
Photograph 7.2 and its enlarged section photograph 7.3 show the topograph of a c-plate of an \((\text{NH}_4)_2\text{ZnCl}_4\) crystal at room temperature. Photograph 7.4 shows the same c-plate being in phase V for the first time.
Using the polarizing microscope we observed that the \(\beta\)-domains of this crystal have domain walls perpendicular to the c-axis, so the topograph shows only the \(\gamma\)-domains with the domain walls perpendicular to the a-axis. The angle differences between the crystal structures of the domains must be small, since not all the Laue spots show the domain structure. Only hkl planes making an angle near 90° with the incident beam show orientation contrast in their respective "Laue spots".
Passing several times the phase transitions IV \(\rightarrow\) V and V \(\rightarrow\) VI the \(\gamma\)-domain structure fades away, no more orientation contrast is observed.
With the polarizing microscope another crystal shows β-domains with domain walls perpendicular to the a-axis. A topograph of this crystal shows the β-domains in some "Laue spots" (photo 7.5, 7.6, 7.7).

On cooling down the crystal for the first time into phase V both the β- and the γ-domains are observed (photo 7.8, 7.9, 7.10). The crystal shows its triclinic symmetry. The γ-domains show a sharp pattern if the diffracted beam is approximately parallel to the γ-domain walls. In case the diffracted beam intersects many domain walls the pattern gets blurred.

Photograph 7.9 is an enlarged part along the a*-axis of the topograph of photograph 7.8, β- and γ-domains are visible.

Photo 7.10 is an other enlarged section along the b*-axis of the same Laue pattern. Here the β-domains manifest themselves in a sharp pattern, the diffracted beam hardly intersects domainwalls. Remarkably is the direction of the domain walls, not a straight line on the photographs. We shall discuss that in § 7.5. Blurred orientation contrast of the γ-domain structure is not observed in the "Laue spots" because the γ-domains are small; the diffracted beam intersects many domain walls.

Passing again several times through the phase transitions IV → V and V → VI the γ-domains are no more observed, just as in the first crystal. However, the orientation contrast of the β-domains is still there (photo 7.11).

Remarkable is the orientation contrast in the "Laue spot" with hkl indices (0,2,1). This spot belongs to a set of (vertical) planes parallel to the β-domain walls. The crystal cannot show orientation contrast as result of a β-domain structure. The contrast in this (0,2,1) spot must be the consequence of an acute angle γ.
Photo 7.2. Topograph of the a,b plane of (NH$_4$)$_2$ZnCl$_4$ at room temperature.
Photo 7.3.
Enlarged section of photo 7.2.
No domains are observed, only some defects of the crystal plate are visible.

Photo 7.4.
The same section as in photograph 7.3.
The c-plate of (NH₄)₂ZnCl₄ being for the first time in phase V. The γ-domains with domain walls perpendicular to the b-axis are only observed in "Laue spots" in the neighbourhood of the a*-axis.
Photo 7.5. Topograph of a c-plate of (NH₄)₂ZnCl₄ at room temperature. The sections A and B are enlarged, see photograph 7.6 and 7.7.
Photo 7.6. Enlarged section A.
β-domains with domain walls perpendicular to the $a$-axis can be observed in some "Laue spots".

Photo 7.7. Enlarged section B.
Photo 7.8. The e-plate of (NH₄)₂ZnCl₄ in phase V. Section A and B are enlarged (see photograph 7.9 and 7.10) to show the different domain structures. The crystal was for the first time in phase V.
Photo 7.9. Enlarged section A of photograph 7.8. 
β- and γ-domains are visible.

Photo 7.10. 
Enlarged section B of photograph 7.8. The domain walls are not straight lines.
Photo 7.11. Enlarged section B. The crystal has passed several times the phase IV $\to$ V and V $\to$ VI.
7.5. Discussion and conclusion.

Repeated birefringence experiments show that phase V is stable in a temperature region only 8° C wide. The hysteresis of about 5° C at the phase transitions IV $\rightarrow$ V and V $\rightarrow$ VI explains the discrepancy in the phase transition temperatures in the literature.

Phase V is an intermediate phase between the monoclinic phase IV and the orthorhombic phase VI. From the work of van Koningsveld and Matsunaga the structures of the phases IV and VI are known in detail (fig. 1.3). In these structure determinations the modulation consists of a periodic rotation about the c-direction as far as regards the ZnCl$_4$ tetrahedra. This modulation wave has a nearly stepwise character. If we compare the structures of phases IV and VI the difference is merely a difference in modulation wavelength. So phase V is a phase with a modulation between $q = 1/4$ c* and $1/3$ c*.

In presenting the modulation in one string as a "spinwave", it is easy to imagine how an intermediate phase between $q = 1/4$ c* and $q = 1/3$ c* would look like. As is illustrated in fig. 7.5, by decreasing the wavelength continuously from $4c$ to $3c$, we will pass a phase with $\lambda = 3.5$ c. With a stepwise waveform we can reach exactly the same result by an alternation of the wavelengths of $q = 1/4$ c* and $q = 1/3$c*.

![Diagram](image_url)

**Fig. 7.5.** By decreasing the wavelength from $4c$ to $3c$ we will pass a phase with $\lambda = 3.5$ c.
An extension of this procedure shows that a Farey-sequence of \( q \)-vectors can subsequently be found. In between two structures with \( q = n/m \text{ c}^* \) and \( q = p/l \text{ c}^* \) we find an intermediate structure with \( q = (n+p)/(m+l) \text{ c}^* \). In between \( q = 1/4 \text{ c}^* \) and \( q = 1/3 \text{ c}^* \) the rational value of \( q \) with the lowest denominator is 2/7 \( \text{ c}^* \); in the field of numerical mathematics 2/7 is called the mediant between 1/4 and 1/3. All of the possible rational \( q \)-vectors can be constructed in this way. A set with denominators smaller than 20 are given in the sequence below:

\[
\frac{1}{3} \quad \frac{6}{19} \quad \frac{5}{16} \quad \frac{4}{13} \quad \frac{3}{10} \quad \frac{5}{17} \quad \frac{2}{7} \quad \frac{5}{18} \quad \frac{3}{11} \quad \frac{4}{15} \quad \frac{5}{19} \quad \frac{1}{4}.
\]

The measurements of the profiles of hkl reflections in § 7.3 learn that phase V has only satellite reflections at 2/7 \( \text{ c}^* \) when the phase is stable, after passing several times the phase transition. Before the phase is stable we saw in fig. 7.3 satellites at 1/4 \( \text{ c}^* \), 2/7 \( \text{ c}^* \) and about 1/3 \( \text{ c}^* \). Accurate observation of this last satellite learns that the \( q \)-vector of this satellite is not exactly 1/3 \( \text{ c}^* \) (fig. 7.6). Before the structure stabilizes it is possible that the modulation wave passes other modulations. But the mediant of 1/3 \( \text{ c}^* \) and 2/7 \( \text{ c}^* \), that is 3/10 \( \text{ c}^* \), is too far away.

![Fig. 7.6](image)

The intensities of the three satellite reflections of main reflection (1,3,2) in phase V.
The structure model of chapter 4 shows that a stable phase V with satellites at 2/7 c* maximally can have the space group P 1 1 (2/1/n). However, because new ferroelastic domains are created at the phase transition IV \( \rightarrow \) V, and phase IV already has point group m, the pointgroup of phase V must be lower. That agrees with the literature, Deguchi\(^1\) concluded space group P1 for phase V.

With the theory of Aizu and Sapriel there are two possibilities for the orientation of the new domains created at a phase transition m F 1: First domains with domain walls perpendicular to the b-axis, corresponding with the lost symmetry operation m of phase IV. Secondly W' walls, domains walls of which the direction varies with temperature. From Sapriel\(^6\) we know the direction of this W' wall: the wall is parallel to the b-axis and makes an angle \( \theta \) with the c-axis, with \( \tan \theta = s_{12}/s_{23} \); \( s_{12} \) and \( s_{23} \) are the elements \( \neq 0 \) of the spontaneous strain tensor belonging to the phase transition m F 1.

With the above possibilities for the domain walls, our interpretation of the observations in §7.4 must be corrected, just as the interpretation of Deguchi.

When a c-plate in the stable phase V shows domain walls perpendicular to the a-axis then the domain walls are not parallel to the a,c plane, they must be the above described W' walls.

That is in agreement with our observation in the "Laue spot" of the (0,2,1) reflection (photo 7.11). In paragraph 7.4 we already concluded that the orientation in this "Laue spot" only can be the result of an acute angle \( \gamma \) and not of an acute angle \( \beta \).

So, the description of the domain walls in § 7.4 is as follows:

In phase IV there are two possibilities for the domain walls: perpendicular to the a-axis or perpendicular to the c-axis, the so-called \( \beta \)-domain walls. At the first phase transition IV \( \rightarrow \) V new domains, the so-called \( \gamma \)-domains, with domain walls perpendicular to the b-axis are created, while parts of the \( \beta \)-domains may still be there (see for example photo 7.9). At this phase transition the above W' walls can be created too (see photo 7.10). Passing several times the phase transition phase V loses its \( \beta \)-domains, the \( \gamma \)-domains are fully twinned and, if present, the W' domains can still be observed.

All the discussed domains are ferroelastic. The waving pattern of the domain walls at photograph 7.10 and, less prominent, at photograph 7.11 are the effect of inter-wall interactions (see fig. 2.2, 2.3 and 2.4 of § 2.3) between the different ferroelastic domains, namely the \( \gamma \)-domains and the W' walls.
We conclude:
Phase V of \((\text{NH}_4)_2\text{ZnCl}_4\) is a triclinic phase between -2 °C and -10 °C with a modulation vector of \((2/7)c^*\). Only when the crystal has passed through the phase transitions several times, and the γ-domains are fully twinned, this phase is stable. Before that, when the crystal has passed the phase transitions IV → V and V → VI for the first time, parts of the crystal are still in phase IV and other parts are already in phase V (and possible VI), so that the satellite reflections of phase IV, V and VI, and possible medians in between, are observed together. The complex domain structure, as a consequence of the ferroelastic phase transitions mmmF2/m and mF1, frustrates the stabilization of phase V, and may have caused the discussion in the literature.

References

CHAPTER 8. PHASE VII of (NH₄)₂ZnCl₄.

8.1. Introduction.

Below - 79° C (NH₄)₂ZnCl₄ has another low temperature phase. There is not much knowledge of this phase VII:
Agarwal¹ measured Raman spectra of a single crystal (NH₄)₂ZnCl₄ at - 168° C.
Because the NH₄⁺ ions occupy three different sites he supposed phase VII to be triclinic. The thermosensitive bands show a discontinuity at - 79° C.

Phase VI has space group Pca₂₁n with satellites at 1/3 c⁺. Keeping in mind the model structure of chapter 4 a change from the modulation vector from \( q = 1/3 \text{c}^+ \) in phase VI to \( q = 2/5 \text{c}^+ \) in phase VII could be expected since 2/5 is the median of 1/3 and 1/2.

8.2. Precession photographs.

With an X-ray precession camera we have made precession photographs of the a.b plane (photograph 8.1) and the b.c plane (photograph 8.2) of (NH₄)₂ZnCl₄ at - 170° C. Precession photographs of the b.c plane at - 100° C and - 115° C show the same pictures as at 170° C.

The first striking thing is the place of the satellites, at 1/3 c⁺, the same as in phase VI. With our model structure of chapter 4 we know that phase VII has maximally space group Pca₂₁n. However, Pca₂₁n is the space group of phase VI. Comparison of photograph 8.3 of phase VI and photograph 8.2 of phase VII learns that in phase VII less systematic absences of X-ray reflections in the b.c plane exist than in phase VI. So the space group of phase VII must be lower than Pca₂₁n.

What kind of systematic absences are there in phase VII?
All 0kl reflections are present, except the 0k0 reflections with k = odd and the 00l reflections with l = odd.
So, there is no glide plane perpendicular to the a-axis. The c-glide of phase VI has disappeared, but a 2₁-axis parallel to the b-axis is possible. And a 2₁-axis parallel to the c-axis may be there.
Photo 8.1. Precession photograph of the $a,b$ plane of $(NH_4)_2ZnCl_4$ at -170° C.

Photo 8.2. Precession photograph of the $b,c$ plane of $(NH_4)_2ZnCl_4$ at -170° C.
All hko reflections are present, except the h00 reflections with h = odd and the 0k0
reflections with k = odd.
So, there is no glide plane perpendicular to the c-axis. The n-glide of phase VI has
disappeared, but a 2_1-axis parallel to the a-axis is possible.
Only the h0l reflections cannot be observed. A glide-plane perpendicular to the b-axis
can be there.

Photo 8.3. Precession photograph of the b,c plane of (NH₄)₂ZnCl₄ in phase VI.
8.3. Conclusion.

The space group of phase VII maximally can be P212121 or P1(21/glide plane)1, but there is an uncertainty. One cannot discriminate between reflections with low intensities and systematically absent reflections.

If the space group of phase VII is acentric, Sundaram2 supposed ferroelectric activity, then P21, P1 or P(glide) are the possible space groups. P1 is in agreement with the literature1.

It will be interesting to check this with a structure refinement at -170° C. Before starting this experiment one must realize that the phase transition VI → VII possibly is a phase transition of the species m2mF1. With the theory of Aizu we know this phase transition can deliver ferroelastic and ferroelectric domains, and thus a lot of problems!

References.

Summary.

This thesis is an experimental study of domain structures in \((\text{NH}_4)_2\text{ZnCl}_4\). These domain structures have an important influence and cause many problems in the detection of phases and phase transitions of \((\text{NH}_4)_2\text{ZnCl}_4\).

\((\text{NH}_4)_2\text{ZnCl}_4\) belongs to the large family of \(A_2\text{BX}_4\) crystals having the distorted \(\beta\)-\(K_2\text{SO}_4\) structure. Many of the \(A_2\text{BX}_4\) compounds have a normal high temperature phase, an incommensurate phase and a lock-in phase with a superstructure. In addition to the three mentioned phases \((\text{NH}_4)_2\text{ZnCl}_4\) has four other phases (see fig. 1.3 of this thesis).

The present work is an exploration of the border region between the single crystalline state and the multiple twin structures, incommensurate phases, and sequences of lock-in phases. For the investigations in this region we have chosen the compound \((\text{NH}_4)_2\text{ZnCl}_4\), which may be assumed to form a link between the classical \(A_2\text{BX}_4\) substances such as \(\text{K}_2\text{SeO}_4\), \(\text{Rb}_2\text{ZnBr}_4\), \(\text{Rb}_2\text{ZnCl}_4\) on one hand and \([\text{N(CH}_3)_4]_2\text{ZnCl}_4\) and its isomorphs on the other hand.

To tackle the problems of this investigation, different X-ray diffraction instruments are used: an X-ray topography set up, a photographic precession camera and two different four-circle diffractometers. Beside that, different optical methods with the polarizing microscope are used and the non-linear optical method of second harmonic generation (SHG).

If a crystal undergoes a (nearly) second order phase transition which lowers the point group symmetry, the lower symmetry phase is called a ferroic phase and the crystal is said to be ferroic. In chapter 2 Aizu's theory of ferroic crystals is discussed. The theory predicts that the lock-in phase of \((\text{NH}_4)_2\text{ZnCl}_4\) below 91° C is ferroelastic, i.e. \((\text{NH}_4)_2\text{ZnCl}_4\) has different orientation states in the absence of a mechanical stress and these orientation states can be shifted from one to another by a mechanical stress.

We have performed manipulation experiments which confirm that the domain structure of \((\text{NH}_4)_2\text{ZnCl}_4\) is ferroelastic between room temperature and 91° C.

In chapter 3 the X-ray topographic method of Guinier-Tennevin is discussed. For Guinier and Tennevin this topographic method was a method to get information about
the degree of perfection of certain crystals, but we have used it to study different domain structures of (NH₄)₂ZnCl₄. The method is extensively discussed and calculations are performed to know the resolution of this topographic method for our measurements. An angle difference of 0.01° between crystal axes of two different domains can be visualized very well.

In chapter 4 a model of the A₂BX₄ crystal structures is described. In all of the A₂BX₄ structures layers of tetrahedra normal to the c-axis can be distinguished. In each of the layers the distortions are such that the tetrahedra are rotated about the c-axis all in the same sense. The modulation wave can be characterized by the amplitudes of the rotations in the subsequent layers and by its wavelength. The wavelength of the modulation can either be a rational multiple of the c-axis of the prototype or an irrational multiple resulting in a commensurate or an incommensurate phase respectively. The starting point for the model structure development is that the rotations of tetrahedra within a layer preferably are in the same sense. The result of the model is that the space group of a modulated structure with wave vector \( \mathbf{q} = 1/4 \mathbf{c}^* \) is maximally P1 21/c 1, with wavevector \( \mathbf{q} = 1/3 \mathbf{c}^* \) is Pca 2 1 n and with \( \mathbf{q} = 2/7 \mathbf{c}^* \) is P1 1 2 1/n. The actual symmetry can be lower.

In chapter 5 the thermal behaviour of the ferroelastic domain structure of (NH₄)₂ZnCl₄ is studied from room temperature to the incommensurate phase. An attempt is made to detect the phase transition at 46° C by optical experiments, X-ray diffraction and X-ray topography. However, the conclusion must be that there is no phase transition at 46° C and from room temperature to 91° C there is only one phase with space group P1 c 1.

Chapter 6 describes a study of the phase transition at \( T = 91° \) C from the lock-in phase to the incommensurate phase. The behaviour of the modulation vector is studied and special reflections are measured. The result is that the 4-dimensional space group of the incommensurate phase of (NH₄)₂ZnCl₄ is Pcmn(00\(\gamma\))(s s \(\bar{1}\)). The lower temperature part of the incommensurate phase shows domain walls (discommensurations) and differs from the upper temperature part of the incommensurate phase. The transition to the ferroelastic phase starts in the lower temperature part of the incommensurate phase and not at 91° C. The \( \mathbf{q} \)-vector shows steps that look like a devil's staircase, but passing the phase transition to the incommensurate phase several times makes the steps to disappear.
In chapter 7 the domain structure in another phase, between -5° C and -10° C, is observed with X-ray topographic experiments. An accurate study of the satellite positions is done with an X-ray diffractometer. The conclusion is that this phase is a triclinic phase with a modulation vector of 2/7 e*. Only when the crystal has passed through the phase transition several times this phase is stable. Before that, satellite reflections are observed at 1/4 e*, 2/7 e* and 1/3 e*, because parts of the crystal are in other phases. The complex domain structures, as a consequence of two different ferroelastic phase transitions, frustrate the stabilization of the phase.

Chapter 8 shows some experiments with a precession camera of another low temperature phase, below -79° C. P1 is a possible space group for this phase.
Samenvatting.

Dit proefschrift is een experimentele studie van de domein structuren van (NH₄)₂ZnCl₄. Deze domeinen hebben een belangrijke invloed en veroorzaken veel problemen bij het vaststellen van fasen en fasenovergangen van (NH₄)₂ZnCl₄.

(NH₄)₂ZnCl₄ behoort tot de grote familie van A₂BX₄ kristallen die de verstoorde β-K₂SO₄ structuur hebben. Veel A₂BX₄ kristallen hebben een hoge temperatuur fase, een incommensurabele fase en een "lock-in" fase met een superstructuur. Buiten deze drie genoemde fasen heeft (NH₄)₂ZnCl₄ nog vier andere fasen (zie fig. 1.3 van dit proefschrift).

Dit werk is een onderzoek in het grensgebied van eenkristallen en tweelingen (of veelingen), incommensurabele fasen en opeenvolgingen van "lock-in" fasen. We hebben (NH₄)₂ZnCl₄ uitgekozen om dit grensgebied te onderzoeken. (NH₄)₂ZnCl₄ kan beschouwd worden als de link tussen aan de ene kant de klassieke A₂BX₄ substanties zoals K₂SeO₄, Rb₂ZnBr₄, Rb₂ZnCl₄ en aan de andere kant [Ni(CH₃)₄]₂ZnCl₄ en zijn isomorfismen

Om de problemen van dit onderzoek aan te pakken zijn verschillende röntgen diffractie apparaten gebruikt: een meetopstelling voor röntgen diffractie topografie, een fotografische precessie camera en twee verschillende vier-cirkel diffractometers. Verder zijn verschillende optische meetmethoden met de polarisatie microscoop gebruikt en de niet-lineaire optische methode van tweede harmonische generatie (SHG).

Indien een kristal een (vrijwel) tweede orde fase overgang passeert waarbij de puntgroep verlaagd wordt, dan wordt de lagere symmetrie fase een ferroïsche fase genoemd en van het kristal zegt men dan dat het ferroïsch is. In hoofdstuk 2 wordt de theorie van Aizu over ferroïsche kristallen besproken. De theorie voorspelt dat de "lock-in" fase van (NH₄)₂ZnCl₄ is ferro-elastisch, d.w.z. (NH₄)₂ZnCl₄ heeft bij afwezigheid van een mechanische spanning verschillende orientatie toestanden die in elkaar overgevoerd kunnen worden door het aanleggen van een mechanische spanning.

We hebben manipulatie experimenten uitgevoerd en die bevestigen dat tussen kamertemperatuur en 91⁰C de domein structuur van (NH₄)₂ZnCl₄ ferro-elastisch is.

In hoofdstuk 3 wordt de röntgen diffractie topografie methode van Guinier-Tennevin besproken. Voor Guinier en Tennevin was deze topografische methode een methode
om de kwaliteit van kristallen te beoordelen, maar wij hebben de methode gebruikt om de verschillende domein structuren van \((\text{NH}_4)_2\text{ZnCl}_4\) te bestuderen. De methode wordt uitgebreid besproken en berekeningen worden uitgevoerd om de resolutie van deze methode te bepalen voor onze metingen. Een hoekverschil van 0.01° tussen kristal assen van twee verschillende domeinen is gemakkelijk zichtbaar te maken.

In hoofdstuk 4 wordt een model voor \(A_2BX_4\) kristal structuren beschreven. In al deze \(A_2BX_4\) structuren kunnen loodrecht op de c-as lagen tetraeders waargenomen worden. De verstoring in elk van deze lagen is zodanig dat alle tetraeders in zo'n laag dezelfde kant op draaien. De modulatie golf kan gekarakteriseerd worden door de amplituden van de rotaties in opeenvolgende lagen en door zijn golflengte. De modulatie golflengte kan een rationaal of een irrationaal aantal malen de c-as zijn, wat een commensurabele of incommensurabele fase oplevert.

Als startpunt voor de ontwikkeling van een model structuur is genomen dat de rotaties van de tetraeders in één laag bij voorkeur in dezelfde richting gebeuren. Dat levert als model op dat een gemoduleerde structuur met golfvector \(q = 1/4\ c^*\) maximaal ruimtegroep \(P1 2_1/c\ 1\) heeft, met golfvector \(q = 1/3\ c^*\) ruimtegroep \(Pc 2_1\ n\) en met golfvector \(q = 2/7\ c^*\) ruimtegroep \(P1 1 2_1/n\).

De werkelijke symmetrie kan lager zijn.

In hoofdstuk 5 wordt het thermisch gedrag van de ferro-elastische domein structuren bestudeerd van kamertemperatuur tot aan de incommensurabele fase. Met optische experimenten, röntgen diffractie en röntgen topografie is getracht de fase overgang bij 46° C waar te nemen. De conclusie is echter dat er geen fase overgang bij 46° C is en dat er tussen kamertemperatuur en 91° C slechts één fase is, met ruimtegroep \(P1\ c\ 1\).

Hoofdstuk 6 bestudeert de fase overgang bij 91° C van de "lock-in" fase naar de incommensurabele fase. Het gedrag van de modulatie vector is bestudeerd en speciale reflecties zijn gemeten. De 4-dimensionale ruimtegroep van \((\text{NH}_4)_2\text{ZnCl}_4\) blijkt \(Pcmn(00\gamma)(s\ s\ 1)\) te zijn.

Het lagere temperatuur gebied van de incommensurabele fase laat domein wanden (discommensuraties), zien en verschilt van het hogere temperatuur gebied. De overgang naar de ferro-elastische fase begint niet bij 91° C maar in het lagere temperatuur gebied van de incommensurabele fase. De q-vector laat stappen zien in zijn curve die op een "devil's staircase" lijken, maar wanneer de fase overgang naar de incommensurabele fase een aantal malen gepasseerd is verdwijnen deze stappen.
In hoofdstuk 7 wordt de domein structuur van een andere fase, tussen -50° C en -100° C, met röntgen diffractie topografie waargenomen. Met een röntgen diffractometer wordt nauwkeurig de positie van satellieten bepaald. De fase blijkt trikliëne te zijn met een modulatievector van 2/7 c*. Deze fase is pas stabiel wanneer de fase overgang een aantal malen gepasseerd is. Voor die tijd worden satellieten waargenomen op 1/4 c*, 2/7 c* en 1/3 c*, omdat delen van het kristal zich in andere fasen bevinden. De ingewikkelde domein structuren, die een gevolg zijn van twee verschillende ferroelastische fase overgangen, houden de stabilisatie van deze fase tegen.

In hoofdstuk 8 worden een aantal opnamen met de precessie camara getoond van een andere lage temperatuur fase van (NH4)2ZnCl4, beneden -79° C. P1 is mogelijk een ruimtegroep voor deze fase.
Nawoord.

Veel personen hebben bijgedragen aan het tot stand komen van dit werkstuk. Een aantal van hen wil ik met name bedanken. Mijn ouders in het bijzonder wil ik bedanken dat ze mij lieten studeren. Mijn promotor, prof. dr. ir. F. Tuinstra, dank ik voor zijn begeleiding in de afgelopen jaren, maar bovenal dank ik hem voor het feit dat hij bereid was een part-time promovendus op zijn afdeling aan te stellen. Wim Peterse en Henk van Koningsveld bedank ik voor de uitleg over de werking en de kuren van diffractometers, jullie bereidheid om op "Truusloze " dagen de diffractometers door te starten en vooral het feit dat jullie altijd bereid waren mee te denken en te discussiëren over mijn onderzoek. Charles Laman bedank ik voor zijn veelzijdige technische hulp en uitermate plezierige samenwerking bij het opbouwen en draaiende houden van de meetopstellingen. Ad van den Berg kan ik helaas niet meer bedanken. Hij zal in mijn herinnering blijven als een fijne collega, die mij de eerste beginzelen van de kristallografie bijbracht en die altijd bereid was mee te denken, te rekenen en te puzzelen. Het werk van hem en zijn studenten is op verschillende plaatsen in dit proefschrift terug te vinden. Ruud Staakman bedank ik voor het vele enthousiaste werk dat hij heeft geleverd om alle apparatuur en met name de Hilger & Watts diffractometer electronisch in werking te houden. Mirjam van der Geur bedank ik dat ze bereid was om intermediair te zijn. Daarnaast bedank ik je natuurlijk voor alle gezellige gesprekken. De mensen in Groningen en Nijmegen wil ik bedanken voor de prettige en nuttige bijeenkomsten van de "incommensurabele" werkgroep. Daarnaast bedank ik alle mensen binnen de faculteit en de vakgroep die ik hier niet met naam noem maar die hun hulp en bijdrage aan dit onderzoek hebben gegeven. Ik heb de werksfeer binnen het gebouw van Technische Natuurkunde altijd zeer plezierig gevonden. Daarnaast zijn er een aantal mensen die ik moet bedanken omdat ze voor kortere of langere tijd bereid waren om op mijn kinderen te passen. Zonder jullie was dit werkstuk er niet geweest. Tot slot bedank ik Hein, die er altijd van overtuigd geweest is dat dit werk af zou komen.

Truus.
Curriculum vitae.

Geboren 15 maart 1953 te Vlaardingen.


Examen bij de Stichting Opleiding Leraren te Utrecht afgelegd, februari 1977, tweede graads lesbevoegdheid voor natuurkunde, derde graads lesbevoegdheid voor wiskunde.

Insluizingsprogramma bij de Rijksuniversiteit Utrecht gevolgd om toegelaten te worden tot de doctoraalstudie.

Het afstudeerwerk is verricht bij de vakgroep Vaste Stof Fysika van de Vrije Universiteit te Amsterdam.

Tijdens de doctoraalstudie werd lesgegeven op een mavo school.


Sinds juni 1986 in deeltijd werkzaam geweest aan een promotie onderzoek bij de vakgroep Vaste Stof/Fysische Kristallografie van de Technische Universiteit Delft.