Studies of Nematic to Smectic-A Phase Transitions using Synchrotron Radiation Experimental Techniques and Experiments

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Publication date:
1981

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Studies of Nematic to Smectic-A Phase Transitions using Synchrotron Radiation Experimental Techniques and Experiments

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Risø National Laboratory, DK 4000 Roskilde, Denmark
October 1981
STUDIES OF NEMATIC TO SMECTIC-A PHASE TRANSITIONS USING SYNCHROTRON RADIATION.
EXPERIMENTAL TECHNIQUES AND EXPERIMENTS

Finn Christensen

Abstract. High-resolution X-ray diffraction on liquid crystals, with a triple-axis spectrometer, was initiated 4-5 years ago, using rotating-anode sources. The natural extension of this work was to use the same kind of spectrometer at the much more powerful source provided by synchrotron radiation. This work was initiated during excursions to the DORIS storage ring in Hamburg in 1979-1980. The triple-axis spectrometer, built at Risø, is now permanently positioned at DORIS in HASYLAB and series of dedicated beam time are used by the solid-state physics group at Risø. The triple-axis X-ray spectrometer work in general and especially at the synchrotron source is a new field and a portion of this thesis is devoted to a description of the techniques it uses.

(Continue on next page)
The experiments described here are studies of the nematic to smectic-A phase transition in liquid crystals. The first study is a 2S5 (C_{8}H_{17}O-->COS-->C_{5}H_{11}, where $\phi$ denotes a benzene ring). The results of this experiment are compared to those on the bimolecular compounds 8CB (C_{8}H_{17}-->CN), 8OCB (C_{8}H_{17}O-->CN), and CBOOA (C_{8}H_{17}O-->NCH-->CN). The second experimental study is one of the reentrance phenomenon in the ternary mixture: 5CT:09:7CB:x; 8OCB:91-x, where 5CT(C_{5}H_{11}-->CN) and 7CB(C_{7}H_{15}-->CN) have only a nematic phase and not the smectic-A phase. The results are interpreted in terms of Landau theory, which also explains a pressure-driven reentrance phenomenon in certain pure bilayer compounds (e.g. 8OCB).

Finally, a frame is given for discussing the nature of the smectic-A phase and an experiment is proposed to explore the nature of the smectic-A phase together with detailed calculations of (001)- and (002)-lineshapes for the smectic-A phase.

UDC 539.26:548.73

This report is submitted to the Technical University of Denmark in partial fulfilment of the requirement for obtaining the lic. tech. (Ph.D.) degree.

ISBN 87-550-0823-2
ISSN 0106-2840

Risø repro 1982
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ACKNOWLEDGEMENTS

The experimental work, reported on in this thesis, was carried out at the DORIS-storage ring in Hamburg. The author wishes to thank scientists and technicians in HASY-LAB for their skilful guidance, especially Dr. G. Waterlik, who provided information on crystal cutting.

The author also wishes to express his deep gratitude to the group of technicians in the Physics Department at Risø, especially S. Bang, E. Dahl Petersen, J. Linderholm, and J. Munck, all of who never refused to spend a night of hard work in Hamburg whenever needed.

I would also like to thank the secretaries in the Physics Department, especially K. Kjoller, and Lis Vang for their patience and skill in typing the draft of the manuscript.

Privately I am greatly indebted to may parents for their support throughout my whole education.

Last, but not least, I gratefully acknowledge the inspiring guidance from and collaboration with Dr. J. Als-Nielsen.
1. INTRODUCTION

Synchrotron radiation has become a powerful tool in experimental physics in recent years, especially since the possibility of dedicated beamtime is growing. A number of well-known experimental techniques in solid-state physics such as X-ray diffraction, EXAFS, photoemission, etc. have been reconsidered in order to match the experimental equipment to the properties of the synchrotron radiation, and a whole new era of experiments have started within the various fields.

In order to pursue the advantages of synchrotron radiation, Dr. J. Als Nielsen at Risø built a triple-axis spectrometer for general-purpose X-ray diffraction in 1978. At the same time construction of a rotating anode was funded. The advantage of having two complementary scattering probes (X-rays and neutrons) at the same place is obvious, and secondly the rotating anode set-up provided the home base for the testing of the triple-axis spectrometer, the development of new experimental equipment, routines, and the training of experimenters, until the triple-axis spectrometer could be moved permanently to the experimental hall of HASYLAB at DORIS in Hamburg. This took place in October 1980. During the 1-1/2 years from May 1979 to October 1980 the spectrometer was brought to EMBL (European Molecular Biology Laboratory) at DORIS for test experiments and actual experiments. During these excursions we worked in a parasitic mode (high-energy physics experiments deciding the energy and the lifetime of the electrons/positrons), but nevertheless we gained valuable experience. All in all everything was well prepared for the dedicated beamtime at HASYLAB in October-November 1980 and it was possible to utilize the dedicated beamtime fully from the start.

This thesis reports on high-resolution X-ray diffraction studies of the nematic to smectic-A phase transition in liquid crystals, using primarily synchrotron radiation. The renewed theoretical
and experimental interest in liquid crystals started in the begining of the seventies, especially with the theoretical work of de Gennes, W.L. McMillan, and K.K. Kobayashi. The interest was parallel to the breakthrough in the theory of phase transitions. The new approach to phase transitions, known as renormalization group theory (R.G.T.), provides a number of simple concepts. One of the salient features of the theory is the recognition that critical phenomena associated with continuous phase transitions in two quite different condensed material systems have some fundamental features in common, provided they belong to the same universality class. This basically means that the interaction space dimensionality $d$ and the order parameter space dimensionality $n$ are the same for the two systems. This leads to a unified picture of the phenomena of continuous phase transitions in condensed matter, regardless of the origin of the physical interaction between the basic constituents of the system. The theory is thus not designed to solve exactly any particular many-body problem in condensed matter physics, but rather describe the critical behaviour. This is done through symmetry considerations, dimensionality considerations and a few basic assumptions. An important concept is that of marginal dimensionalities, $d_L$ being the lower marginal dimensionality and $d_U$ is the upper marginal dimensionality. For $d < d_L$ thermal fluctuations destroy the long-range order otherwise favoured by the interactions among the basic constituents. For $d > d_U$ the behaviour in the critical regime can be calculated from mean field theory (M.F.T.). For most condensed matter systems $d_U = 4$ and $d_L = 2$.

The phases and phase transitions of liquid crystals have properties which make them uniquely suited for testing these new ideas. The smectic-A phase is namely thought to be a system exactly at lower marginal dimensionality. Furthermore, the nematic to smectic-A transition belongs to the same universality class as superfluid helium and the superconductor in a magnetic field, which lead to predictions for the critical exponents. The analogy between the nematic to smectic-A phase transition and the normal-to-superconducting transition for a metal in an external magnetic field is an even closer one. This analogy
manifests itself in isomorphous (phenomenological) free energy expressions for the spatial fluctuations.

The experimental studies, reported on in this thesis, have been performed on the liquid crystal 8S5, and a ternary mixture of liquid crystals of the following composition: $5\text{CB}_3:7\text{CB}_7:8\text{OCB}_{91-x}$, where the index $x$ means weight percent. This mixture exhibits a $T-x$ phase diagram with a reentrant nematic phase for $x < 76.7\%$. 8S5 is out of the family $\text{B}:_{n+1} \text{C}:_{n+1} \text{C}:_{n+1}$, where $\text{B}$ denotes a benzene ring. This family exhibits the following sequence of phases for $0 < n < 12$: isotropic - nematic - smectic-A - smectic-C - smectic-B - solid. 8S5 was chosen because of its monomolecular smectic-A structure, as opposed to the bimolecular structure of materials such as 8CB, 8OCB, and CBOOA, which have been studied in great detail by J.D. Litster et al.\textsuperscript{5}.

The reentrant behaviour of the mixture is analogous to the pressure-driven reentrant behaviour in pure compounds like 8OCB which have been studied by P.E. Cladis\textsuperscript{6}. There are a number of mixtures which display reentrant behaviour. The one we studied has the advantages of good chemical stability, the reentrant nematic phase being stable, not supercooled, with a completely reversible and second-order phase transition\textsuperscript{7}.

The plan of the thesis is the following:

**Chapter 1:** Introduction.

**Chapter 2:** An overview over liquid crystals, phases and phase transitions, displaying various analogies and theoretical predictions, as briefly outlined in the introduction.

**Chapter 3:** A discussion of the use of perfect single crystals in high-resolution X-ray diffraction.

**Chapter 4:** The resolution function of the triple-axis spectrometer. Detailed measurements are shown for a typical liquid crystal set-up at the rotating anode.
Chapter 5: The properties of synchrotron radiation as a radiation source in high-resolution X-ray diffraction. Its measured properties (DORIS - HAMBURG) are compared with calculated ones and with the rotating-anode source at Risø.

Chapter 6: An experimental study of the nature of the second-order nematic-smectic-A phase transition in the monolayer smectic-A component 8S5, performed at the EMBL-outstation at DORIS. The obtained results are compared with similar studies on bilayer compounds such as 8OCB, 8CB, and CBOOA.

Chapter 7: An experimental study of the ternary mixture 5CTg:7CBx:80CB91-x, exhibiting reentrant nematic behaviour for x < 76.74. The study determines the phase diagram, critical exponents for different values of x, and absolute values of correlation lengths. The experimental results are compared with available theoretical predictions.

Chapter 8: Different models for the nature of the smectic-A phase, including calculations of molecular form factors and calculations of the (001)-lineshape and the (002)-lineshape in the smectic-A phase of 8OCB for a specific experimental set-up.

Appendix A: The calculation of the anomalous scattering singularities in the smectic-A phase.

Appendix B: A description of the transformation from one set of conjugate diameters to another.

Appendix C: The numerical deconvolution procedure that is used to obtain correlation-length-data close to Tc.

Appendix D: A description of the combination of resolution ellipses for the triple-axis spectrometer.

Appendix E: The effect of mosaicity of the sample on the resolution function.
REFERENCES

2. LIQUID CRYSTAL MATERIALS, PHASES, AND PHASE TRANSITIONS. ANALOGIES AND THEORETICAL PREDICTIONS

The materials exhibiting liquid crystal behaviour have certain fundamental features in common. As is well known, they are all elongated, rodlike molecules consisting of two or more benzene rings and hydrocarbon chains. Typically, the length of these molecules falls in the 20–30 Å range. There are of course quite a number of materials meeting these requirements, and the spectrum of liquid crystals is quite rich. A table of various liquid crystal materials together with their chemical formula and other relevant information is listed below. These materials have been used quite extensively in the study of the nematic to smectic-A phase transition during the last five years. From the table it is evident that the d-spacing of the smectic-A phase is incom­mensurable with the molecular length for the compounds CBOOA, CBOA, 80CB, 8CB and CBNA, but on the other hand, \( l = d \) for 885 and 40.8. This fact has led to a division of smectic-A compounds into two categories, namely: Bilayer smectic-A compounds and monolayer smectic-A compounds.

2.1. Liquid crystal materials and phases

The basic building block of the bilayer smectic-A compounds is thought to be an overlapping configuration of two molecules\(^2\),\(^3\), while in monolayer compounds the basic building block is one molecule. The bilayer compounds are typically molecules with head-tail structure. To be specific let us consider 8CB. Here the \( \text{C}_8\text{H}_{17} \) constitutes the nonpolar tail and \( \text{O}–\text{O-CN} \) constitutes the polar head (core). \( \text{O} \) denotes a benzene ring.

From this model, assuming a complete overlap of the heads, one may infer that \( d = a + 2b^2 \) for bilayer smectic-A compounds where \( a \) and \( b \) are the lengths of the head and tail, respectively. This is in qualitative agreement with the observed
Table 2.1. A survey of some smectic-A compounds. The symbol \( \Theta \) denotes a benzene ring. The superscript on \( l \) and \( d \) refers to references. The \( d \)'s and \( l \)'s are measured and calculated values, respectively. The spread in \( d \) reflects the accuracy of the measurements and the spread in \( l \) reflects the lack of precise knowledge of all interatomic distances and some degrees of freedom in the molecular formation.

<table>
<thead>
<tr>
<th>NAME(S)</th>
<th>CHEMICAL FORMULA</th>
<th>( l ) ( \equiv ) MOLECULAR LENGTH (Å)</th>
<th>( d ) ( \equiv ) D-SPACING IN SMECTIC-A PHASE</th>
<th>TRANSITION TEMPERATURES ( ^{\circ}C )</th>
</tr>
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<tr>
<td>JOOA</td>
<td>( C_{8}H_{17}O-\Theta-NCH-\Theta-CN )</td>
<td>( 26.4^{(3)}/25.6^{(2)} )</td>
<td>( 35.10^{(1)}/35.0^{(2)} )</td>
<td>C( 21 ) S( 98 ) 5( 2 ) N( 10 )6.51</td>
</tr>
<tr>
<td>CBOA</td>
<td>( C_{8}H_{17}O-\Theta-NCH-\Theta-CN )</td>
<td>( 25.8^{(3)} )</td>
<td>( 34.7^{(3)} )</td>
<td>S( 61 ) 8( 8 ) N( 2 )2.51</td>
</tr>
<tr>
<td>8OCB+COOB</td>
<td>( C_{8}H_{17}O-\Theta-CN )</td>
<td>( 23.1^{(3)}/23.4^{(2)} )</td>
<td>( 31.89^{(1)}/32.0^{(2)} )</td>
<td>C( 54 ) S( 67 ) N( 8 )01</td>
</tr>
<tr>
<td>8CB+COB</td>
<td>( C_{8}H_{17}O-\Theta-CN )</td>
<td>( 22.4^{(3)}/22.1^{(2)} )</td>
<td>( 31.73^{(1)}/31.6^{(2)}/31.0^{(5)} )</td>
<td>C( 21 ) S( 93 ) 6( 6 ) N( 10 )8.51</td>
</tr>
<tr>
<td>8S5</td>
<td>( C_{8}H_{17}O-COS-\Theta-C_{5}H_{11} )</td>
<td>( 27.5^{(4)} )</td>
<td>( 28.5^{(4)} )</td>
<td>S( 85 ) S( 55 ) S( 36 ) N( 8 )2.51</td>
</tr>
<tr>
<td>40.8</td>
<td>( C_{4}H_{9}O-\Theta-CN-\Theta-C_{8}H_{17} )</td>
<td>( 25.4^{(4)} )</td>
<td>( 28.5^{(4)} )</td>
<td>S( 89 ) S( 54 ) N( 7 )2.51</td>
</tr>
<tr>
<td>CBNA</td>
<td>( C_{9}H_{19}O-\Theta-NCH-\Theta-CN )</td>
<td>( 27.0^{(3)} )</td>
<td>( 38.1^{(3)} )</td>
<td>C( 99 ) S( 25 ) 5( 1 ) N( 27 )5.51</td>
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</table>
d-spacings. The model has been used in attempts to describe the reentrance phenomena in liquid crystals under pressure qualitatively\(^3\) and has led to a quantitative Landau-theory for the reentrance phenomena (to be discussed later). The monolayer compounds differ from the bilayer compounds chemically by the addition of a carbon-tail, so the general structure is two or more benzene rings in the middle of the molecule and the carbon-tails stretching out to either side.

The liquid crystal phases and phase transitions one observes in these materials are due to the extra, orientational, degree of freedom of the rodlike molecules compared to isotropic molecules/atoms. The phases of principal interest and currently under active study, are: Nematic, Smectic-A, Smectic-C and Smectic-B. All these phases (with the possible exception of Smectic-B, which can probably be classified as a three-dimensional solid) constitute intermediate states of matter (mesophases), between that of the isotropic liquid phase (I) and the three-dimensionally ordered solid phase (S).

A material exhibiting all phases will usually have the following sequence of phases:

\[
T_c^1 \quad T_c^2 \quad T_c^3 \quad T_c^4 \quad T_c^5
\]

(*) S \(\leftrightarrow\) Sm B \(\leftrightarrow\) Sm C \(\leftrightarrow\) Sm A \(\leftrightarrow\) Nem \(\leftrightarrow\) I

with \(T_c^1 < T_c^2 < T_c^3 < T_c^4 < T_c^5\), reflecting the decrease of the order (usually) with increasing temperature. (See also Table 2.1). There exist, however, mixtures of liquid crystals which exhibit a reentrant nematic phase (N*) giving a phase sequence of \(\ldots N^* \leftrightarrow\) Sm-A \(\leftrightarrow\) N\ldots\). One example is the ternary mixture, reported on in this thesis, 5CTg:7CB\(_x\):8OCB\(_{91-x}\). Also pure compounds may exhibit the same sequence under pressure, e.g. 8OCB.

The structural characteristics of the three mesophases nematic, Sm-A, and Sm-C are the following:

Nematic: In this phase the centres of gravity of the molecules are distributed at random as in a liquid, but the rodlike molecules are orientationally ordered with their long axes, on the
average, in the same direction, the optical axis of the nematic phase. The variation in space of the direction of the long axes is commonly described by the unit vector \( \mathbf{n}(r) \), called the director, giving at point \( r \), the average direction of the long axes. (See Figure 2.1a, where the nematic phase is shown schematically together with the density-variation along the optical axis, here denoted the z-direction.) The order parameter describing the \( \text{N} \leftrightarrow \text{I} \) transition is \( S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \), where \( \theta \) is the angle between the optical axis and the long axis of the molecules. \( S = 1 \) for total alignment and 0 for the isotropic phase. The parameter \( \langle \cos \theta \rangle \) is not the correct order parameter because the directions +n and -n are equivalent, leading to \( \langle \cos \theta \rangle = 0 \).

A phenomenological theory for the nematic order parameter \( S \) has been given by W. Maier & A. Z. Saupe \(^{15}\).
Smectic-A: This phase is characterized by the orientational order of the nematic phase and in addition a density-ripple along the z-axis. (See Figure 2.1b.) This gives rise to a layered structure indicated on the schematic drawing. The nature of the layering is discussed in detail in Chapter 8. As will be apparent there exists to this day no conclusive evidence for the exact nature of this layering. Within these layers the positional order of the molecule is still liquidlike. The order parameter for the Sm-A ↔ N transition is the two-component complex order parameter

$$\psi(\mathbf{r}) = a(\mathbf{r}) \cdot e^{i\mathbf{q}_0 \cdot \mathbf{u}(\mathbf{r})},$$

where:

$$\rho(\mathbf{r}) = \rho_0 \cdot [1 + \text{Re}(\psi(\mathbf{r}) \cdot e^{i\mathbf{q}_0 \cdot \mathbf{r}})] \; ; \; \mathbf{q}_0 = \frac{2\pi}{d}$$ (2.1)

$\rho(\mathbf{r})$ being the density. Clearly $a(\mathbf{r})$ is the amplitude of the density ripple and $u(\mathbf{r})$ is the displacement in the $z$-direction of the layer at $\mathbf{r}$. The expression for $\psi(\mathbf{r})$ assumes a sinusoidal density-ripple. More rigorously, one could regard $\text{Re}[\psi(\mathbf{r})e^{i\mathbf{q}_0 \cdot \mathbf{r}}]$ as the first harmonic term in a Fourier-series expansion of the density. (See Chapter 8, Section 8.5.)

An extension of the Maier-Saupe mean field theory covering both the nematic-isotropic transition and the nematic smectic-A transition has been outlined by McMillan. He assumes the following expression for the pairwise interaction between the constituent molecules:

$$V_{12}(r_{12}, \cos \theta_{12}) = -V_0 \cdot e^{-(r_{12}/r_0)^2 [(3/2\cos^2 \theta_{12} - 1/2)+\delta]}$$

where $r_{12}$ is the distance between centers of mass and $\theta_{12}$ is the angle between the long axes of the two molecules. $V_0, r_0$ and $\delta$ are the model parameters. The term $r_0$ is of the order of the length of the rigid section of the molecule, and $0<\delta<1$. The next step is to assume the following mean field expression for the one-particle potential:

$$V_1(z, \cos \theta) = -V_0 [\eta(3/2\cos^2 \theta - 1/2) + a \delta \cos(2\pi z/d)$$

$$+ a \cos(2\pi z/d)(3/2\cos^2 \theta - 1/2)]$$
where $z$ is the position of the center of mass along the $z$-axis and $\theta$ is the angle between the long axis of the molecule and the preferred direction. $\alpha$ is the McMillan parameter:

$$\alpha = 2e^{-\left(\frac{\tau_0 z}{d}\right)^2}$$

A more general mean field expression for $V_1$ would contain higher Fourier components\(^{18}\), but these are neglected. Using $V_1, V_{12}$ is recalculated and self-consistency demands that:

$$n = \langle 3/2 \cos^2 \theta - 1/2 \rangle ; \tau = \langle \cos(2\pi z/d) \rangle ;$$

$$\sigma = \langle \cos(2\pi z/d)(3/2 \cos^2 \theta - 1/2) \rangle$$

where the thermal average is calculated using the one-particle distribution function $f = e^{-\left(V_1(z, \cos \theta) / kT\right)}$.

$n$ is identical to $S$ the orientational order parameter of the nematic phase, $\tau$ is the density wave amplitude or the smectic order parameter, $\sigma$ is a mixed order parameter. The three expressions above can be solved numerically to obtain $n, \tau, \sigma$ vs. temperature for different values of model parameters $V_0, \tau_0$ (or $\alpha$) & $\delta$. $V_0$ determines the N-Isotropic transition temperature and fixes the temperature scale of the model. $\alpha$ is a dimensionless interaction strength for smectic ordering. $\delta$ is a parameter which allows the translational order to be decoupled from orientational order. McMillan has determined the phase diagram for $\delta = 0$, which means that the translational order cannot be decoupled from the orientational. Setting $\delta = 0.65$ and without assuming the specific form of the one-particle potential $V_1$, which neglects higher Fourier components, Lee et al\(^{17}\) have used the McMillan form of $V_{12}$ and minimized the free energy with respect to the distribution function $f$, using a variational form of $f$, thus obtaining the I-N-SmA phase diagram. The results of McMillan and Lee et al. are in qualitative agreement, but Lee et al. predictions for the phase diagram are in closer agreement with experiment\(^{17}\). Regarding the onset of second-order phase transitions, the two calculations differ very little. McMillan's calculation predicts the following:
The transition is first order for $0.7 < \alpha < 1$ and second order for $\alpha < 0.7$, or equivalently the transition is first order if $T_{NA}/T_{NI} > 0.87$ and second order if $T_{NA}/T_{NI} < 0.87$. It is worth noting that experimentally the compounds 8CB, 8OCB and CBOOA all exhibit second-order transitions, with $T_{NI}/T_{NA} < 0.87$ as predicted. Lee et al. predicts 0.88 instead of 0.87. The upper limit on $T_{NA}/T_{NI}$ for second-order transitions reflects the nearly saturated form of the nematic order within the mean field theory, before the nematic to smectic-A transition can take place in a continuous manner.

Smectic-C: This phase is optically biaxial, but otherwise resembles the Sm-A phase. This is microscopically interpreted as a result of a tilting of the molecules within the layers, as sketched in Figure 2.1.c. The order parameter for the Sm-C ↔ Sm-A transition is again a two-component complex scalar of the following form: $\Phi(\vec{r}) = \omega(\vec{r}) \cdot e^{i\phi(\vec{r})}$ is the tilt angle and $\phi(\vec{r})$ is the azimuthal angle of the projection of the molecule on the layer. The tilting of the molecules (or $\hat{n}$) drives the layer distance $d_C$ away from this distance in the Sm-A phase, by the simple geometric relation $d_C = d_A (1-\cos \omega)$.

The fundamental static distortions of the nematic phase are described by the phenomenological Frank free energy $F_N$, which is an expansion in the spatial derivatives of $\hat{n}(\vec{r})$, including only terms which are compatible with the symmetry of the phase. It turns out$^6$ that $F_N$ can be written:

$$F_N = F_O + 1/2 K_1((\hat{v} \cdot \hat{n})^2 + 1/2 K_2((\hat{n} \cdot (\hat{v} \times \hat{n}))^2 + 1/2 K_3((\hat{n} \times (\hat{v} \times \hat{n}))^2$$

(2.2)

where $K_1$, $K_2$, and $K_3$ are the Frank elastic constants. Each term in the expansion corresponds to a fundamental distortion. These are:
Fig. 2.2. The static distortions of the nematic phase.

<table>
<thead>
<tr>
<th>Distortion</th>
<th>Vector Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Splay</td>
<td>$\nabla \cdot \mathbf{n} \neq 0$</td>
</tr>
<tr>
<td>Twist</td>
<td>$\nabla \cdot (\nabla \times \mathbf{n}) \neq 0$</td>
</tr>
<tr>
<td>Bend</td>
<td>$\nabla 	imes (\nabla \times \mathbf{n}) \neq 0$</td>
</tr>
</tbody>
</table>

Splay which corresponds to $(\nabla \cdot \mathbf{n})^2 \neq 0$

Twist which corresponds to $(\nabla \cdot (\nabla \times \mathbf{n}))^2 \neq 0$

Bend which corresponds to $(\nabla \times (\nabla \times \mathbf{n}))^2 \neq 0$
(See Figure 2.2 where these distortions are drawn schematically.) The elastic constants $K_1$, $K_2$, and $K_3$ can be measured by light wave scattering. In fact, the fluctuations of \( \hat{n} \) give rise to strong scattering of light, which makes the nematic phase seem turbid.

The long wavelength fluctuations of the Sm-A-phase can be described using a phenomenological free energy $F_S$ (analogous to the Frank free energy $F_N$ for the nematic phase), which is an expansion in the spatial derivatives of $u(\vec{r})$, compatible with the symmetry of the Sm-A-phase and a few basic assumptions. $F_S$ has the following form:

$$F_S = F_0 + 1/2 \bar{B} \left( \frac{\partial u}{\partial z} \right)^2 + 1/2 K_1 \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2$$

(2.3)

where $\bar{B}$ is a stiffness constant and $K_1$ is the SPLAY-elastic constant. It is important to understand this form of $F_S$. The crucial symmetry points and assumptions made in writing down $F_S$ are:

i) $-z$ and $+z$-directions are equivalent (excludes uneven powers of derivatives)

ii) Simultaneous rotations of layers and molecules do not change the free energy (excluding terms $= (\partial u/\partial x)^2$ and $(\partial u/\partial y)^2$).

A term $1/2 D [ (n_x + \partial u/\partial x)^2 + (n_y + \partial u/\partial y)^2 ]$, giving the energy associated with fluctuations of the director away from the layer normal is neglected. Fluctuations away from the layer normal are associated with BEND & TWIST-deformations. To a first approximation these are forbidden in the smectic-A phase. (See later.) Formally the neglect of the D-term leads to:

$$\frac{\partial u}{\partial x} = -n_x << 1$$

(2.4)

$$\frac{\partial u}{\partial y} = -n_y << 1$$
which immediately shows that the term:

\[ \frac{1}{2} K_1 \left[ \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial x^2} \right] = \frac{1}{2} K_1 \nabla \cdot (\nabla \times n)^2 \]

is just the SPLAY-term of the nematic phase. The reason for the absence of the TWIST and BEND terms is that, as a first approximation, the layer distance is a constant \( d \), simply because changing the layer distance requires compression of layers which costs too much energy. The proof that \( n \cdot (\nabla \times n) \) and \( n \times (\nabla \times n) \) vanishes completely when \( d \) is constant is simple as shown below:

\[ n_{AB} = \frac{1}{d} \int_A^B n \cdot dl \]

measures the number of layers crossed when moving from \( A \) to \( B \). This means immediately

\[ \frac{1}{d} \int_A^B n \cdot dl = \frac{1}{d} \int A^B \nabla \times n \, ds \] (according to Stokes's theorem)

which completes the proof.

Terms involving \( \nabla^2 = (\partial^2 u/\partial z^2) \) are neglected as the dominant term is \( 1/2 \mathcal{B}(\partial u/\partial z)^2 \). On the other hand, the SPLAY-term cannot be neglected on the same grounds (since, if \( \partial u/\partial z = 0 \), the splay-term is then the only term left).

In comparison with the nematic phase the layering in the smectic-A phase introduces the new term \( 1/2 \mathcal{B}(\partial u/\partial z)^2 \) in the free energy and at the same time only the SPLAY-term survives this layering. In Figure 2.1 the two fundamental distortion configurations are sketched. Figure 2.3a shows a longitudinal displacement distortion, where \( \partial u/\partial z \neq 0 \) and \( \partial^2 u/\partial x^2 = \partial^2 u/\partial y^2 = 0 \). Figure 2.3b shows a transverse displacement distortion (undulation mode), where \( \partial u/\partial z = 0 \) and either \( \partial^2 u/\partial x^2 \) or \( \partial^2 u/\partial y^2 \neq 0 \) (or both).
Fig. 2.3. The static distortions of the smectic-A phase.

The peculiar form of $F_s$ has a fundamental implication on the smectic-A phase, which is most easily seen by calculating $\langle u^2(r) \rangle$. Using equipartition on $F_s$ yields:

$$ F_s = \frac{V}{2} \sum (B q_2^2 + K_1 q_4^4) u^2(q) \Rightarrow \langle u^2(q) \rangle = \frac{k_B T}{B V(q_2^2 + \lambda^2 q_1^4)} ; \lambda = \sqrt{\frac{K_1}{B}} $$

(2.5)

$\lambda$ is the penetration depth for SPLAY-deformations and $1/(\lambda k)^2$ measures how far an imposed undulation mode of wavelength $k$ will penetrate into a smectic-A phase. One gets for $\langle u^2(r) \rangle$: 
\[ \langle u^2(t) \rangle = \frac{V}{(2\pi)^3} \int \langle u^2(q) \rangle dq \]

\[ = \frac{k_B}{8\pi^2} \left( \int_{-2\pi/d}^{2\pi/d} dq_2 \int_{2\pi/L}^{2\pi/d} dq_1 \right) \frac{2q_1 dq_1}{q_2^2 + q_1 q_2^4} \]

\[ = \frac{k_B}{4\pi^2 d} \ln \left( \frac{L}{d} \right) \]

where \( L \) is the sample dimension and \( d \) the layer spacing. This logarithmic divergence of the layer displacement indicates the unique feature of this phase, namely that the Sm-A phase is a system at low marginal dimensionality. The lack of long-range order (L.R.O.) is frequently referred to as the Landau Peierls instability of the smectic-A phase.\(^{14}\)

The divergence of \( \langle u^2(t) \rangle \) does not, however, mean that the peaks in \( S(q) \): The Fourier transform of the correlation function \( G(\ell) \) totally disappears. There remain singularities in \( S(\mathbf{q}) \), which are weaker than conventional \( \delta \)-function Bragg-peaks. The calculation of \( G(\ell) \) and \( S(\mathbf{q}) \) was first worked out by Caillé\(^{8}\) and is done carefully in Appendix A for completeness and because it differs significantly from the usual calculations of thermal diffuse scattering. The result is the following for \( q_z = nq_0 \), i.e. near the "pseudo" reciprocal lattice points:

\[ G(\ell) = \langle e^{iq_z(u(r) - u(o))} \rangle = e^{-2\gamma n \frac{2dn}{2\pi n}} e^{-nE_1\left(\frac{\rho^2}{4\lambda^2}\right)} \]

\[ (2.6) \]

where: \( \gamma = \text{Euler const.} = 0.577 \); \( \rho^2 = x^2 + y^2 \); \( d \) = layer spacing
\[ n = \frac{k_B T q_0^2 \cdot n^2}{16 - B \lambda}; \quad E_1(x) = \int_{x}^{\infty} \frac{e^{-t}}{t} dt; \quad \lambda = \frac{\sqrt{K_1}}{B}; \quad n q_0 = n \cdot \frac{2\pi}{d} \]

for \( p << z \):

\[ G(r) = e^{-\gamma n} \left( \frac{d^2}{4n^2 \pi^2 \lambda} \right)^n \] (2.7)

for \( p >> z \):

\[ G(r) = e^{-2\gamma n} \left( \frac{2d}{2\pi n p} \right)^{2n} \] (2.8)

which gives for \( S(\kappa) \):

\[ S(0,0,q_z) = \frac{1}{(q_z-q_0)^{2-n}} \quad \text{and} \]

\[ S(q_\perp,0) = \frac{1}{q_\perp^{4-2n}} \] (2.9)

The power law decay of \( S(q) \) has been experimentally verified by high-resolution x-ray scattering on 80CB by Als-Nielsen et al.\(^9\)&\(^10\).

In this study the \( S(0,0,q_z) \)-lineshape has been measured for a number of temperatures close to \( T_c \). It shows, as expected, an increase of \( n \) as \( T \rightarrow T_c \). \( K_1 \) is constant over the narrow temperature range.

### 2.2. The nematic to smectic-A phase transition. Analogies - theoretical predictions

\( F_N \) and \( F_S \) describe well the static distortions of respectively the Nematic and Sm-A phases, whereas the phase transition is described using the complex order parameter \( \psi(\vec{r}) = a(\vec{r}) \cdot e^{i\eta(\vec{r})} \) which indicates that the \( N \leftrightarrow \text{Sm-A} \) transition belongs to the \( n = 2; \, d = 3 \) universality class. The full free energy
functional used to describe the phase transition is:

\[ F = F_0 + \alpha |\psi|^2 + \beta |\psi|^4 + \frac{1}{2} M_y \left( \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \xi^2} \right) + \nabla^2 \psi + \mathcal{O}(\psi^2) \]

\[ + \frac{1}{2} M_t \left[ \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + a^2 q_o^2 \left( n_y + \frac{\partial u}{\partial y} \right)^2 \right] + F_N \]

(2.10)

Inserting \( \psi = a(x) \cdot e^{i q_0 n(x)} \) yields

\[ F = F_0 + \alpha \cdot a^2 + \beta \cdot a^4 + \frac{1}{2} M_y \left[ \left( \frac{\partial a}{\partial x} \right)^2 + a^2 q_o^2 \left( \frac{\partial a}{\partial z} \right)^2 \right] + \nabla^2 \psi + \mathcal{O}(\psi^2) \]

\[ + \frac{1}{2} M_t \left[ \left( \frac{\partial a}{\partial x} \right)^2 + \left( \frac{\partial a}{\partial y} \right)^2 + a^2 q_o^2 \left( n_y + \frac{\partial u}{\partial y} \right)^2 \right] + F_N \]

(2.11)

by comparing with the free energy expression p. 20, where spatial fluctuations in \( a \) were neglected, one can identify: \( \overline{B} = 1/2 \cdot M_y \cdot a^2 q_o^2 \) and \( D = 1/2 \cdot M_t \cdot a^2 q_o^2 \).

The physical meaning of each of these terms is the following: The first three terms are the usual Landau theory terms, which are the only ones left when neglecting spatial fluctuations. The fourth is the energy cost of longitudinal amplitude fluctuations and longitudinal phase fluctuations. The fifth term, in curly brackets, consists of two different contributions: The first \( (\partial a/\partial x)^2 + (\partial a/\partial y)^2 \) is simply the energy cost of transverse amplitude fluctuations. The second the energy cost associated with fluctuations of \( n(\xi) \) away from the normal to the layers. The sixth hand term is the Frank elastic energy of the nematic phase.
It is worth noting the difference between this free energy functional and the sum of $F_S$ and $F_N$. One notices that all the terms of $F_S$ and $F_N$ are present, but new ones have appeared. Basically because the order parameter used is a two-component one and because fluctuations of $n(r)$ away from the layer normal are generally allowed.

The form of $F - F_N$ provides the basis for the analogy with superconductors. $F - F_N$ will namely describe a superconductor in a magnetic field $H(r) = \nabla \times A(r)$ where $A(z) = 0$, provided one makes the identification:

$$q_0(n_x, n_y) = -e^*/\hbar (A_x, A_y); \quad e^* \equiv \frac{2e}{c}$$

which is easily checked by noting that the Landau-Ginzburg free energy for the superconductor is

$$F_{s.c} = F_{s.c}^N + a|\psi|^2 + \beta|\psi|^4 + \frac{1}{2} M|(-i\hbar \nabla - e^* A)\psi|^2.$$

It is now interesting to look upon the pretransitional effects which can emerge from $F - F_N$ and compare these with analogous effects in the superconductor. One of the most interesting is the anomalous increase in $K_2$ and $K_3$ as $T$ approaches $T_C$. This effect can be explained in the following manner: Far above $T_C$ the correct description is provided by $F_N$ and for a specific material one has Frank elastic constants $K_{10}$, $K_{20}$, and $K_{30}$. As $T$ approaches $T_C$ fluctuations in $\psi$ will lead to resistance against deformations, as they are not allowed in the smectic-A phase. This effect, which has been measured by D. Litster et al.\cite{1}, is the analogy of fluctuation diamagnetism in superconductors as first calculated by Schmid\cite{11}). This pretransitional analogy was pointed out by de Gennes\cite{12}).

The magnitude of the effect can be calculated using $F - F_N$; formally it leads to an increase of $K_2$ and $K_3$ of the order:

$$\delta K_2 = \frac{k_B}{(2\pi)^n} q_0^2 \left( \frac{\xi^2}{\xi_{||}} \right) \quad \xi_{||} = \frac{\sqrt{M_N}}{2\alpha}$$
The most striking advantage of the N → Sm-A phase transition in liquid crystals, as compared to the superconducting transition in metals is the possibility of probing the magnitude of the fluctuation in $\psi$ directly via x-ray measurements and thus follow the divergence of $\xi_\parallel$ and $\xi_\perp$ in the critical region. To see this one must calculate $S(\delta \mathbf{q}) = \langle |\rho(\mathbf{q})|^2 \rangle$, where $S(\delta \mathbf{q})$ is the scattering cross-section and $\rho(\mathbf{q})$ is the Fourier transform of the density. Around $\mathbf{q} = \mathbf{q}_0 = (0,0,2\pi/d)$ one finds via the relation between $\rho(\mathbf{r})$ and $\psi(\mathbf{r})$: $\langle |\rho(\mathbf{q})|^2 \rangle = \langle |\psi(\mathbf{q}-\mathbf{q}_0)|^2 \rangle$. Neglecting the fourth-order term, $F_N$, director fluctuations and phase fluctuations in (2.10) gives upon Fourier transforming and equipartition:

$$S(\mathbf{q}) = \frac{k_B T}{\alpha [1 + \xi_\parallel^2 (q_x-q_o)^2 + \xi_\parallel^2 q_y^2]}$$  \hspace{1cm} (2.12)

where: $q_\perp^2 = q_x^2 + q_y^2$ and $\xi_\parallel$, $\xi_\perp$ are defined as in the expressions for $\delta K_2$ and $\delta K_3$.

The Lorentzian structure factor reflects the Ornstein-Zernike form of $\langle \psi(0) \psi(\mathbf{r}) \rangle$:

$$\langle \psi(0) \psi(\mathbf{r}) \rangle \sim \frac{e^{-r/\xi}}{r}$$  \hspace{1cm} (2.13)

and clearly $\xi_\parallel$ is a measure of the range of correlation along the long axis of the molecule and $\xi_\perp$ measures the range of correlation perpendicular to the long axis of the molecules. High-resolution x-ray measurements have been performed on a number of bilayer smectic-A compounds (80CB, 8CB, CBOOA) by D. Lister et al.\(^1\). In these studies it was shown, however, that a fourth-order term $c \cdot \xi_\parallel^4 q_\perp^4$ in the denominator of $S(\mathbf{q})$ was essential in de-convoluting experimental data.
The analogy with superfluid helium manifests itself only in that this transition belongs to the same universality class \((d = 3, n = 2)\) as the \(N \leftrightarrow \text{Sm-A}\) transition. The R.G.T. predictions for this universality class gives for the divergence of \(\delta K_{2, 3}\) and \(\xi_{||, 1}^{12}\) and \(\xi_{1}^{19}\):

\[
\delta K_{2, 3} = \xi_{||, 1} = t^{-v}; t = \left(\frac{T - T_c}{T_c}\right)
\]

where the critical exponents \(v, \gamma,\) and \(n\) are predicted to be:

\[
\begin{align*}
v &= \gamma/(2-n) = 0.66 \\
\gamma &= 1.30 \\
n &= 0.04
\end{align*}
\]

The Landau approach, where \(a \sim (T - T_c)\), predicts the mean-field exponents

\[
\begin{align*}
v &= 0.5 \\
\gamma &= 1.0 \\
n &= 0.0
\end{align*}
\]

The detailed x-ray scattering experiments\(^1\) on 8CB, 80CB & CBOOA show that

\[
\nu_{||} = 0.70 \pm 0.04 > \nu_{\perp} = 0.60 \pm 0.04 \text{ and } \gamma = 1.30 \pm 0.04
\]

Thus \(\nu_{||}\) and \(\gamma\) are in agreement with the liquid He analogy, but \(\nu_{\perp}\) is not. This subtle difference between theory and experiment is currently under active study, theoretically as well as experimentally. On the theoretical side there are attempts to explore the effect of the Landau-Peierls instability on the critical behaviour. On the experimental side experiments on monolayer smectic-A materials like 40.8 and 885 are made in order to establish whether or not the tendency from the bilayer compounds is true also for the monolayer compounds.

In the experimental studies on 885 and the mixture 5CT\(_9\):7CB\(_x\):80CB\(_{91-x}\), the expression \(2.12\) has been used to analyze the data.
REFERENCES

3. PERFECT SINGLE-CRYSTAL TECHNIQUES IN TRIPLE-AXIS X-RAY DIFFRACTION

The development and use of perfect single crystals in triple-axis X-ray diffraction is fairly new. Specifically, the construction of monochromator crystals specially suited for the white synchrotron radiation is a new field, which has emerged in recent years parallel to the growth in synchrotron radiation facilities. This chapter will summarize the basic techniques employed in triple-axis X-ray diffraction, as it has been used at Risø at the rotating anode and at the DORIS synchrotron in Hamburg during the last three years.

3.1. The perfect crystals

A typical experimental set-up employed in triple-axis, elastic, X-ray diffraction is shown in Figure 3.1, where M is the monochromator and A the analyzer.

For a set-up like the one shown in Figure 3.1, one will almost always use identical crystals as monochromator and analyzer. There is generally no point in using a fixed good collimation on one side of the sample and a fixed bad collimation on the other. On the other hand, one can think of set-ups where an excellent fixed collimation, given by a perfect crystal on the incoming side of the sample, is matched with a slit-system on the outgoing side, which provides a continuously tuneable in-plane resolution. A set-up like this is optimal if one wants to look for weak reflections, since one can relax the collimation on the outgoing side until a reasonable signal can be obtained.
Table 3.1. Scattering angles for commonly used wavelengths and reflections. λ is the wavelength of the radiation, $k = \frac{2\pi}{\lambda}$, $d$ the distance between scattering planes, $a$ the length of the cubic unit cell vector and $\theta$ the Bragg angle.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>$\lambda/\AA$</th>
<th>$k/\AA^{-1}$</th>
<th>$\theta_{Si(111)}/\deg$</th>
<th>$\theta_{Si(220)}/\deg$</th>
<th>$\theta_{Ge(111)}/\deg$</th>
<th>$\theta_{Ge(220)}/\deg$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuK$_{a1}$</td>
<td>1.5405</td>
<td>4.0787</td>
<td>14.221</td>
<td>23.651</td>
<td>13.642</td>
<td>22.654</td>
</tr>
<tr>
<td>CuK$_{a2}$</td>
<td>1.5443</td>
<td>4.0686</td>
<td>14.257</td>
<td>23.713</td>
<td>13.677</td>
<td>22.713</td>
</tr>
<tr>
<td>CuK$_{a}$</td>
<td>1.5424</td>
<td>4.0736</td>
<td>14.239</td>
<td>23.682</td>
<td>13.656</td>
<td>22.683</td>
</tr>
<tr>
<td>CuK$_{b2}$</td>
<td>1.3810</td>
<td>4.5497</td>
<td>12.722</td>
<td>21.078</td>
<td>12.207</td>
<td>20.199</td>
</tr>
<tr>
<td>CuK$_{g}$</td>
<td>1.3866</td>
<td>4.5314</td>
<td>12.775</td>
<td>21.167</td>
<td>12.257</td>
<td>20.285</td>
</tr>
<tr>
<td>MoK$_{a1}$</td>
<td>0.7093</td>
<td>8.8583</td>
<td>6.495</td>
<td>10.644</td>
<td>6.234</td>
<td>10.215</td>
</tr>
<tr>
<td>MoK$_{a2}$</td>
<td>0.7135</td>
<td>8.8061</td>
<td>6.533</td>
<td>10.708</td>
<td>6.272</td>
<td>10.276</td>
</tr>
<tr>
<td>MoK$_{a}$</td>
<td>0.7114</td>
<td>8.8321</td>
<td>6.514</td>
<td>10.676</td>
<td>6.253</td>
<td>10.246</td>
</tr>
<tr>
<td>MoK$_{b1}$</td>
<td>0.6323</td>
<td>9.9370</td>
<td>5.787</td>
<td>9.478</td>
<td>5.555</td>
<td>9.096</td>
</tr>
<tr>
<td>MoK$_{b2}$</td>
<td>0.6210</td>
<td>10.1179</td>
<td>5.683</td>
<td>9.307</td>
<td>5.456</td>
<td>8.932</td>
</tr>
<tr>
<td>MoK$_{g}$</td>
<td>0.6267</td>
<td>10.0275</td>
<td>5.736</td>
<td>9.393</td>
<td>5.506</td>
<td>9.015</td>
</tr>
</tbody>
</table>
Fig. 3.1. A typical experimental set-up employed in triple-axis, elastic, X-ray diffraction.

The most commonly used crystals are silicon & germanium. Together they cover a rather wide range of resolution. The reflections most often used are Si(111), Si(220), and Ge(111). In Table 3.1 some useful information is given for several of the most frequently used wavelengths.
As shown in the next chapter, the in-plane resolution is determined by the \((\Delta \lambda/\lambda)\)-content and the shape of the direct beam profile for the two crystals. For two absolutely perfect crystals, the latter is determined by the Darwin width of the reflection, but also depends on whether the crystals are channel cut or not. In Figure 3.2 two channel-cut crystals are shown, together with the track of the X-rays. On the same figure what is meant by a direct beam profile is shown.

![Channel cut crystals. Direct beam profile. \(\theta_0\) is the Bragg angle corrected for refraction.](image)

3.2. Calculation of reflectivities and direct beam profiles

We have used \(m = 1\) and \(m = 3\) for \(\text{Si}(111)\) and \(\text{Si}(220)\) and \(m = 1\) for Ge. It is a straightforward calculation to derive the direct beam profile from dynamical diffraction theory. In several textbooks on X-ray diffraction, like the one of W.H. Zachariasen\(^1\)), one can find excellent accounts of this theory. Since this
theory is essential to the resolution considerations given in Chapter 4, I will briefly recall the essential results of dynamical diffraction theory, and also some numerical calculations will be presented.

The scattering geometry for diffraction in a perfect crystal is displayed in Figure 3.3, where a ray of wavevector \( \hat{k}_i \) is incident on the crystal surface and a ray of wavevector \( \hat{k}_o \) is diffracted from the crystal. (Bragg geometry)

![Fig. 3.3. Diffraction of a ray of wavevector \( \hat{k}_i \) by an asymmetrically cut crystal.](image-url)
As is shown in Figure 3.3 the scattering planes need not be parallel to the surface; there may be an angle \( \phi \) between the surface and the scattering planes. In dynamical diffraction theory this asymmetry is expressed by the asymmetry parameter \( b \),

\[
b \equiv \frac{n \cdot \hat{k}_i}{n \cdot \hat{k}_o}
\]

where \( \hat{n} \) is an inward unit vector normal to the surface. \( \hat{k}_i \) and \( \hat{k}_o \) are unit vectors along the incident and the diffracted rays, respectively.

The wavelength is connected to the kinematical Bragg angle \( \theta_B \) by:

\[
\lambda = 2d \sin \theta_B
\]

where \( d \) is the spacing of the diffracting planes.

Basically the dynamical diffraction theory predicts the following: A monochromatic beam incident on a perfect crystal will be almost totally reflected within a narrow angular range, the Darwin width. The center of this angular range \( \equiv \theta_0 \) will be displaced from the kinematical Bragg angle \( \theta_B \), and if the angle of incidence is \( \theta_i \) (\( \equiv \) angle between diffracting planes and incident ray), the angle of reflection \( \equiv \theta_r \) (\( \equiv \) angle between diffracting planes and diffracted ray) will be:

\[
\theta_r = \theta_B - b(\theta_i - \theta_B)
\]

Thus it is only for \( b = -1 \) (corresponding to \( \phi = 0 \)) that \( \theta_r = \theta_i \).

The physical origin of the displacement from \( \theta_B \) to \( \theta_0 \) is that even X-rays will be refracted slightly when entering a crystal. The existence of an angular range of almost total reflection is due to the contribution to the diffraction by only a finite number of layers, simply because the intensity in the incoming beam will decay much faster than dictated by true absorption, when the reflection condition is satisfied.
The following set of equations, taken from W.H. Zachariasen\(^1\), gives the reflectivity \( R_h(\theta) \) for the \( \bar{h} \)-reflection when true absorption in the crystal is taken into account.

\[
R_h(\theta) = \frac{(L - \sqrt{L^2 - (1 + 4\kappa^2))} \cdot \frac{1}{|c|}}{H}
\]

\[
L = |\sqrt{(y^2 - g^2 - 1)^2 + 4(g \cdot y - \kappa)^2} + y^2 + g^2|
\]

and

\[
y = \frac{(1-b) \cdot \psi_o^* + (\theta_B - \theta) \sin(2\theta_B)}{K|\psi_o^*| \sqrt{|b|}} \cdot \frac{b}{2}
\]

\(\theta\) is the angle of incidence.

\[
g = \frac{(1-b) \cdot \psi_o^*}{K|\psi_o^*| \sqrt{|b|}} ; \quad \kappa = \frac{-i}{\psi_o^*}
\]

\(\psi_o^*\), \(\psi^*_H\) & \(\psi^*_o\) are real quantities given by:

\[
\psi_o^* = -\Gamma \cdot P_o^* ; \quad \psi^*_o = -\Gamma \cdot P^*_o ; \quad \Gamma = \frac{r \cdot \xi^2}{w}
\]

\[
\psi^*_H = -\Gamma \cdot P^*_H ; \quad \psi^*_o = -\Gamma \cdot P^*_o
\]

\(P_o^* = P^*_o + i P^*_n\) is the structure factor for the \(H\)-reflection.
\[ (f_0 + \Delta f' + i \Delta f'') \cdot F_{\text{Geo}} \cdot e^{-M} \]

with the sum extending over the basis of the unit cell. \( r_j \) is the position of the \( j \)'th atom in the basis. \( r_e \) is the classical electron radius and \( v \) is the volume of the unit cell. \( f_0 = \) the atomic formfactor. \( \Delta f' \) & \( \Delta f'' \) are dispersion corrections to the atomic formfactor.

\( M \) is the Debye-Waller factor and \( K \) a polarization factor given by:

\[
k = \begin{cases} 
1 & \text{; polarization of incoming beam \( \perp \) to scattering plane} \\
|\cos(2\theta)| & \text{; polarization of incoming beam in the scattering plane} \\
\frac{1+|\cos 2\theta|}{2} & \text{; incoming beam unpolarized.}
\end{cases}
\]

The formula for \( R_+() \) in the Bragg geometry is valid for strong reflections, where \( \psi' \gg \psi'' \), provided that the crystal has a center of inversion and that \( F_{\text{Geo}} \) is calculated with the origin of the unit cell in this inversion center.

As mentioned earlier there are a number of general features of the reflection curves. From the above formulas\(^1\&4\) one may deduce the following:

Due to refraction the center of the reflection curves (corresponding to \( y = 0 \)) shown on Figure 3.4 is not identical to the kinematical Bragg angle, but is displaced towards higher angles: \( \theta_0 \) on Figure 3.4 is given by

\[
\theta_0 = \theta_B + (1 - 1/b) \cdot \frac{|\psi'|}{2 \sin(2\theta_B)}
\]

If the angle of incidence is \( \theta_i \) the angle of reflection \( \theta_r \) will be (see Figure 3.8)

\[
\theta_r = \theta_B - b(\theta_i - \theta_B)
\]
Thus, it is for the $b = -1$ case alone that $\theta_r = \theta_i$. A measure for the width of the reflection curves is the angular range for which $-1 < y < 1$, or explicitly:

$$2K|\psi_i| \over H \Delta \theta_i = \sqrt{|b|} \sin(2\theta_B)$$

and $\Delta \theta_r = |b| \cdot \Delta \theta_i$

where $i$ refers to angle of incidence and $r$ refers to angle of emergence.

Since $|\psi_i|$ depends critically on the wavelength $\lambda$ the reflection curves for higher-order reflections, like Si(333) and Si(440), will be displaced from the fundamental and have a different width. Furthermore, the parameter $b$ is freely adjustable and can be used to enhance the inherent properties of the reflection curves. Section 3.3 will show an example of this.

Table 2. Parameters used to calculate reflectivities. $f_0 \cdot \Omega$ (No. of electrons) for $8\cdot 0$.

<table>
<thead>
<tr>
<th></th>
<th>Si(111)</th>
<th>Si(220)</th>
<th>Ge(111)</th>
<th>Ge(220)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a/A$</td>
<td>5.4307</td>
<td>5.4307</td>
<td>5.65635</td>
<td>5.65635</td>
</tr>
<tr>
<td>$f_0$</td>
<td>11.2</td>
<td>8.75</td>
<td>27.1</td>
<td>23.6</td>
</tr>
<tr>
<td>$\Delta f'$</td>
<td>0.2</td>
<td>0.2</td>
<td>-1.3</td>
<td>-1.3</td>
</tr>
<tr>
<td>$\Delta f''$</td>
<td>0.4</td>
<td>0.4</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>$\lambda/A$</td>
<td>1.542</td>
<td>1.542</td>
<td>1.542</td>
<td>1.542</td>
</tr>
</tbody>
</table>
Fig. 3.4. Calculated reflectivities from Si/Ge(111/220); \( m = 1 \) & \( m = 3 \). Full lines correspond to (111)-reflections. Dotted lines correspond to (220)-reflections. a), c) & e): Si, b), d) & f): Ge. a), b) \( \hat{E} \parallel \) to scattering plane. c) & d) unpolarized incoming beam. e) & f) \( \hat{E} \parallel \) in the scattering plane.
With the scattering planes parallel to the surface, the asymmetry parameter \( b \) is \(-1\) and the reflectivity after \( m \) reflections in a channel-cut crystal is simply given by \((R(\theta))^m\). In Figure 3.4 the results of a numerical calculation are shown for \( m = 1 \) and \( m = 3 \) for three different polarizations of the incoming beam. i) The electric field \( \mathbf{E} \) parallel to the scattering plane, ii) unpolarized and iii) the electric field \( \mathbf{E} \) in the scattering plane. i) corresponds to a synchrotron with the scattering plane in the vertical plane, ii) to the rotating anode, and iii) to a synchrotron, with the scattering plane in the horizontal direction.

The calculations show that the reflectivity is asymmetric, square-like, and with a width which depends somewhat on \( m \). By performing the direct profile scan, it is the convolution of these curves with themselves (for identical \( M \) and \( A \)) one measures. The result of a numerical convolution of the reflectivities in Fig. 3.4 is shown in Figs. 3.5 and 3.6. In these same two figures, available data from experiments performed at Risø and in Hamburg are compared with the theoretical calculations. Since the spectrometer can step only 0.5 m deg, the data-points are rather scarce, especially for the Si(220)-reflections. This makes the normalization of the data to the calculated curves uncertain, but nevertheless the agreement is generally excellent and one can conclude that the crystals we have used are truly perfect.
Fig. 3.5. Calculated and measured direct beam profiles for Si(111/220). Full lines correspond to unpolarized incoming beam. (Rot. anode) Dotted lines correspond to \( \hat{E} \) in the scattering plane (DORIS). Filled points are data taken at DORIS. Empty points are data taken at the rotating anode.
Fig. 3.6. Calculated and measured direct beam profiles for Ge(111/220). Full lines correspond to unpolarized incoming beam. (Rot. anode). Dotted lines correspond to $E$ in the scattering plane (DORIS). Data points are taken at DORIS.
The width of the calculated curves is given in Table 3.3. For later reference these will be called D.B.-FWHM (Direct Beam FWHM).

Table 3.3. FWHM in mdeg of direct beam profiles for Si/Ge (111/220)-reflection. Note that (FWHM (l-pol) + FWHM (||-pol))/2 = FWHM (unpol). \( \lambda = 1.542 \text{ Å} \).

<table>
<thead>
<tr>
<th></th>
<th>Si(111)</th>
<th>Si(220)</th>
<th>Ge(111)</th>
<th>Ge(220)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m = 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>l-pol</td>
<td>2.80</td>
<td>2.10</td>
<td>6.12</td>
<td>4.82</td>
</tr>
<tr>
<td>un-pol</td>
<td>2.65</td>
<td>1.78</td>
<td>5.67</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-pol</td>
<td>2.48</td>
<td>1.45</td>
</tr>
<tr>
<td>m = 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>l-pol</td>
<td>1.95</td>
<td>1.45</td>
<td>4.24</td>
<td>3.43</td>
</tr>
<tr>
<td>un-pol</td>
<td>1.84</td>
<td>1.23</td>
<td>4.01</td>
<td>? 80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-pol</td>
<td>1.73</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The great advantage in using the channel-cut crystals is not the factor \( \sim 1.5 \) reduction in D.B.-FWHM one obtains when going from \( m = 1 \) to \( m = 3 \). So far we have dealt only with the reflectivity close to \( \theta_0 \). It is well known\(^1\)&\(^2\) that \( R(\theta) \), if the thermal motion of the atoms is included, has thermally diffuse wings going like \( e^{-\xi^2} \), where \( \xi \equiv \theta - \theta_0 \) or equivalently \( q^{-2} \); where \( q \equiv k - \tau \) (\( \tau \) is the relevant reciprocal lattice vector). Going from \( R(\theta) + (R(\theta))^3 \) will change the \( q \)-dependence of the reflectivity to \( q^{-6} \) and thereby also drastically influence the wings of the direct beam profile. Even though the direct beam profile is a convolution of reflectivities, this will not alter the \( q^{-6} \)-dependence very much.

In Figure 3.7 the investigation of the tails of the direct beam profile is shown for two sets of crystals: \( 2 \times \text{Si}(111); m = 3 \) and \( 2 \times \text{Si}(220); m = 3 \). One can clearly see the effect. It is this effect which has made it possible to probe the detailed lineshape of the smectic-A phase\(^3\).
3.3. Design and cutting of a monochromator crystal, especially suitable for white synchrotron radiation

The continuous spectrum of the synchrotron radiation has called for the need of monochromators, which are perfect and which can eliminate higher-order reflections. A recently developed solution to this problem is described in reference 4). The basic idea is to use either Silicone or Germanium, preferably (Si(111) or Ge(111), since the second harmonic is forbidden in this case, and cut a channel-cut crystal with one of the reflecting surfaces cut at an angle $\sim 5^\circ$ with respect to the scattering
planes, and furthermore introduce a weak link in the crystal, thereby making it possible to offset one of the reflecting surfaces, slightly. Figure 3.8 shows a lay-out for a Si(111) channel cut crystal of this kind.

As noted in the previous section the dependence of $\Delta \theta_1, \Delta \theta_r$, and $\theta_o$ on the wavelength, and the asymmetry parameter $b$, can be used to discriminate against higher orders. This is achieved with the arrangement in Figure 3.8. This is most easily seen by calculating the reflectivity curves for the two reflections in the channel-cut crystal. The result is shown in Figure 3.9.

It is clear from Figure 3.9 that the essential trick is to separate the reflectivity regions for higher-order reflections by letting the first crystal be cut asymmetrically.
Fig. 3.9. Calculated reflection curves for a double crystal as shown in Figure 7. Parts (a) and (b) give the intensity distributions tied to crystal C1 for incidence and emergence respectively. Part (c) for crystal C2 for incidence. Note that the curves for C2 are shifted with respect to the curves for C1, \( \Delta \beta = 0.001^\circ \), thus getting rid of the higher order (333)-reflection. The offset is facilitated by bending C2 using a piezoelectrical translator.
With $\Delta \beta \sim 1$ mdeg it is essential to be able to bend $C_2$ with high accuracy. This is obtained by letting a piezoelectrical translator, commercially available, push on the far end of $C_2$, as shown in Figure 3.8. The piezoelectrical device we used can be set continuously between $0-10$ $\mu$m by varying the voltage input from $0-1000$ volt. This gives a full range for $\Delta \beta$ of approximately $20$ mdeg for our final arrangement with the piezo-device $\sim 30$ mm from the weak link.

The disadvantage of the arrangement in Figure 3.8 is that, since the synchrotron radiation is white, a number of other reflections, $Si(\alpha, \beta, \delta); \alpha, \beta, \delta \neq 1,1,1$, may accidentally be reflected and be parallel to the $Si(111)$-reflection on the outgoing side. It is also clear that this effect is not present for $m = 1$ & $m = 3$ channel-cut crystals (see Figure 3.10).

![Fig. 3.10. A spurious reflection.](image)

Even though the above-mentioned so-called spurious reflections are parallel to $Si(111)$-reflection, they will be spatially separated as shown in Reference 4 and a slit system on the outgoing side of crystal can separate these from $Si(111)$.
For the kind of diffraction experiments reported on in this thesis it has not been necessary to eliminate higher-order reflections. The elimination of higher-order reflections is crucial in experiments like EXAFS. For future use I have cut a crystal like the one in Figure 3.8. This was done using a diamond saw in HASYLAB in Hamburg.

After cutting, the crystal must be etched in order to remove surface impurities and dislocations. The etching procedure is done in the following steps:

i) Cleaning: This is done by putting the crystal in sulphuric acid for ~ 12 hours.

ii) Etching: After cleaning in sulphuric acid the crystal is flushed with distilled water and acetone and lastly flushed with methanol. When the crystal is dry it is etched by putting it in a solution of 95% HNO₃ and 5% HF (volume concentration), without touching the crystal with one's fingers. The total amount of solution should not be less than 30 ml per cm² of crystal. During etching, which takes approx. 1/2 hour, it is essential to rotate and "bump" the plastic container with crystal and solution all the time. This ensures that the crystal is turned around in the solution, thus getting a uniform etching; furthermore, the "bumping" will remove air bubbles that continuously form on the crystal surface. If these bubbles are not removed the crystal surface will resemble orange peel afterwards, with small grooves all over the surface. Also the crystal should not contact the air above the solution. The whole etching procedure must take place in a ventilated-fume cupboard and every now and then the tightly closed plastic container must be opened to remove the pressure. After etching, the crystal is flushed with acetone and distilled water. The final crystal is shown in Figure 3.11.
Fig. 3.11. The crystal cut and etched in Hamburg. Dimensions in mm.
REFERENCES

4. THE RESOLUTION OF THE TRIPLE-AXIS SPECTROMETER

The perfect crystals with Darwin widths $= 1$ mdeg, provide a high resolution of the triple-axis spectrometer in the scattering plane. This chapter is dedicated to the calculation of the resolution function of the triple-axis spectrometer, when the set-up is as shown in Figure (3.1) in Chapter 3. It will be assumed throughout that the scattering in the sample is elastic and that the monochromator crystal is identical to the analyzer crystal.

4.1. Introduction

The resolution one will obtain depends on the following:

i) The characteristics of the source (spectral distribution, collimation of radiation, etc.) and slit system before the monochromator.

ii) The monochromator crystal and the analyzer crystal.

iii) Collimators and slits in the vertical plane. Note no collimators and slits are necessary in the scattering plane, as the crystals also provide the collimation in the scattering plane apart from monochromatization.

iv) The sample and the scattering angle $\theta_s$.

The resolution function is generally defined via the expression for the measured intensity, when the spectrometer is set to measure at point $\mathbf{q}$ (often close to a reciprocal lattice vector $\mathbf{q}_o$):

$$ I(\mathbf{q}) = \int S(\mathbf{q} - \mathbf{q}') R(\mathbf{q}', \mathbf{q}_o) d\mathbf{q}' $$

where $R$ is the resolution function and $S$ the scattering cross-section. Expression (4.1) states, simply that $R(\mathbf{q}', \mathbf{q}_o)$ is the probability of detecting a scattering process at $\mathbf{q}'-\mathbf{q}$ when the
spectrometer is set to detect scattered radiation at \( \mathbf{q} \) (close to \( \mathbf{q}_0 \)).

\( R(\mathbf{q}', \mathbf{q}_0) \) can be decomposed into two uncorrelated contributions, the out-of-plane, vertical, resolution \( R_v(q_0^v) \) and the in-plane resolution \( R_i(q_i^v) \).

The in-plane resolution is determined by i), ii), and iv) and the out-of-plane resolution, the vertical resolution, will be determined by iii). Note that \( R \) generally varies throughout reciprocal space, indicated by the \( \mathbf{q}_0 \) in the argument.

4.2. The in-plane resolution

The finite energy-bandwidth of the incoming radiation (i) and the finite collimations in the scattering plane (ii), make it impossible to set the spectrometer to detect radiation of one energy \( E \) at one point in reciprocal space \( \mathbf{q} \). There will always be a certain amount of uncertainty in the direction and the magnitude of the detected wavevector \( k \) in the scattering plane. This uncertainty, or probability distribution, can be separated into two contributions: one tied to the monochromator and another, similarly, tied to the analyzer crystal\(^1\). Once these two contributions are calculated it is possible to combine them using the condition of elastic scattering in the sample, to a final in-plane resolution function \( R_i \).

In the following it will be assumed that all probability distributions are Gaussian, thus making it possible to use the concepts of half contour ellipses and conjugate diameters\(^1\).

The basic problem is then to calculate the conjugate diameters \( X_1, X_2 & X_3, X_4 \) in the language of reference 1 \& 2. The perfect crystal set-up is shown in Figure 4.1. \( \sigma_0, \sigma_1 \) are the effective in-plane collimations before and after the monochromator, respectively. Similarly \( \sigma_3, \sigma_4 \) are the collimations before and after the analyzer crystal. To be specific \( \sigma_0, \sigma_1, \sigma_3, \sigma_4 \) are
defined by the probability expression for a ray deviating \( u \) degrees from the central ray:

\[
P(u) = e^{-\frac{1}{2} \left( \frac{u}{\sigma_{0,1,3,4}} \right)^2}
\]

As there are no collimators between the monochromator and the sample, \( \sigma_1 \) is determined by the size of the sample or the monochromator drum-exit slit and the distance between the monochromator and the sample.
The collimations before and after the analyzer crystal are determined in a manner analogous to \( \sigma_1 \). Thus, generally \( \sigma_1, \sigma_3, \) and \( \sigma_4 \) represent wide angular acceptance collimators, compared to the angular acceptance of a monochromatic beam by a perfect crystal. Representing the square-like reflectivity curves in Figure 3.4 in Chapter 3 by Gaussian functions with the same FWHM, one can introduce, the probability of transmission of a photon of wavevector \( k \) in a perfect crystal as:

\[
P(m) = e^{-\frac{m^2}{2\sigma_D^2}}
\]

where \( m \) is the deviation from the Bragg angle corrected for refraction \( \equiv \theta_0 \) (see Chapter 3) and according to the above:

\[
\sigma_{1,3,4}^2 \gg \sigma_D^2
\]

The characteristics of the source, specifically the energy content of the emerging radiation, play a significant role. In this respect, the synchrotron source and the rotating anode, or simply the X-ray tube, represent two extreme cases. At the synchrotron, where the wavelength of the emerging radiation extends over several decades, one may essentially treat the source as white or in the appropriate language as follows. The probability of emergence of a photon of wave \( k+\Delta k \), where \( k \) is the mean \( k \)-value picked out by the monochromator crystal, can formally be written as

\[
P(\Delta k) = e^{-\frac{(\Delta k)^2}{2k^2\sigma_{k-s}^2}}
\]

where \( \sigma_{k-s}^2 \gg \sigma_{0,1,3,4}^2 \). The subscript \(-s\) in \( \sigma_{k-s} \) refers to the source. Since the synchrotron radiation is white, the degree of monochromatization in the monochromator is determined by \( \sigma_0 \), which is given by the distance between the source and monochromator, and the spot size or width of the beam-defining slit (whichever is larger. See Fig. 4.6). With a typical distance of 20 m (DORIS-HASYLAB) between the source and monochromator and a typical source size/width of beam-defining slit of 2-5 mm, one sees that at the synchrotron:
At the rotating anode the characteristic $k\alpha_1$, $k\alpha_2$, $k\beta$, ... lines of the anode material are sharply confined in energy or $k$, and for a rotating anode:

$$\sigma_0^2 \ll \sigma_{1,3,4}^2$$  \hspace{1cm} (4.6)

Also it is essentially to note that before the monochromator the slit system usually served only to help separate $k\alpha_1$- from $k\alpha_2$- radiation and thus all of the collimations represented by $\sigma_0$, $\sigma_1$, $\sigma_3$, and $\sigma_4$ obey:

$$\sigma_{0,1,3,4}^2 \gg \sigma_D^2$$  \hspace{1cm} (4.8)

The above considerations are summarized in Table 4.1.

**Table 4.1. Relations among the essential parameters determining the resolution function at the synchrotron and at the rotating anode.**

<table>
<thead>
<tr>
<th>Synchrotron</th>
<th>Rotating anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{k-s}^2 \gg \sigma_{0,1,3,4}^2 \gg \sigma_{0,D}^2$</td>
<td>$\sigma_{0,1,3,4}^2 \gg \sigma_{k-s,D}^2$</td>
</tr>
</tbody>
</table>

From Table 4.1 one sees that at the synchrotron the essential parameters are $\sigma_0$ and $\sigma_D$, while at the rotating anode the essential parameters are $\sigma_{k-s}$ and $\sigma_D$, results which agrees with what one would expect a priori. In the next section the conjugate diameters $\chi_1, \chi_2, \chi_3$ and $\chi_4$ are determined using the above relations.
4.3. Calculation of $X_1$, $X_2$, $X_3$, $X_4$ - the conjugate diameters

The following calculation is based on lecture notes from summer-school in Vienna 1980 on "X-ray scattering with synchrotron radiation". The notes are written by Dr. J. Als Nielsen and deals with resolution in diffraction. During the summer school it became clear that the results for the conjugate diameters for the case of an imperfect crystal with a mosaicity distribution much broader than the Darwin width, could not be carried over directly to the case of a perfect crystal with only the Darwin range of reflectivity. What follows is a calculation of the conjugate diameters for the perfect monochromator crystal and the perfect analyzer crystal. The calculation of the conjugate diameters is based on the method outlined in the above-mentioned notes.

Starting with the monochromator crystal and assuming that the Darwin width is zero gives the situation in Fig. 4.2a, for the central ray and a slightly deviating one.

One has generally:

$$P(u) = e^{-1/2 \left( \frac{u}{\sigma_M^2} \right)^2 - 1/2 \left( \frac{u \cdot \cot \theta_M}{\sigma_{k-s}} \right)^2} ; \quad \sigma_M^2 = \frac{\sigma_k^2 \sigma_0^2}{\sigma_k^2 + \sigma_0^2}$$

where it is used that $\Delta k = k \cdot u \cdot \cot \theta_M$. Using the relations in Table 4.1 one gets at the two sources of interest:

Synchrotron: $P(u) = e^{-1/2 (u/\sigma_0)^2}$

Rot. anode: $P(u) = e^{-1/2 \left( \frac{u}{\sigma_{k-s}/\cot \theta_M} \right)^2}$

(4.9)

Giving the conjugate diameter $X_1$ parallel to the scattering planes (Als-Nielsen 1980):
Fig. 4.2. a) Negligible Darwin width. b) Finite Darwin width.
Introducing a Darwin width \( \neq 0 \) or equivalently \( \sigma_D \neq 0 \) gives the picture in Figure 4.2b, provided that the asymmetry parameter of the reflection \( \varepsilon b = -1 \) (see Chapter 3, Section 3.2). Maintaining \( \chi_1 \) as one of the conjugate diameters the direction and magnitude of the other \( \chi_2 \), can be found by looking at the probability distribution \( P(u,m) \) (see Figure 4.2b).

\[
P(u,m) = e^{-\frac{u+m}{\sigma_0} - \frac{m^2}{\sigma_D} - \frac{u^2}{\sigma_{K-S}/\cot \theta_M}},
\]

(4.11)

Using the relation \( \sigma_{K-S}^2 \gg \sigma_0^2 \gg \sigma_D^2 \) for the synchrotron and the relation \( \sigma_{0,1}^2 \gg \sigma_{K-S}^2 \) for the rotating anode, one gets:

\[
\text{Synchrotron: } P(u,m) = e^{-\frac{u+m}{\sigma_0} - \frac{m^2}{\sigma_D}} - \frac{u^2}{\sigma_{K-S}/\cot \theta_M},
\]

\text{Rot. anode: } P(u,m) = e^{-\frac{u}{\sigma_{K-S}/\cot \theta_M} - \frac{m^2}{\sigma_D}} - \frac{u+m}{\sigma_M}.
\]

These two expressions may be brought on a common form:
The direction and magnitude of the other conjugate diameter $X_2$ can now be found by letting $u = \gamma m$ and setting $m = C \cdot \sigma_D$; $C = 2 \sqrt{2} \sigma_D$.

For the synchrotron this leads to the following:

$$u = -m \Rightarrow u + m = 0$$

Noting that $\Delta k = k \cot \theta_M$ one gets that $X_2$ for the synchrotron is along $k$ with a magnitude:

$$X_{2, \text{syn}} = C \cdot k \cdot \sigma_D \cdot \cot \theta_M$$ \hspace{1cm} (4.12)

For the rotating anode one gets:

$$u = \gamma m \Rightarrow u = 0$$

Noting again that $\Delta k = k \cot \theta_M$ one gets that $X_2$ for the rotating anode is perpendicular to $k$ with a magnitude:

$$X_{2, \text{rot.anode}} = C \cdot k \cdot \sigma_D$$ \hspace{1cm} (4.13)

Table 4.2 and Figure 4.3 summarize the result for the conjugate diameters for the monochromator at the synchrotron and at the rotating anode.
Table 4.2. The conjugate diameters for the monochromator at the synchrotron source and at the rotating anode.

<table>
<thead>
<tr>
<th></th>
<th>( x_1 )</th>
<th>dir. of ( \vec{x}_1 )</th>
<th>( x_2 )</th>
<th>dir. of ( \vec{x}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synchrotron</td>
<td>( C \cdot \frac{k_0}{\sin \theta_M} )</td>
<td>along scatt. planes</td>
<td>( Ck_0 \cot \theta_M )</td>
<td>along ( \vec{k} )</td>
</tr>
<tr>
<td>Rotating anode</td>
<td>( C \cdot \frac{k_0 k - 1}{\sin \theta_M} )</td>
<td>(- -)</td>
<td>( Ck_0 \dot{D} )</td>
<td>( \perp ) to ( \vec{k} )</td>
</tr>
</tbody>
</table>

Fig. 4.3. The conjugate diameters \( \vec{x}_1 \) & \( \vec{x}_2 \) at the synchrotron and at the rotating anode.
Concerning the difference between the two sources it is inter-
esting to notice that if one transforms the \( \hat{x}_{1, \text{syn}}, \hat{x}_{2, \text{syn}} \) set
of conjugate diameters to a \( \hat{x}_{1, \text{syn}}, \hat{x}_{2, \text{syn}} \) set, where \( \hat{x}_{2, \text{syn}} \perp \hat{k} \)
just like \( \hat{x}_{2, \text{rot.anode}} \perp \hat{k} \), one finds, by using the formulae in
Appendix B, that if \( \sigma_0^2 \gg \sigma_D^2 \):

\[
\hat{x}'_{1, \text{syn}} = C \cdot \frac{\sigma_0}{\sin \theta_M}; \quad \hat{x}_1 \parallel \text{scatt. planes}
\]

\[
\hat{x}'_{2, \text{syn}} = C \cdot \sigma_D; \quad \hat{x}_2 \perp \hat{k}
\]

or exactly the same as at the rotating anode. The only differ-
ence is that \( \sigma_{k-s}/\cot \theta_M \) is substituted with \( \sigma_0 \). This result tells
us that if \( \sigma_D \) represents the most narrow collimation in the
whole set-up, then the two sets of conjugate diameters are alike
except that \( \sigma_0 \) plays the role of \( \sigma_{k-s}/\cot \theta_M \) and vice versa. This
is a perfectly reasonable and expected result.

For the analyzer crystal, the analogue of \( \sigma_0 \) is \( \sigma_4 \) and the ana-
logue of \( \sigma_{k-s} \) is the energy discrimination of the detector
\( \equiv \sigma_{k-d} \), where subscript \( -d \) refers to detector. Thus, for a scin-
tillation detector one has:

\[
\sigma_{k-d}^2 \gg \sigma_D^2 \quad \text{and} \quad \sigma_{3, 4}^2 \gg \sigma_D^2
\]

which in accordance with the above gives the conjugate diameters
\( \hat{x}_3, \hat{x}_4 \) or \( \hat{x}'_3, \hat{x}'_4 \) for the analyzer crystal, where:

\[
\hat{x}_3 = "\sigma" \quad \text{(or rather} \hat{x}_3 \gg \hat{x}_{1, 2, 4}) \quad ; \quad \hat{x}_3 \parallel \text{scatt. planes}
\]

\[
\hat{x}_4 = C \cdot \sigma_D \cdot \cot \theta_M \quad ; \quad \hat{x}_4 \parallel \hat{k}
\]

or equivalently:
$X_3^i = \text{"" (see above)}$ \quad ; \quad \hat{X}_3 \text{ is parallel to scatt. planes}

$X_4^i = C \cdot \kappa \cdot \sigma_D$ \quad ; \quad \hat{X}_4 \perp \hat{k}$

**Fig. 4.4.** The four different configurations of the spectrometer.
The orientation of the two ellipses, the \(X_1\), \(X_2\)- and \(X_3\), \(X_4\)-ellipses, relative to each other is determined by the configuration of the triple-axis spectrometer. There are four different configurations of the spectrometer. These are shown in Figure 4.4. 1 & 2 will be called nondispersive or parallel set-ups and 3 & 4 will be called dispersive- or antiparallel set-ups. For each configuration two rays are shown Bragg reflected in \(M\), \(S\), and \(A\). For these reflections it is assumed that \(\varnothing = 0\). This uniquely determines how the sample and analyzer must be rotated in order to allow the ray of wavelength \(\lambda + \Delta \lambda\) to be transmitted through the system, and evidently \(\Delta \theta_M\) and \(\Delta \theta_S\) is related to \(\Delta \lambda\), \(\theta_S\) and \(\theta_M\) by:

\[
\Delta \theta_M = (\Delta \lambda/\lambda) \cdot \tan \theta_M; \quad \Delta \theta_S = (\Delta \lambda/\lambda) \cdot \tan \theta_S; \quad \Delta \theta_S = \text{tan} \theta_5 = \text{tan} \theta_{5e}/\text{tan} \theta_M \cdot \Delta \theta_M.
\]

The in-plane resolution will, apart from \(X_1\), \(X_2\), \(X_3\), \(X_4\), also depend on which set-up is chosen.

4.4. Combination of the two resolution ellipse in the synchrotron case

The two resolution ellipses must be combined under the condition of elastic scattering in the sample and it is straightforward, though somewhat lengthy, to combine the two resolution ellipses. Therefore, the detailed combination is derived in Appendix D in the synchrotron case, where general formulae for the in-plane resolution are given. It is a simple matter to carry over the result to the rotating anode case. In fact, as we have seen, if \(\varnothing_0^2 \gg \varnothing_0^2\) at the rotating anode, the results are readily applicable if \(\varnothing_0\) for the synchrotron is substituted with \(\varnothing_0^2/\cot \theta_M\) for the rotating anode. The result is expressed in terms of the two conjugate diameters \(Y_1\) and \(Y_2\) and angles \(\alpha\) and \(\delta\) (see Figure 4.5).

As expected, the resolution function depends only on \(\varnothing_S\), \(\varnothing_M\), \(\varnothing_0\), \(\varnothing_D\) and the set-up that is chosen. It is easy to derive expression for \(Y_1\), \(Y_2\), \(\alpha\) & \(\delta\) in a number of limits, from the general formulae of Appendix D. Among the interesting limiting cases at the synchrotron are the ones in Table 4.3. Since one often deals with the limit \(\varnothing_\delta^2 \gg \varnothing_0^2\) in practice, I have concentrated on
this. For example, at DORIS $q_0 = 4 \text{ mm}/20 \pi = 0.2 \text{ mrad} \sim 11 \text{ mdeg}$ (see next chapter) and $a_{Si(111)} = 2 \text{ mdeg}$.

![Diagram](image)

**Fig. 4.5.** A schematic drawing of the in-plane resolution ellipse. The conjugate diameters $\hat{y}_1, \hat{y}_2$, $s$ = the angle from $\hat{q}_0$ to $\hat{y}_1$ going counterclockwise and $a$ = the angle from $\hat{y}_1$ to $\hat{y}_2$ going counterclockwise, determines the ellipse relative to $\hat{q}_0$.

It is obvious from Table 4.3 that one will choose one of the two non-dispersive set-ups if $\theta_s \ll \theta_M$, and only if $\theta_s = \theta_M$ will one choose the $++$ configuration.

In the case of the liquid crystal set-up, where $\theta_s \ll \theta_M$ and where $\theta_M \ll \pi/2$ for $\text{Si}(111/220)$ and Cu-$k\alpha$-radiation, a rather good approximation to $R_I$ can be obtained by neglecting the lack of parallelism of $y_1$ with the $q_\|$-axis. In this case $R_I$ can be written:

$$R_I = R(q_\|) \cdot R_T(q_T)$$
Table 4.3. Interesting limiting cases of the resolution ellipse. $\hat{Y}_1$ & $\hat{Y}_2$ are the conjugate diameters of the resolution ellipse. $\delta$ = angle from $q_0$ to $\hat{Y}_1$ going counterclockwise. $\alpha$ = angle from $\hat{Y}_2$ to $\hat{Y}_1$ going counterclockwise. $k$ is the wavevector and $C = 2\sqrt{2}\cdot\tan 2$.

<table>
<thead>
<tr>
<th>Conf.</th>
<th>limit</th>
<th>$Y_1^2$</th>
<th>$Y_2^2$</th>
<th>$\alpha$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+++- 1</td>
<td>$\sigma_0^2 \gg \sigma_D^2$</td>
<td>$\sigma_0^2 \gg \sigma_D^2$</td>
<td>$(2Ck\cdot\frac{\sin \theta_S}{\sin \theta_M})^2$</td>
<td>$2\cdot(C\cdot k\sigma_D)^2$</td>
<td>$\theta_M$</td>
</tr>
<tr>
<td>+++- 2</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
</tr>
<tr>
<td>+++- 3</td>
<td>$\sigma_0^2 \gg \sigma_D^2$</td>
<td>$\sigma_0^2 \gg \sigma_D^2$</td>
<td>$(C\cdot k\cdot \sigma_D)^2$</td>
<td>$(C\cdot k\cdot \sigma_D)^2$</td>
<td>$2\theta_S$</td>
</tr>
<tr>
<td>+++- 4</td>
<td>$\sigma_0^2 \gg \sigma_D^2$</td>
<td>$\sigma_0^2 \gg \sigma_D^2$</td>
<td>$(2Ck\sigma_0)^2$</td>
<td>$0$</td>
<td>irrelevant</td>
</tr>
</tbody>
</table>

where $R_T(q_T)$ is a delta function and $R^*(q^*)$ is a Gaussian with width $Y$ given by:

$$Y^2 = 2(C\cdot k\sigma_D)^2 + (2Ck\sigma_0 \cdot \frac{\sin \theta_S}{\sin \theta_M})^2; \quad C = 2\sqrt{2}\cdot\tan 2$$

$R^*$ then corresponds to a convolution of the direct beam profile, the first term, with the $\Delta\lambda/\lambda$-contribution (as it will be called), the second term.

Since $\theta_M \ll \pi/2$ the second term can further be approximated by:

$$2\cdot(C\cdot \sigma_0 \cdot k \cdot \frac{\sin \theta_S}{\sin \theta_M})^2 = (2\Delta \theta_M \cdot k \cdot \frac{\tan \theta_S}{\tan \theta_M})^2 = (2\Delta \theta_M \cdot k)^2$$

where $\Delta \theta_S$ and $\Delta \theta_M$ are defined in Figure 4.4. and $\Delta \theta_M$ is set to be $C\cdot \sigma_0$, or in words, $\Delta \theta_M$ is the FWHM of the angular acceptance.
of the slit system before the monochromator. As mentioned earlier, if $a^2_k - a^2_\text{D}$ for the rotating anode, one can substitute $a_0$ with $a_k - a_\text{D}/\cot \theta_\text{M}$ in the above formula. Doing so gives the same result as above, with $\Delta \theta_\text{M} = \tan \theta_\text{M} \cdot (\Delta \lambda/\lambda)_{\text{FWHM}}$, where $(\Delta \lambda/\lambda)_{\text{FWHM}}$ is the FWHM-$\lambda$ content of the specific anode line.

Within the above-mentioned approximation, $R_m$ can be measured. This can be seen from Figure 4.4. If the sample is left out in either of configurations 1) or 2), scanning the analyzer-crystals will give the direct beam profile. The $\lambda$-content will not broaden this curve. Leaving out the sample in any of 3) or 4) will give $\Delta \theta_\text{M}(\text{FWHM})$, or equivalently at the rotating anode, $(\Delta \lambda/\lambda)_{\text{FWHM}}$ provided that $(2 \cdot \Delta \theta_\text{M}(\text{FWHM}))^2 \gg (\text{D.B.-FWHM})^2$ or equivalently at the rotating anode $(2 \cdot \Delta \lambda/\lambda(\text{FWHM}) \tan(\gamma_\text{M}) \cdot 180/\pi)^2 \gg (\text{D.B.-FWHM})^2$. If $\Delta \theta_\text{M}(\text{FWHM})$ has been measured in this way, the line distribution & from Appendix D, can be obtained by scaling the abscissa with the ratio $\tan \theta_s/\tan \theta_\text{M}$. If $2 \Delta \theta_s \gg \text{D.B.-FWHM}$ one may directly measure the line distribution. This cannot be done with liquid crystal samples since $2 \Delta \theta_s \sim \text{D.B.-FWHM}$. To check the scaling procedure one can put in a perfect crystal, as sample, with a Bragg angle fulfilling the condition that $(2 \Delta \theta_s, \text{test})^2 \gg (\text{D.B.-FWHM})^2$. One can then scale the abscissa of these data with the ratio $\tan \theta_s/\tan \theta_s, \text{test}$, which is the procedure normally used in case of the liquid crystal set-up.

These detailed measurements may reveal non-Gaussian behaviour of the two elements contributing to $R_i$. Depending on the wanted degree of accuracy, it is reasonable to assume that it is still a good approximation to represent $R_m$ by a convolution of the two contributions (the direct beam profile and $\Delta \lambda/\lambda$-line distribution).

4.5. The out-of-plane resolution

The out-of-plane resolution is not correlated to the in-plane resolution and can be calculated independently. $R_v(q_v, q_\text{O})$ is determined by the out-of-plane divergence of the beam on either side of the sample. This divergence can be calculated as shown
in Figure 4.6, that is, in case the divergence is determined by two slits only. If the trapezoidal curve in Figure 4.6 is approximated with a Gaussian of $FWHM = \sigma_{i,v}$ for the incoming side and a $FWHM = \sigma_{o,v}$ for the outgoing side, then the out-of-plane resolution function is a convolution of two Gaussians, yielding a Gaussian of $FWHM = \sqrt{\sigma_{i,v}^2 + \sigma_{o,v}^2}$.

**Fig. 4.6.** The angular acceptance of a two-slit system.
Note that the FWHM is given by the largest slit only.

The resolution function is now determined in terms of the in-plane resolution function $R_i$ and the out-of-plane resolution function $R_o$. One more contribution may be added to the total resolution function if the sample is imperfect. The effect of mosaicity in the sample is to add an extra component to the in-plane resolution in the transverse direction and to add an extra one to the out-of-plane resolution as outlined in Appendix E.

4.6. The resolution for a typical liquid crystal set-up

To make the previous considerations concrete one can take one of the two nondispersive set-ups at the rotating anode and put in a liquid crystal sample, like 80CB ($q_o = 0.197 \text{ Å}^{-1}$), and try to
see what resolution this will give if the radiation is CuK$_{\alpha 1}$-radiation and $M \equiv A = \text{Si}(220)$; $m = 3$. For this set-up, the following conditions approximately apply:

$$\frac{2}{s-k} \gg \frac{2}{D}; \theta_s \ll \theta_M \ll \frac{\pi}{2}.$$ 

From Appendix E and Section 4.4 it is clear that the transverse in-plane resolution is given by the mosaicity and for intensity reasons one will have to open up the vertical slits to get a large vertical resolution $R_v$. $R_v$ is, as noted earlier, approximately a convolution of the direct beam profile and the $(\Delta \lambda/\lambda)$-contribution. For a realistic calculation the mosaicity $M_T$ is assumed to be Gaussian with FWHM = 0.00515 Å$^{-1}$ and $R_v$ is assumed to be Gaussian with FWHM = 0.00807 Å$^{-1}$. (see Table 4.4, where functions and parameters are given for the resolution function at $q_Q$ and $2q_Q$.)

The longitudinal resolution function $R_\ell$ has been experimentally measured by performing a direct beam profile scan, putting in a perfect Si(111)-crystal as test-sample, and rotating the analyzer crystal. The Si(111)-crystal was rotated along with the analyzer-crystal, the ratio of rotations being $-2 \tan \theta_{\text{Si}(111)}/(\tan \theta_{\text{Si}(220)} - \tan \theta_{\text{Si}(111)})$ (see Figure 4.4). In Figure 4.7 the scaled Si(111)-data numerically convoluted with the direct beam profile, is compared with two analytic curves. The sharpest one approximates the experimental data well down to $\sim 10\%$ of the peak-value. This curve is simply the convolution of two Gaussians, one with the width $\equiv \alpha$ of the direct beam profile and one with the width $\equiv \beta$ of the scaled Si(111)-curve. The convolution gives a Gaussian with width $= \sqrt{\alpha^2 + \beta^2}$. The second curve, which approximates the experimental points quite well down to $10^{-3}$ of the peak-value is a convolution of a Gaussian with the width of the direct beam profile and an exponential which describes very well the scaled Si(111)-curve. The parameters are given in Table 4.4. Figure 4.8 shows the result and two components of this convolution, together with experimental points. Clearly the exponential wings of $R_\ell$ seems to be a property of the natural lineshape of the CuK$_{\alpha 1}$-line. Theoretically the lineshape should have the form:
Fig. 4.7. The longitudinal resolution function. The points are the direct beam profile convoluted, numerically, with the scaled Si(111)-data, giving the ($\Delta \lambda / \lambda$)-contribution. The two curves are analytical approximations. See text.

$$I(\lambda) = \frac{a}{b + \left(\frac{1}{\lambda} + \frac{1}{\lambda_0}\right)^2}$$

where $\lambda_0$ is the nominal CuK$_{\alpha 1}$ wavelength and $a$ & $b$ are constants. With $(2\cdot\text{FWHM of the unscaled Si(111)-data})^2 \gg (\text{D.B.-FWHM of the two Si(220); } m = 3\text{-crystals})^2$ the unscaled (and scaled) Si(111)-data should be a Lorentzian intensity distribution versus the offset-angle $\Delta \theta$.
Fig. 4.8. The result and the two components of the longitudinal resolution function. Measured points and analytic curves. Parameters for the analytic curves are given in Table 4.4.

\[
\Delta q_z \equiv q_z - q_0 \quad (\text{Å}^{-1})
\]

\[
\begin{align*}
I(\Delta \theta) &= \frac{4\pi^2 a}{4\pi^2 b + (k-k_0)^2} \\
&= \frac{a}{\cot^2 \theta_M} \cdot (\Delta \theta)^2 \quad ; \quad \Delta k \equiv k-k_0 = k_0 \cdot \cot \theta_M \Delta \theta \\
\Delta \theta &= \theta - \theta_M
\end{align*}
\]
The reason for the apparent exponential lineshape is unclear. An attempt to fit the unscaled Si(111)-data to a Lorentzian is unsuccessful. The goodness of fit parameter $\chi^2 = 2.9 \times 10^4$.

It is often unnecessary to know the resolution function accurately down to $10^{-3}$ of the peak-value. In these cases one can use the Gaussian approximation. At the synchrotron the $(\Delta \lambda/\lambda)$-contribution will probably not have the exponential wings and in this case the Gaussian approximation may be better than at the rotating anode.

Fig. 4.9. Experimental points and analytical curves for the longitudinal resolution function at $\xi = \xi_0$ and $\xi = 2\xi_0$. Filled points are for $\xi = 2\xi_0$.
Figure 4.9 shows \( R^* \) at \( q_0 \) and at \( 2q_0 \). Experimental data are shown together with the analytic curves used to deconvolute exp. data.

The typical functions and parameters from Table 4.4 are the ones used to calculate experimental line shapes in Chapter 8. This calculation has not used (4.1) directly in the numerical convolution. This is so because no analytical form of \( S(q) \) is known, but the Fourier transform \( G(r) \) is known (Appendix A). Therefore, the convolution was performed in real space, using the folding theorem, followed by a Fourier transformation (see also Ref.3).
Table 4.4. A typical resolution for high-solution liquid crystal X-ray experiments at the rotating anode.

<table>
<thead>
<tr>
<th>Res.fct.</th>
<th>ANALYTICAL FORM</th>
<th>Parameters</th>
<th>FWHM (in q-space)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transverse $R_T$</td>
<td>$q - q_0$</td>
<td>$q - 2q_0$</td>
<td>$\sigma_T = 0.0111 \cdot q_0 = 2.1867 \cdot 10^{-3} \text{ Å}^{-1}$</td>
</tr>
<tr>
<td>Vertical $R_V$</td>
<td>$-q^2/2q_0^2 e^{-q^2/2q_0^2}$</td>
<td>$-q^2/2q_0^2 e^{-q^2/2q_0^2}$</td>
<td>$\sigma_V = 0.0174 \cdot q_0 = 3.4278 \cdot 10^{-3} \text{ Å}^{-1}$</td>
</tr>
<tr>
<td>Longitudinal $R_L$</td>
<td>convolution of: $-q^2/2q_0^2$ and $-\sqrt{2}</td>
<td>q</td>
<td>=1 e^{\sigma_2}$</td>
</tr>
<tr>
<td></td>
<td>$e^{\sigma_2}$</td>
<td>$e^{\sigma_2}$</td>
<td>$\sigma_1 = 1.446$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$q_2 = 2.89$</td>
</tr>
</tbody>
</table>
4.7. The two-axis spectrometer with P.S.D.

The foregoing discussion has dealt with the X-ray spectrometer in the horizontal triple-axis mode. Another high-resolution set-up can be obtained by the use of a position-sensitive detector (P.S.D.). The Physics Department at Risø bought a P.S.D. a few years ago and it has been used mainly to study the adsorption of two-dimensional layers of gases on graphite-substrates. With the P.S.D. the spectrometer operates essentially as a two-axis spectrometer, with a monochromator part that may be either one crystal or a set of crystals and where the scattered radiation is detected in a certain angular range by the P.S.D. The collimation between the sample and P.S.D. is determined by the resolution of the detector-wire (typically < 100 μ), the distance between the sample and the P.S.D. and the slit-system after the sample.

The in-plane resolution one obtains for this set-up can be found using the standard procedure for the two-axis spectrometer, which in short involves the following steps:

1) Construct the $X_1, X_2$-set of conjugate diameters for the monochromator part. For perfect crystal(s) the method in Figure 4.2 must be used. For crystals with a mosaicity $>>$ Darwin width, the method in reference\(^2\) can be used.

2) Transform this resolution-ellipse to the end of $\Delta_0$, under the assumption of infinitely good collimation between the sample and the detector. (see Reference\(^2\)).

3) The effect of a finite collimation of the detecting system can then be included simply by the use of transformation of conjugate diameters and the rule of sum-of-squares for Gaussian distributions. (see Reference\(^2\)).

The out-of-plane resolution is determined similarly to the triple-axis case.
REFERENCES


5. TRIPLE-AXIS X-RAY DIFFRACTION AT THE SYNCHROTRON; THE TECHNIQUES AND QUALITATIVE AND EXPERIMENTAL COMPARISONS WITH THE ROTATING ANODE

The radiation emitted by accelerated electrons or positrons with ultrarelativistic velocities in a storage ring is well suited to the study of condensed matter. The wavelength of the radiation extends from the visible to the hard X-ray region. One of the dedicated synchrotron laboratories is HASYLAB in Hamburg. This laboratory uses the radiation from the DORIS storage ring, which is part of the hierarchy of electron/positron rings at the high-energy physics center DESY (Deutsches Elektronen Synkrotron).

This chapter will describe the techniques employed when working with the triple-axis spectrometer at DORIS and further describes the properties of the synchrotron radiation and compares them, partly experimentally, with a conventional source, a 12-kW rotating anode.

5.1. General properties of synchrotron radiation

When electron/positrons, with ultra-relativistic energy $E$, traverse a circular trajectory, they emit radiation tangential to the orbit. The electron/positron is confined to the circular orbit of radius $R$ by a magnetic field $B$ perpendicular to the horizontal orbit plane. Figure 5.1 shows a schematic drawing of the set-up.

If the electron beam is perfectly confined to the orbit plane, the vertical collimation (FWHM) of radiation with wavelength $\lambda$ is given by:

$$
\Delta \psi = 2 \cdot \sqrt{2 \ln 2} \cdot \sigma_\gamma(\lambda) = 2 \cdot \sqrt{2 \ln 2} \cdot \frac{0.289}{k(\text{GeV})} \cdot \frac{\lambda}{\lambda_c}^{0.425} \text{ mrad}
$$

(5.1)
\[ \Delta \psi = \frac{0.5 \text{MeV}}{E} \quad (E-\text{electron energy}) \]

Ex.: \( E = 5 \text{GeV} \)
\[ \Delta \psi = 10^{-4} \text{ rad} = 0.1 \text{ mrad} \]

Fig. 5.1. The synchrotron radiation.
where the critical wavelength $\lambda_c$ is given by:

$$\lambda_c = 5.59 \cdot R(a) \cdot \frac{1}{[E(GeV)]^3} \mu m; \ R \ is \ orbit \ radius$$

(5.2)

The spectral intensity distribution from the storage ring can be calculated exactly from theory, and the result can be expressed in terms of simple, universal, functions. The function relating to a typical horizontal triple-axis set-up at the synchrotron is:

$$N(\lambda) = \text{number of photons/sec./}0.1\% \text{ energy bandwidth/mrad horizontal}$$

$$= 2.236 \cdot 10^{10} \cdot I \cdot E \cdot G(\frac{\lambda_c}{\lambda})$$

(5.3)

where $I$ is the beam current in mA and $E$ is the electron energy in GeV, and where $G(\lambda_c/\lambda)$ is given by:

$$G(\frac{\lambda_c}{\lambda}) = 1.1 \cdot \left(\frac{\lambda_c}{\lambda}\right) \int_{\frac{\lambda_c}{\lambda}} \ K_{5/3}(x) dx; \ K_{5/3} \ is \ the \ modified \ Bessel \ function \ of \ degree = 5/3.$$

(5.4)

Figure 5.2 shows calculations\(^1\) of $N(\lambda)$ for DORIS, NSLS (National Synchrotron Light Source–design, Brookhaven, U.S.A.); ESRF (European Synchrotron Radiation Facility design).

The electrons/positrons are not completely confined to the average orbit plane. They perform oscillations in and out of the average orbit plane; furthermore, the electron beam is not infinitely thin, but has a spatial distribution. This is shown in Figure 5.1, where Gaussian distributions are assumed in the $x$ and $z$-directions with FWHM$_{x,z} = 2\sqrt{2ln2}\cdot \sigma_{x,z}$. The above-mentioned oscillations give rise to an electron beam divergence, characterized by the standard deviation $\sigma_z$. The full divergence of the X-ray beam in the vertical plane is then given by:
Fig. 5.2. $N(\lambda)$ for DORIS, NSLS and ESRF.

$$q^2_{z,\text{tot}} = \sigma_y^2 + \sigma_z'^2 \quad (5.5)$$

At DORIS $2\sqrt{2\ln 2} \cdot q_{z,\text{tot}}$ is $\approx 0.3$ mrad for $E = 3$ GeV.

If one assumes that the intensity distribution in the x-direction is uniform within a range $2\sqrt{2\ln 2} \cdot \sigma_x$ and zero outside, then the beam divergence in the horizontal direction is determined by the slit width before the experimental apparatus or $2\sqrt{2\ln 2} \cdot \sigma_x$, whichever is the larger (see Figure 5.5 in Chapter 4). $q_x$ is shown in Table 5.1 for DORIS, NSLS, and ESRF. During a dedicated running period, the energy of the electrons/positrons is fixed, while the current gradually decays. This decay is due to collisions between electrons/positrons and residual gas molecules in the ring. The lifetime of the current at a storage ring like DORIS can be as high as $\sim 12$ hours under optimal conditions, but normally new electrons/positrons are injected after 3-4 hours, thus maintaining a high intensity level. After a new filling of the ring the source might have moved, both in the horizontal and vertical directions. For the DORIS storage ring a typical energy
is 3.3 GeV with the current, typically, decaying from 100 mA to 20 mA.

In Table 5.1, DORIS is compared to an NSLS- and ESRF-design.

### Table 5.1. DORIS-, NSLS- and RDTG-parameters.\(^1\)

<table>
<thead>
<tr>
<th></th>
<th>DORIS</th>
<th>ESRF</th>
<th>NSLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \cdot 2\pi n^2 \cdot \sigma_x)</td>
<td>4.0 mm</td>
<td>0.49 mm</td>
<td>0.94 mm</td>
</tr>
<tr>
<td>(2 \cdot 2\pi n^2 \cdot \sigma_z)</td>
<td>2.8 mm</td>
<td>0.28 mm</td>
<td>0.235 mm</td>
</tr>
<tr>
<td>ELECTRON-BEAM DIVERGENCE</td>
<td>0.26 mrad</td>
<td>0.021 mrad</td>
<td>0.0235 mrad</td>
</tr>
<tr>
<td>R(radius)</td>
<td>12.12 m</td>
<td>22.4 m</td>
<td>6.93 m</td>
</tr>
<tr>
<td>MAX. CURRENT</td>
<td>100 mA</td>
<td>500 mA</td>
<td>500 mA</td>
</tr>
<tr>
<td>MAX. ENERGY</td>
<td>5 GeV</td>
<td>5 GeV</td>
<td>2.5 GeV</td>
</tr>
</tbody>
</table>

5.2. General properties of the rotating-anode radiation

The radiation generated by electrons striking a metal anode, like Cu, consists of the well-known line spectrum superimposed on a low-intensity bremsstrahlung. The bremsstrahlung comes from the deceleration of the electrons in the target. The line spectrum is generated by a process where an electron has enough energy to remove, say, a K-electron from a Cu-atom whereupon an L-electron jumps to the K-shell. This latter process is followed by the generation of X-rays with the characteristic Cu,Kα₁ and Cu,Kα₂ lines. Typical anode materials are Cu and Mo. The origin of the Kα₁ and the Kα₂-splitting is the spin-orbit coupling in the L-shell, which splits up into two energetically close eigen-
states, giving rise to the Ka₁ and the Ka₂-lines. The Ka₁-line is approximately two times more intense than the Ka₂.

The intensity from the anode is limited, in practice, by anode heating. This can be reduced by letting the anode rotate, thus distributing the heat over a larger area.

The radiation from the anode is almost completely uncollimated and both the vertical and the horizontal divergence of the radiation incident on the monochromator is determined by slit widths or source dimensions (see Figure 5).

The characteristic lines from the rotating anode are not infinitely sharp but have a natural line width. For the CuKa₁-line this is:

\[ \frac{\Delta \lambda}{\lambda} \text{CuK}_{\alpha_1} = 4 \times 10^{-4} \text{ (FWHM)} \]

When running properly, the rotating anode is an extremely stable source with the possibility of controlling the intensity over at least 1 decade of the full range, by varying the voltage over the anode and filament and/or varying the current from the anode to the filament.

5.3. Detection of the X-ray beam at the storage ring and rotating anode

There are a number of ways one can detect an X-ray beam. X-ray detectors are available for different purposes. Among these are scintillation detectors, solid state detectors, and position sensitive detectors. When an actual experiment is running, one of these will be used to collect data, but during alignment of the spectrometer they are not very useful. The main reason is that during alignment it is often necessary to detect very intense X-ray beams and all the detectors mentioned will either be destroyed or become saturated if the intensity gets beyond 10⁴-10⁵ photons/sec. To deal with this, one could use various
beam attenuators. Since it is crucial to be able to align the spectrometer at either source, fast and accurately, one can alternatively use other ways of detecting intense X-ray beams. One of these is the ion-chamber, which at the same time can be used as a beam monitor, when doing the actual experiment. The beam monitor is shown in Figure 5.3. It has been constructed by Dr. J. Als-Nielsen at Risø and used at the rotating anode and, especially at the storage ring.

![TOP VIEW](image1)

![SIDE VIEW](image2)

**Fig. 5.3.** The ion chamber. Note the outer ring, which will catch possible leak currents. 3)
The detector is filled with gas of 90% argon and 10% methane to a pressure of 0.1 atm. If necessary, the pressure can be changed easily. An example of its use is given in Figure 5.5 and Table 5.2. The transmission of the detector is 92% for CuKα₁-radiation. The current generated in the ionization chamber is converted to a voltage by a Keithley-amplifier. The maximum gain of the amplifier is $10^{11}$ V/A, thus $10^{-12}$ ampere can be detected.

Other ways of detecting intense X-ray beams employ what could be called visual detectors. Among these are: films, fluorescent screens, and X-ray sensitive paper ("green paper"). Any of these can be very helpful when aligning the spectrometer. In the direct beam from the storage ring, they will all give a signal almost immediately. The fluorescent screen will light up so brightly that a precise determination of the beam spot is impossible due to the smearing out of the picture. At the rotating anode, both films and the fluorescent screen can detect the direct beam. The "green paper" is too insensitive to be useful at the rotating anode. In a monochromatic beam ($\lambda = 1.542$ Å) from the storage ring, where the monochromator is either a perfect Si-crystal or a perfect Ge-crystal, both the film and the fluorescent screen will show a sharp spot with well-defined edges. In the monochromatic CuKα-radiation from the rotating anode, sensitive films can be used and to some extent the fluorescent screen.

5.4. A procedure for aligning the triple-axis spectrometer at the storage ring

For a universal X-ray spectrometer it is crucial to develop techniques which can facilitate a rapid alignment of the spectrometer, especially at the storage ring where source movements during refilling of DORIS calls for the need of ways to trace the beam and perhaps realign the spectrometer rapidly. The following alignment procedure is for a triple-axis, nondispersive, elastic, X-ray experiment at the storage ring (see Figure 3.1 in Chapter 3).
Fig. 5.4. Devices and/or techniques for aligning the spectrometer. a) The beam colouring of a X-ray sensitive paper, placed in front of the beam definer. b) The pin cross. c) The arrangement of the fluorescence screen and the camera behind the pin cross.
The direct beam from the storage ring DORIS at the spectrometer site in HASYLAB is limited in the vertical plane by its natural divergence. In the horizontal plane the beam is limited by a 10-mm wide Cu-aperture, approximately 14 meters from the source. This leads to a beam with the intensity distribution just before the beam-defining slit shown in Figure 5.4a.

This can be checked by exposing X-ray sensitive paper for ~ 10 seconds. Since the source moves every now and then, it is essential to be able to trace the beam without having to realign the whole spectrometer. For this purpose a beam-finder is installed in front of the beam-defining slit. The beam-finder is essentially four small ion-chambers, one above, one below, one to the right, and one to the left of the beam-defining slit. The beam-defining slit and the beam-finder are fixed to the monochromator axis, and the beam-defining slit and monochromator axis are aligned once and for all, so that when the current in the ion-chambers is balanced two and two, the spectrometer is in the correct position, meaning that the center of the intense, white synchrotron beam is exactly over the monochromator axis. The spectrometer can be brought into this central position by moving the spectrometer floor up or down, which can be done by remote motor control and by moving the whole spectrometer horizontally perpendicular to the beam. This is done by gliding the spectrometer along a sledge bolted to the spectrometer floor.

When the spectrometer as a whole is brought into the right position and a beam-defining slit, typically with dimensions 2-mm wide and 5-mm high, is chosen, the spectrometer is aligned by the following steps:

1) With the center of the direct beam over the monochromator axis, the next step is to direct the center of the direct beam over the sample axis or, equivalently, find the zero-position of the monochromator arm (M.A.). This may be done by placing X-ray sensitive paper after a 1 mm pin cross on the sample goniometer (see Figure 5.4b).

2) M.A. is moved to $2 \cdot \theta_M$, twice the Bragg angle of the monochromator for the chosen wavelength.
3) The monochromator crystal is set in place, rotated (N.R.) and tilted until the monochromatic beam falls over the sample axis at the correct height. This can be checked using the 1-mm pin cross and the fluorescent screen arrangement in Fig. 5.4c). The picture of the beam spot on the fluorescent screen of the TV-monitor should look exactly like the sensitive paper colouring of Figure 5.4b).

4) The zero-position of the sample arm (S.A.) can now be determined by bringing the analyzer axis into the center of the monochromatic beam. This is done in the same way as under point 3). The only difference being that in this case, the beam is fixed in space and the pin cross is moved through the beam to find the correct position, whereas under 3) the beam is moved and the pin cross is fixed.

5) The analyzer arm (A.A.), with the ion chamber as far back as possible, is scanned through the monochromatic beam to find the zero-position of A.A.

6) The analyzer arm is rotated nondispersively to $2\theta_A$, twice the Bragg angle of the analyzer crystal, for the chosen wavelength.

7) The analyzer crystal is put in and rotated (A.R.) until the monochromatic beam is reflected into the ion chamber of the analyzer arm.

8) The analyzer crystal is tilted until the intensity in the ion chamber is maximised.

Unfortunately, 7) and 8) are coupled, since the narrow Darwin-width of the perfect crystals makes it impossible, with the present goniometer, to tilt the crystal and at the same time maintain the position of the rotation to within 1 mdeg. The solution to this is to scan A.R. for a number of settings of the tilt of the analyzer crystal, thus finding the position of the tilt which gives maximum intensity. The spectrometer is aligned, and the sample can be placed in position. The alignment procedure at the rotating anode is similar, but films and ion chamber would be used instead of fluorescent paper. The full alignment can be completed in ~ 20 minutes.
5.5. Measurement of properties of the synchrotron radiation and rotating-anode radiation relevant to triple-axis X-ray diffraction

The properties measured and compared in this section are related specifically to the demands of a triple-axis X-ray spectrometer. In X-ray diffraction experiments it is crucial to obtain a high resolution of the spectrometer, while maintaining the necessary intensity.

**ROT. ANODE RISØ**

![Diagram of the rotating anode setup showing S₀, S₁, S₂, and M, with sizes and material specifications.]

**DORIS-SYNCHROTRON**

![Diagram of the synchrotron setup showing S₀, S₁, S₂, and M, with sizes and material specifications.]

*Fig. 5.5.* The experimental set-up at the rotating anode and at the synchrotron referring to Table 5.2.
Table 5.2. Intensity comparison between the rotating anode and the synchrotron source. The set-ups are shown in Figure 5. The intensity is \( \sim 500 \) times larger at the synchrotron than at the rotating anode. Furthermore, the vertical and horizontal beam divergence is reduced by a factor \( \sim 10 \). Note the difference in beam size.

<table>
<thead>
<tr>
<th></th>
<th>ROT. ANODE</th>
<th>DORIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\Delta \lambda}{\lambda} ) FWHM</td>
<td>( 3.1 \times 10^{-4} ) (^4)</td>
<td>( 1.06 \times 10^{-3} )</td>
</tr>
<tr>
<td>Horizontal beam divergence (FWHM)</td>
<td>( \frac{1}{600} = 1.4 \text{ mrad} )</td>
<td>( \frac{4}{20} \text{ mrad} = 0.2 \text{ mrad} )</td>
</tr>
<tr>
<td>Vertical beam divergence (FWHM)</td>
<td>( \frac{5}{600} = 8.3 \text{ mrad} )</td>
<td>( 0.32 \text{ mrad} )</td>
</tr>
<tr>
<td>Intensity in I.C.</td>
<td>15 kc/sec</td>
<td>7.8 kc/sec</td>
</tr>
<tr>
<td>Gain in current to voltage amp.</td>
<td>( 10^{11} \text{ V/A} )</td>
<td>( 10^{8} \text{ V/A} )</td>
</tr>
<tr>
<td>Beam size</td>
<td>( w \times h ) ( 1 \times 5 )</td>
<td>( w \times h ) ( 2 \times 10 )</td>
</tr>
<tr>
<td>Source</td>
<td>Tube voltage</td>
<td>Electron energy</td>
</tr>
<tr>
<td></td>
<td>55 kV</td>
<td>3.3 GeV</td>
</tr>
<tr>
<td></td>
<td>Electron current:</td>
<td>Electron current: ( 190 \text{ mA} ) ( 50 \text{ mA} )</td>
</tr>
</tbody>
</table>

The entire set of critical data for the mixture 5CT9:7CB\(_x\):80CB9\(_{1-x}\) were taken during a 10-day period at the DORIS-ring. A complete set of data for one mixture could be obtained in 3-4 hours. In these experiments the monochromator and analyzer were Si(111), \( m=3 \) crystals. Similar critical data have been obtained over much longer time scales and with a somewhat relaxed longitudinal resolution given by \( m=1 \) Ge-crystals at the rotating anode. A more direct measurement of the intensity difference between similar
set-ups at the synchrotron and at the rotating anode is displayed in Figure 5.5 and Table 5.2. The transmission of the ion chamber for $\lambda = 1.5422\ \text{Å}$-radiation is calculated to be 91%. The transmission has been measured at the rotating anode to be 92%.

Higher-order contributions to the synchrotron intensity in Table 5.2 are negligible, since the transmission of the third-order reflection Si(333) is 99% and from Figure 5.2 the third-order $\lambda = 0.5\ \text{Å}$ intensity is at least a factor of 10 lower than $\lambda = 1.54\ \text{Å}$ radiation. (Note that the spectrum in Figure 5.2 for DORIS must be shifted to the left for $E = 3.3\ \text{GeV}$.)

When calculating $\Delta\lambda/\lambda$ for the synchrotron it is assumed that the source is uniform within $2\sqrt{2} \ln 2 \cdot \sigma_x$ and zero outside. The measured values, both at the synchrotron and rotating anode, were obtained by rotating the analyzer crystal in the dispersive mode without a sample. (See Figure 4.3 in Chapter 4). The good agreement between the measured and calculated values of $\Delta\lambda/\lambda$ at the synchrotron indicates that the FWHM of the source width is given rather accurately by $2\sqrt{2} \ln 2 \cdot \sigma_x$ from Table 5.1. The measurements indicate that it is slightly broader. Preliminary, independent measurements of the source width, performed by scanning a photodiode across the beam close to the source, agree with our measurements to within 10%. The photodiode measurements were made by Dr. Zietz in HASYLAB.

The characteristic exponential decay of the $\Delta\lambda/\lambda$-curve for the CuK$\alpha$-line (see Figure 4.7 in Chapter 4) is not expected to be found at the synchrotron, if the Gaussian approximation holds for the spatial distribution of the source, but a detailed experimental check still needs to be made.

Clearly, Table 5.2 shows that the synchrotron is by far a better X-ray source on all points apart from the bandwidth ($\Delta\lambda/\lambda$). This bandwidth for the synchrotron can be reduced by moving further away from the source. The effect of moving further away is displayed in Figure 5.6, which shows measurements of ($\Delta\lambda/\lambda$) at two different sites. While the triple-axis spectrometer was located at EMBL-outstation next to HASYLAB, the distance to the ring was
Fig. 5.6. The effect of moving further away from the synchrotron source. The monochromator and the analyzer are Si(111); m = 3-crystals.
35 m. This reduces \( \Delta \lambda / \lambda \) to a value comparable to the intrinsic line width of the CuK\( \alpha \)-line.

REFERENCES

1) European synchrotron radiation facility (ESRF)-design as outlined by a European Science Foundation (ESF)-committee. Supplements II and III. May 1979.
6. HIGH-RESOLUTION X-RAY STUDY OF THE SECOND-ORDER NEMATIC-SMECTIC-A PHASE TRANSITION IN THE MONOLAYER LIQUID CRYSTAL 8S5

The second-order phase transition from nematic to smectic-A in liquid crystals has been studied in detail in recent years using different experimental techniques. Until recently\textsuperscript{2) the x-ray studies have concentrated on the so-called bilayer liquid crystals. Examples of these materials are CBOOA, 8OCB (see Chapter 2).

This chapter reports on a study of the monolayer liquid crystal 8S5, performed at the DORIS storage-ring in Hamburg, using synchrotron radiation. The material 8S5 is out of the \( C_nH_{2n+1-\text{\ding{59}}-\text{COS-\text{\ding{59}}-C}_5H_{11} \) family, where \( \text{\ding{59}} \) denotes a benzene ring. For \( 12 > n > 8 \) these materials exhibit the following sequence of phases: isotropic + nematic + smectic-A + smectic-B + solid.

\( T_{\text{NS}}/T_{\text{NI}} = 0.72 \) well below the limiting value of 0.87 above which the transition should become first order as predicted by McMillan\textsuperscript{3)\textsuperscript{0}}.

To some extent the monolayer nature of this compound in the smectic-A phase will change the length/width-ratio of the basic building block. See Figure 6.1 and an increase of the ratio of longitudinal correlation length to transverse correlation length is expected (\( \xi_\parallel/\xi_\perp \); see Chapter 2), compared to the bilayer compounds. In Figure 6.1 a schematic picture of the nematic phase in the critical region is also shown. In this figure \( \xi_\parallel/\xi_\perp = 4 \). The situation in bilayer compounds such as CBOOA, 8OCB, and 8CB is that \( \xi_\parallel/\xi_\perp = 5-8 \textsuperscript{2)\textsuperscript{0}}\).
The theoretical model for the transition from the nematic to smectic-A phase is outlined in Chapter 2. In short, the following theoretical predictions are made: The scattering cross section is given by:

\[ S(q) = \frac{S(q_0)}{1 + \xi_{\parallel}^2(T)(q_{\parallel} - q_0)^2 + \xi_{\perp}^2(T) \cdot q_{\perp}^2} \]  

where
\[ q_\perp^2 = q_x^2 + q_y^2 \; ; \; q_\parallel = q_z \; ; \; q_o = \frac{2\pi}{d} \] and

\[ \xi_\parallel = \sqrt{\frac{M_v}{2a}} \; ; \; \xi_\perp = \sqrt{\frac{M_t}{2a}} \]

\[ S(q_o) = \sigma(q_o) = k_BT/\alpha = \frac{k_BT \cdot \xi_\parallel^2}{2M_v} \equiv a \cdot \xi_\parallel^2 \; ; \; a = \frac{k_BT}{2M_v} \]

The notation refers to the free energy expression, describing the phase transition, given in Chapter 2. In De Gennes's superfluid-helium model for the nematic to smectic-A transition the following exponents are predicted:

\[ \xi_\parallel, \perp \sim t^{-\nu} \; ; \; \sigma(q_o) \sim t^{-\gamma} \; ; \; a \sim t^{-\nu\eta} \]

where

\[ \nu = 0.66 \; ; \; \gamma = 1.30 \; ; \; \eta = 0.04 \]

As opposed to the mean field result:

\[ \nu = 1/2 \; ; \; \gamma = 1 \; ; \; \eta = 0 \]

originating from assuming that: \( a \sim (T-T_c) \).

6.2. Experimental

The experimental set-up is shown in Figure 3.1 in Chapter 3. It basically consists of the triple-axis spectrometer build at Risø. This spectrometer has been described elsewhere and was only (during these initial experiments at the synchrotron) slightly modified to meet the requirements of operation at a storage ring as opposed to a rotating anode. Two important
changes were the addition of a beam monitor and a TV camera. The beam monitor is shown in Figure 6.2. Unfortunately, the magnetic fringe field from the sample magnet made this beam monitor ineffective. It turned out that with the geometry we had to use one gets a decreasing pulse height from the sodium-iodide detector with increasing magnetic fringe field. This effect must be due to electrons being bent away from their normal trajectory in the photomultiplier by the magnetic fringe field. This effect depends critically on the distance between magnet and monitor. Due to lack of space and the rather large magnet we used with a field of approximately 3000 gauss to grow the smectic liquid
crystal, it became impractical to use the beam monitor; thus we had to resort to the storage ring current in normalizing the counts. Later, we used an ion chamber, which have proved extremely useful. The width and height of the beam defining slit were 2 and 3 mm, respectively.

The full experiment took place during two sessions that were a few months apart and under differing beam conditions. During the first session (July 1979) DORIS ran under the following conditions: positron energy = 5.2 GeV giving a critical wavelength of 0.52 Å. The current was from 30 to 100 mA, with a lifetime of approximately 4 hours. During the second session (November 1979) DORIS ran under the conditions: positron energy = 4.73 GeV giving a critical wavelength of 0.57 Å. The current was from 10 to 20 mA with a lifetime of approximately 3-4 hours.

In Table 6.1 the experimental parameters employed in the two sessions are displayed. Note that the influence of the mosaicity of the sample is not included in the resolution function. This is because the convolution of $S(q)$ with the mosaicity distribution was done directly, using a measured mosaicity distribution which was often non-Gaussian. (See Appendix C for a description of the numerical deconvolution procedure.)

The longitudinal resolution function $R_\parallel(q_\parallel)$ is approximated by a Gaussian with a width $W_\parallel^2 = \alpha^2 + \beta^2$, where $\alpha$ is the width of the direct beam contribution and $\beta$ the width of the $\Delta \lambda/\lambda$-contribution. The transverse resolution function $R_\perp(q_\perp) = \delta(q_\perp)$ and the vertical resolution function $R_\| (q_\|)$ are approximated by a Gaussian with a width, calculated from the out-of-plane beam divergence allowed by the Soller-collimator.

The sample was contained in a flat 1.5 × 5 × 10 mm cell made of an Al-frame with Be-windows. The sample oven had two stages. It consisted of two heating elements, an inner and outer one, where the inner element contained the flat Be-cell with the liquid crystal. Each heating element was connected to a separate thermistor-controlled temperature regulator. By setting the outer element approximately 5 K below $T_c$ and keeping an ultra-low gain
Table 6.1. Important experimental parameters during the sessions. The resolution functions are: \( R_{||}(q_{||}) = e^{-(q_{||}/\sigma_{||})^2} \), \( R_{\perp}(q_{\perp}) = e^{-(q_{\perp}/\sigma_{\perp})^2} \), \( R_T(q_T) = \delta(q_T) \) with the same notation as in Chapter 4. The values of \( T_c \) are the best judgement from the FWHM in \( q_{||}-\)scan and \( q_{\perp}-\)scan vs. \( T \), when going up in temperature. (2mr) means that the Soller collimator giving the vertical resolution was a 2 mrad Soller collimator.

|       | \( \lambda/\AA \) | \( k_0 = k_0/\AA^{-1} \) | Monochromator = analyzer | \( \sigma_{||}/\AA^{-1} \) | FWHM of \( R_{||}/\AA^{-1} \) = \( 2/\ln2 \cdot \sigma_{||} \) | \( \sigma_{\perp}/\AA^{-1} \) | FWHM of \( R_{\perp}/\AA^{-1} \) = \( 2/\ln2 \cdot \sigma_{\perp} \) | \( T_c/k \) |
|-------|------------------|--------------------------|-----------------|------------------|------------------|------------------|------------------|------------------|
| Session I (Jul. 79) | 1.54 | 4.07 | Si(111); m=1 | 4.89 \times 10^{-3} (2mr) | 1.22 \times 10^{-2} (5mr) | 8.14 \times 10^{-3} (2mr) | 2.03 \times 10^{-2} (5mr) | 1.71 \times 10^{-4} | 2.85 \times 10^{-4} | 333 060 |
| Session II (Nov. 79) | 1.54 | 4.07 | Si(111); m=3 | 7.35 \times 10^{-3} (3mr) | 1.224 \times 10^{-2} (3mr) | 1.12 \times 10^{-4} | 1.86 \times 10^{-4} | 332 372 |
Fig. 6.3. The FWHM of longitudinal and transverse scans versus temperature.
in its control system, it was possible to control the temperature (near $T_c$) accurately using only the inner element. In this way one was able to obtain a temperature stability of $\pm 10\, \text{mK}$ during the first session and after some modification $\pm 1.5\, \text{mK}$ during the second session.

With the resolution and temperature stability we obtained, it turned out that neither of these became the limiting factor as far as probing close to $T_c$ was concerned. The limiting factor was the difficulty of growing a perfect smectic-A phase. Even with a rather large magnetic field it was not possible to grow a smectic-A phase with a mosaicity lower than $1^\circ$ as can be seen from Figure 6.3, showing the sample-rocking curves versus $T$ from the two sessions.

Since there is no way one can measure the mosaicity above $T_c$ we had to assume a specific mosaicity in deconvoluting the data. As we shall see in the next section the correction, close to $T_c$, one gets by putting in mosaicity above $T_c$ is rather large as opposed to assuming it is zero.

### 6.3. Data-analysis

The data were taken by performing longitudinal ($\hat{q}_l | \hat{q}_o$) and transverse ($\hat{q}_t | \hat{q}_o$) scans going through the critical region. In Figure 6.3 the FWHM's of longitudinal and transverse scans are shown. As one can see, there is a slight hysteresis when going down and going up in temperature indicated by the guide for the eye lines through the $\Delta \phi$ points. The data analysed are for increasing $T$ in both sessions. A rather precise $T_c$ can be read off from Figure 6.3 (the kink in the sample-rocking curves). A typical set of scans is shown in Figure 6.4, indicating the large $\xi_{||} / \xi_{\perp}$-ratio. The data were analysed by fitting the lineshape, convoluted with the mosaicity distribution (if included) and convoluted with the resolution function (Table 6.1) to the experimental data.
The data have thus been analysed for \( T > T_c \) assuming 1) no mosaicity and 2) the same mosaicity as the one at \( T = T_c \).

![Graph showing experimental data and fit]

**Fig. 6.4.** Experimental data and fit for the set of data with the largest resolution correction. \( T = T_c + 0.03^\circ C; t = 9 \cdot 10^{-5} \). FWHM of longitudinal scan is \( 5.8 \cdot 10^{-4} \text{Å}^{-1} \). FWHM of transverse scan is \( 11.4 \cdot 10^{-3} \text{Å}^{-1} \). Mosaicity is included in the fit and the scattering cross section convoluted with the mosaicity is also shown.

In Figure 6.5 the results of the fitting are displayed. The vertical line at the points close to \( T_c \) gives the correction to \( a_{||,1} a_0 \), when mosaicity is included. It is clear from this that the limiting factor in probing close to \( T_c \) is the inability to grow a perfect smectic-A phase.

An attempt to include a term \( + c a_{||,1}^4 q_1^4 \), in the numerator of the scattering cross section as done in the paper of J.D. Litster et al.\(^2\), did not significantly lower the goodness-of-fit-parameter \( \chi^2 \) and in any case \( c \) became negative. \( \chi^2 \) was typically of
Fig. 6.5. The complete set of deconvoluted data from the two sessions.

the order of 2.5. This rather large value of $\chi^2$ one may partly ascribe to the crude normalization of the data. With $T_C$ fixed on the value obtained from Figure 6.3, the full dataset from the two sessions deconvoluted with mosaicity included, were fitted to $\xi_{||,1}^0 t^{-v_{||,1}}$, yielding the following parameters:

\[ v_{||} = 0.77 \pm 0.04 \quad ; \quad v_{\perp} = 0.60 \pm 0.04 \text{ Å} \]
Fig. 6.6. The susceptibility $\sigma_0 \sim t^{-\gamma}$ from the November-run. $\gamma = 1.35$.

The full lines in Figure 6.5 are the fitted curves. It is important to notice that the assumed mosaicity is the mosaicity at $T_C$ and that this probably gives a larger correction to $\xi_{||} q_0$ than it should, since the mosaicity just above $T_C$, due to the magnetic field, probably is smaller than at $T_C$. The quoted uncertainties do not include this, of course, but only the uncertainties in $T$ and $\xi_{||} q_0$. 
Lastly, the bilayer smectic-A compounds are compared to 8S5 in Figure 6.7; furthermore, the $\xi_{\parallel}/\xi_{\perp}$-ratio of 8S5 is shown in Figure 6.8. The difference in magnitude of this ratio for this monolayer smectic-A compound and bilayer smectic-A compounds as 8OCB, CBOOA and 8CB, is, intuitively, in good agreement with the assumption that the basic building block of the smectic-A phase of 8S5 is a single 8S5 molecule, while the basic building block of the smectic-A phase of f.ex. 8OCB is an overlapping...
configuration of two 80CB-molecules, as mentioned in the introduction to this chapter.

![Graph](image)

**Fig. 6.8.** The ratio between longitudinal correlation length $\xi_\parallel$ and transverse correlation length $\xi_\perp$.

### 6.4. Conclusions

This study of the monolayer compound 8S5 deviates slightly from similar studies on bilayer compounds\(^1\) as far as critical exponents are concerned. In all of the bilayer compounds 8CB, 80CB and CBOOA, it was found that $\nu_\perp < \nu_\parallel$, $\nu_\perp$ being close to 0.60 and $\nu_\parallel$ close to 0.70. This is not quite the case for the monolayer compound 8S5, where $\nu_\perp = 0.60 < \nu_\parallel = 0.77$. It must be noted, however, that the mosaicity correction is rather large compared with the case of the bilayer compounds. Pretransitional mosaicity seems to be a characteristic feature of the transition in the current sample geometry. It seems plausible to assume that the mosaicity function $M(q_\perp, T) \approx \delta(q_\perp)$ for $T \gg T_c$. A reasonable assumption to make about $M(q_\perp, T)$ would be that $M(q_\perp, T)$ is a Gaussian with a FWHM = $M_0 \cdot P(T)$ as $T \to T_c$. Without any specific model for the decay rate of $P(T)$ it seems rather dubious to guess at random and try to reanalyze the data with
this kind of $M(q, T)$. A "simple" way to avoid this difficulty in the analysis is to learn to grow better samples.

It was noted in Ref. 2 that the length/width ratio of an associated pair of molecules in a bilayer compound is smaller than $\xi_1/\xi_L$. This also appears to be the case for the monolayer liq. crystals, since $\xi_1/\xi_L$ for 8S5 is in the range 13 to 20 and the length/width ratio of 8S5 is $\sim 10$.

REFERENCES

7. AN EXPERIMENTAL STUDY OF THE NEMATIC TO SMECTIC-A PHASE DIAGRAM OF THE MIXTURE 5CT9:7CBx:80CB1-x

The phenomenon of reentrance in solid-state physics is known from a few, quite different, physical systems. Among these are superconductors, doped with magnetic impurities, and liquid crystals, where the sequence: nematic + smectic-A + nematic is

![Diagram showing reentrance phenomena in 80CB under pressure. Notice the supercooled region.](image)

Fig. 7.1. The reentrance phenomena in 80CB under pressure. Notice the supercooled region.
observed upon cooling. The liquid crystal systems exhibiting the reentrant nematic phase are certain pure bilayer materials\(^1\) under pressure and various mixtures of liquid crystals at atmospheric pressure. One of the pure systems is 8OCB, which has been studied in some detail by P.E. Cladis et al.\(^1\) (see Figure 7.1). One of the mixtures is the ternary mixture: \(5\text{CT}_9:7\text{CB}_x:8\text{OCB}_{91-x}\), which exhibits a reentrant nematic phase for \(x < 76.74\), where \(x\) is weight percent. 5CT is acronym for pentylcyanoterphenyl with the chemical formula \(C_5H_{11}-0-0-0-CN\), 7CB is acronym for heptylcyanobiphenyl with the chemical formula \(C_7H_{15}-0-0-CN\). 8OCB is acronym for oxycyanobiphenyl with the chemical formula \(C_8H_{17}-0-0-CN\). This mixture has the advantage over the P-T phase diagram of the pure systems, like 8OCB, that the re-entrant nematic phase is stable and the phase transitions are second order.

A flow behaviour investigation of the mixture \(5\text{CT}_9:7\text{CB}_x:8\text{OCB}_{91-x}\) has been made by S. Bhattacharya and S. Letcher.\(^3\) It is the purpose of this chapter to report on a high-resolution X-ray study of the same mixture, performed using synchrotron radiation from DORIS in Hamburg. Table 7.1 summarizes the phases and the transition temperatures for the three components of the mixture.

<table>
<thead>
<tr>
<th>Material</th>
<th>(T_C + S_A)</th>
<th>(T_C + N)</th>
<th>(T_S_A + N)</th>
<th>(T_N + I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CT</td>
<td>./</td>
<td>131</td>
<td>./</td>
<td>240</td>
</tr>
<tr>
<td>7CB</td>
<td>./</td>
<td>30</td>
<td>./</td>
<td>42.8</td>
</tr>
<tr>
<td>8OCB</td>
<td>54.5</td>
<td>./</td>
<td>67</td>
<td>80</td>
</tr>
</tbody>
</table>

#### 7.1. Experimental

The full experiment was done during a prolonged session of dedicated beam time at DORIS. The beam conditions were: electron energy = 4.3 GeV, with the electron current typically between
100 mA and 20 mA. The experimental setup was the triple-axis arrangement displayed in Figure 3.1 in Chapter 3, except that there was no Soller collimator after the sample. The monochromator and analyzer were Si(111) m = 3 crystals and the beam-defining slit had the dimensions: \( w \times h = 2 \times 10 \text{ mm} \). The three components of the mixture were purchased from BDH Chemicals, with no additional treatment before use. The sample was mixed on location, heated up to the isotropic phase, and pumped on for approximately one hour. After the sample cell was installed in the oven, the entire oven was evacuated.

The oven had to be cooled down to \( \sim 5^\circ\text{C} \). This was done by water cooling. Figure 7.2 shows the oven.

The fine control of the temperature was performed by using a thermistor-controlled heating element symmetrically placed above and below the sample cell. The gold foil on either side of the sample cell diminished temperature gradients across the sample. A temperature stability of \( \pm 1 \text{ mK} \) could be obtained.

Six mixtures were investigated. Table 7.2 gives relevant experimental parameters for all six.

<table>
<thead>
<tr>
<th>Mixture #</th>
<th>Weight percent</th>
<th>( \lambda ) A</th>
<th>( 2/\ln 2 \cdot a_x ) A(^{-1})</th>
<th>( 2/\ln 2 \cdot a_y ) A(^{-1})</th>
<th>( T_{\alpha-\delta} ) °C</th>
<th>( T_{\gamma-\delta} ) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72.17</td>
<td>1.468</td>
<td>2.62 \times 10^{-4}</td>
<td>1.68 \times 10^{-2}</td>
<td>26.41</td>
<td>7.00</td>
</tr>
<tr>
<td>2</td>
<td>73.03</td>
<td>1.523</td>
<td>– –</td>
<td>– –</td>
<td>– –</td>
<td>25.41</td>
</tr>
<tr>
<td>3</td>
<td>74.92</td>
<td>1.468</td>
<td>– –</td>
<td>– –</td>
<td>– –</td>
<td>22.06</td>
</tr>
<tr>
<td>4</td>
<td>76.45</td>
<td>1.523</td>
<td>– –</td>
<td>– –</td>
<td>– –</td>
<td>18.00</td>
</tr>
<tr>
<td>5</td>
<td>76.80</td>
<td>1.468</td>
<td>– –</td>
<td>– –</td>
<td>– –</td>
<td>/ /</td>
</tr>
<tr>
<td>6</td>
<td>77.05</td>
<td>1.523</td>
<td>– –</td>
<td>– –</td>
<td>– –</td>
<td>/ /</td>
</tr>
</tbody>
</table>

The resolution function is

\[
R(q') = \delta(q') \cdot e^{-(q_x/a_x)^2} \cdot e^{-(q_y/a_y)^2}
\]

\( a_x \) is obtained from the direct beam profile and the \( \Delta \lambda/\lambda \)-contribution as outlined in Chapter 4. \( a_y \) is calculated from the vertical collimation after the sample, given by the height of the detector window and the distance between sample and detector.
Data were taken by performing longitudinal and transverse scans going through the critical region. Correlation lengths were obtained by fitting the experimental data to the Lorentzian scattering cross-section (Chapters 2 and 4, and Appendix C) convoluted with the resolution function.

![Diagram of the sample oven](image)

**Fig. 7.2.** The sample oven. The permanent Cobalt-Samarium magnet gave a magnetic field of approximately 1kG.
7.2. Results

The FWHM of longitudinal and transverse scans versus temperature is displayed in Figure 7.3a) & b) for the total set of data. From this plot, critical temperatures are obtained and the phase diagram determined.

This is shown in Figure 7.3c. $T_c$ is read off from Figure 7.3a & b and a conservative estimate of the uncertainty on $T_c$ is found as 0.2°C. Three more points on the phase diagram have been obtained by a somewhat cruder method. The occurrence of the N-Sm-A transition can namely be seen directly, when cooling down through the transition. This is because the nematic phase, due to director-fluctuations, appears turbid, while the Sm-A phase, with damped director-fluctuations, is transparent. In this way, the following three points, with an uncertainty of 0.5°C, have been found (these are not shown in Figure 7.3c):

i) $x = 0.66$ ; $T_c = 3.5°C$

ii) $x = 0.66$ ; $T_c = 34.0°C$

iii) $x = 0.0$ ; $T_c = 75°C$

The three components were mixed as powders. The uncertainty in $x$ comes from the weighing procedure; a conservative estimate of this uncertainty is 0.01%. Two different fits to the phase boundary are shown. The dotted-line parabola can be predicted by Landau theory and the full-line rotated-parabola represents a better fit.

The raw data were deconvoluted using the procedure described in Appendix C. The fit of experimental data to the scattering cross-section convoluted with the resolution function was generally good with the goodness-of-fit parameter $\chi^2 = 1-2$. In Figure 7.4 this is shown for a set of data of mixture 44. The FWHM of the longitudinal resolution is shown for reference. As can be seen from Figure 7.7, showing a comparison between 80CCP, 8S5, and mixture +2-correlation lengths, the mosaicity correction is not the limiting factor in probing close to $T_c$ for the mixture-experiments. $q_0^{\perp\perp}$ is so large, compared to 8S5 that the
Fiq. 7.3. FWHM of longitudinal and transverse scans versus temperature. Especially interesting are mixtures 5 and 6 where the correlation length grows, but never grows to infinity. The deconvolution of the scans, corresponding to the encircled points, is shown in Figure 7.3c). The T-x phase diagram deduced from a) & b). Two fits are shown. A parabola with axis perpendicular to the temperature axis and a rotated parabola, which represents a better fit to the data.
Fig. 7.4. Longitudinal and transverse scans through the (0,0,1) reciprocal lattice point show the smectic-A fluctuations in the nematic phase of liquid crystal mixtures at 20.17°C. Full lines are least squares fits of the cross section (dashed curve) folded with the resolution.
longitudinal resolution sets the limit for the mixture experiments. Therefore, mosaicity was not included in the fit and the transverse resolution is a delta function.

The correlation lengths versus reduced temperature for the six mixtures are shown in Figures 7.5 and 7.6.
Fig. 7.5. $q_o \xi_{||}$, $q_o \xi_{\perp}$ and $q_o$ for mixtures No. 1-4. Filled points are for the $N^* + A$-transition. The encircled point corresponds to the encircled point in Figure 7.3. The $q_o$ and $q^*$ are $2\pi/d$ at $T_{N-A}$ and at $T_{N^*-A^*}$. 
Fig. 7.6. $q_{0 \text{, } 5\parallel}$, $q_{0 \text{, } 5\perp}$ and $q_0$ for $x = 76.80$ & 77.05%.
7.3. Comparison with theoretical predictions

A Landau theory of the reentrant nematic-smectic-A phase transition is given by P.S. Pershan and J. Prost⁴). Their work is based on the assumption of the existence of an optimum density for smectic ordering; on the microscopic level this means that above the optimum density, the interactions stabilizing smectic order are suppressed by steric effects and the reentrant nematic phase are obtained. The Landau theory was primarily proposed in an attempt to explain the P-T phase diagram of 8OCB¹), but the mixtures are treated by the theory as well.
The Landau theory of P.S. Pershan and J. Prost involves a coupling between the smectic order parameter $|\psi|$ and the two parameters: the density $\rho$ and the relative concentration of one of the components of a binary mixture $x$. The coupling is introduced by adding a term $g(\rho,x)|\psi|^2$ to the usual form of the power expansion in $|\psi|$ of the free energy $F$.

$$F-F_N = \frac{1}{2} A|\psi|^2 + g(\rho,x)|\psi|^2 + \frac{1}{4} B|\psi|^4 + \frac{1}{6} C|\psi|^6$$  \hspace{1cm} (7.1)

where $F_N$ is the nematic free energy. $A = a^*(T-T_0)$.

Expanding $g(\rho,x)$ in a power series in $(\rho-\rho_0, x-x_0)$ and keeping only leading terms yields

$$F-F_N = \frac{1}{2} A'|\psi|^2 + \frac{1}{4} B|\psi|^4 + \frac{1}{6} C|\psi|^6$$  \hspace{1cm} (7.2)

with $A' = a(T-T^*(x,\rho))$ where

$$T^*(x,\rho) = T_0(x) + t_2(\rho-\rho_0)^2 ; t_2 < 0$$  \hspace{1cm} (7.3)

Evidently $T^*$ is a measure of the interactions favouring smectic order and the above relation contains the basic physics of the Pershan-Prost theory, namely the existence of an optimum density $\rho_0$, favouring smectic order. The phase diagram is determined$^4$ by the condition:

$$T-T^*(x^N,\rho^N) = K$$

where $K$ is 0 for a second-order transition or $3B^2/16aC$ for a first-order transition.

With

$$(\rho^N-\rho_0)/\rho_0 = -\alpha_N(T-T_0) + \beta_N(P-P_0)$$

where $\alpha_N$ and $\beta_N$ are, respectively, the thermal expansion and the compressibility for the nematic phase, the following expression for the phase boundary is obtained:
\[ T_3(T_1(x) - T) = (T_2 - T + (\beta_N/\alpha_N) P)^2 \] or

\[(T_n - T_n') (T_n - T) = [(T_n - T) + (\beta_N/\alpha_N) (P - P_n')]^2 \]

where \( T_1(x) \) is either \( T_0(x) \) for a second-order transition or \( T_0(x) + 3B^2/16aC \) for a first-order transition and \( T_2 = T_0 - \beta_N/\alpha_N P_0 \) and

\[ T_3 = -\frac{1}{t_2 P_0^2 \alpha_N^2} \]

and the following relations hold where \((T_n, P_n)\) and \((T_n', P_n')\) are indicated on Figure 7.1.

\[ T_n = T_1(x) = T_0(x) \text{ for a second-order transition}; \ T_n - T_n' = T_3 \]

\[ P_2 = \frac{\alpha_N}{\beta_N} (T_n - T_2); \ P' = \frac{\alpha_N}{\beta_N} [T_n + T_3/4 - T_2] \]

\[ T_1 = T_n - T_3/4 \]

The \( P-T \) phase diagram of 8OCB is fitted accurately by the expression, with the ratio \((\beta_N/\alpha_N)\) close to experimental values.

In order to obtain an expression for the \( x-T \) phase diagram at 1 atm, it is necessary to assume a specific form of \( T_0(x) \). The simplest assumption is to assume that \( T_0(x) \) is linear in \( x \):

\[ T_0(x) = T_1 - t_1 \cdot x \]

Alternatively, one can follow Pershan and Prost and assume \( T_0(x) \) is linear in \( y = \) the weight ratio of the two components of a binary mixture = \( \frac{x}{1-x} \).

Inserting the \( x \)-linearity in the expression for the phase diagram and letting \( P = P_0 \) (1 atm.) gives the \( T-x \) phase diagram.
\[ C(x_0 - x) = (T_M - T)^2 \]  
with
\[ T_M = T_0 - T_3/2 \text{ and } C = t_1 T_3 \]  
\[ t_1 x_0 = T_1 - T_0 + T_3/4 \]  
Thus, the existence of an optimum density for smectic ordering and the simple ad hoc assumption of linearity of \( T_0(x) \) leads to a parabolic \( T-x \)-phase diagram or alternatively a parabolic \( T-y \)-phase diagram.

Carrying over the above theory for a binary mixture to a ternary one like \( 5CT_{0.09}:7CB_x:80CB_{0.91-x} \) should give a parabolic \( T-x' \) phase diagram with \( x' = \text{weight}(7CB)/(\text{weight}(7CB) + \text{weight}(80CB)) \). Since \( x' = x \), one may as well talk of a parabolic \( T-x \) phase diagram. Alternatively, (if \( T_0(x) \) is linear in \( y \)) the theory predicts a parabolic \( T-y \) phase diagram, with \( y = \text{weight}(7CB)/\text{weight}(80CB) = 0.x/(0.91-0.x) \).

When looking at the datapoints obtained over the whole \( x \) or \( y \) range in the present study of the ternary mixture, it is obvious that neither a \( T-x \) nor \( T-y \) fit of the simple form (7.7) is reasonable. Leaving out the points at \( x = 0 \) and \( x = 0.66 \) gave the following parameters in a parabolic \( T-x \) fit of the form (7.7):

\[ T = T_M \pm (C(x_0 - x))^{1/2} ; T_M = 16.29^\circ C ; x_0 = 0.7674 ; C = 2018 \]  
(7.9)

This fit is not too bad but a better fit to the whole set of data could be obtained with a rotated parabola:

\[ T = T_M + K(x_0 - x) \pm (C(x_0 - x))^{1/2} \]  
(7.10)

The fit was acceptable with an uncertainty of \( 0.2^\circ C \) in \( T_c \) and no uncertainty on \( x \). It yielded the following parameters:
$T_M = 15.62^\circ C ; x_O = 0.7674 ; C = 2036 ; K = 26.02 \quad (7.11)$

As is obvious from Figure 7.3c the rotated parabola represents a better fit also to the eight datapoints investigated with X-rays. Thus, one may conclusively infer that the phase diagram is rather well described by a parabola of form (7.7) in the vicinity of $x_O$, but not over the whole range investigated. The experiments reported on for 8OCB-6OCB by A.R. Kortan et al. do in fact exhibit a parabolic phase diagram of the form (7.7) in a $T$-$y$ fit as originally proposed$^4$) by J. Prost and P. Pershan, but not in a $T$-$x$ fit.

One of the most spectacular features of the phase diagram is the apparent doubling of the critical exponents $\nu$ and $\gamma$ when approaching a locally parabolic phase boundary tangentially. This can be seen by writing down the free energy for the $P=P_\sigma$-isobar, the $T=T_\sigma$-isoterm and the $x=x_0$-isodensity curves in case of a second-order phase transition. One gets:

$$P=P_\sigma\text{-isobar:} \quad F-F_N = \frac{a(T-T_\sigma)^2}{2 \cdot T_3} \cdot |\psi|^2 + \frac{1}{4} B |\psi|^4 + \frac{1}{6} C |\psi|^6$$

$$T=T_\sigma\text{-isoterm:} \quad F-F_N = \frac{a^2(P-P_\sigma)^2}{2 \cdot T_3} \cdot \frac{\beta N}{\alpha_N} |\psi|^2 + \frac{1}{4} B |\psi|^4 + \frac{1}{6} C |\psi|^6$$

$$x=x_0\text{-isodensity:} \quad F-F_N = \frac{a}{2} (T-T_M)^2 \cdot \beta |\psi|^2 + \frac{1}{4} B |\psi|^4 + \frac{1}{6} C |\psi|^6$$

These Landau expansions are quite unusual. The coefficient of the quadratic term goes to zero without changing sign or physically the fluctuations go to infinity, but no phase transition takes place.

The critical points $(T_\sigma,P_\sigma)$, $(T_\sigma,P_\sigma)$ and $(T_M,x_O)$ themselves are not special, but the approach along either the $P=P_\sigma$-isobar, or $T=T_\sigma$-isoterm or the $x=x_0$-isodensity is special and leads, accor-
According to the free energy expressions, to an apparent doubling of the critical exponents \( v \) and \( \gamma \) over the usual mean field values 1, 1/2. Note that the critical exponent \( \eta \) is defined at \( T_c \) and is therefore not influenced by the special approach.

The above indicates that there must be dramatic crossover effects when going from \( x \leq x_0 \) to \( x = x_0 \). In order to account for this quantitatively, A.R. Kortan et al. have proposed a modified free energy expansion. To allow for non-mean field exponents and different exponents \( v_\parallel \) and \( v_\perp \) the following expansion is introduced:

\[
F-F_N = \alpha |\psi|^2 + M_V \left( \frac{\partial \psi}{\partial z} \right)^2 + M_t \left[ (\frac{\partial}{\partial x} + i q_o n_x) + (\frac{\partial}{\partial y} + i q_o n_y) \right]|\psi|^2 + \beta |\psi|^4 + ... \tag{7.12}
\]

where:

\[
\alpha = a(T-T*)^\gamma ; \quad \beta = b(T-T*)^\gamma - 2 \beta
\]

\[
M_V = M_{V_0}(T-T*)^{-2v_\parallel} ; \quad M_t = M_{t_0}(T-T*)^{-2v_\perp}
\]

and where \( T* \) is the \( T* \) from the Pershan-Prost free energy. \( F-F_N \) predicts the following expression for the correlation lengths and the susceptibility:

\[
\xi_\parallel = \sqrt{\frac{M_V}{\alpha}} = \sqrt{\frac{M_{V_0}}{\alpha}} (T-T*)^{-v_\parallel} ; \quad \xi_\perp = \sqrt{\frac{M_t}{\alpha}} (T-T*)^{-v_\perp}
\]

\[
\sigma_o = \sqrt{\frac{kT}{\alpha}} = \sqrt{\frac{kT}{\alpha}} (T-T*)^{-\gamma}
\]

where \( T* \) is given by:

\[
T* = T_1 - t_1 x - \frac{1}{T_3} (T-T_0)^2
\]
Noting that (7.7) is actually an equation for a phase boundary the $T$ in this equation is actually $T_c$ (for a specific $x$).

Using the parabolic expression for $T_c$ (7.7) it is easy to derive expressions for $T-T^*$ in the two cases $x > x_o$ and $x < x_o$:

$x < x_o : T-T^* = (T_c \Delta T/T_3) [t + (T_c/\Delta T)t^2] \quad ; \quad t = |(T-T_c)/T_c|$

$x > x_o : T-T^* = 1/T_3 [(T-T_M)^2 + t_1 T_3 (x_0-x)]$

where: $\Delta T = 2 \cdot (C(x_0-x))^{1/2}$ \hspace{1cm} (7.15)

This leads to the following expressions for $q_o^{\xi||}$, $q_o^{\xi_1}$ and $\sigma_o$:

$q_o^{\xi||} = q_o/T_3 \sqrt{\frac{M_{\nu,0}}{a}} (T_c \Delta T/T_3)^{-\nu||} [t + (T_c/\Delta T)t^2]^{-\nu||}$

$q_o^{\xi_1} = q_o/T_3 \sqrt{\frac{M_{\nu,0}}{a}} (T_c \Delta T/T_3)^{-\nu_1} [t + (T_c/\Delta T)t^2]^{-\nu_1} \quad x < x_o$

$\sigma_o = kT/aT_3(T_c \Delta T/T_3)^{-\gamma} [t + (T_c/\Delta T)t^2]^{-\gamma}$ \hspace{1cm} (7.16)

and

$q_o^{\xi||} = q_o/T_3 \sqrt{\frac{M_{\nu,0}}{a}} [(T-T_M)^2 + C(x_0-x)]^{-\nu||}$

$q_o^{\xi_1} = q_o/T_3 \sqrt{\frac{M_{\nu,0}}{a}} [(T-T_M)^2 + C(x_0-x)]^{-\nu_1} \quad x > x_o$

$\sigma_o = kT/aT_3 [(T-T_M)^2 + C(x_0-x)]^{-\alpha}$ \hspace{1cm} (7.17)
Notice that the apparent doubling of critical exponents for $x=x_0$ is inherent in (7.16) & (7.17). The data in Fig. 7.5 & 7.6, where $x<x_0$ were fitted to (7.16). $q_0 \cdot \sqrt{M_{V_0}}/a$, $q_0 \cdot \sqrt{M_{C_0}}/a$ and $kT/a$ were allowed to vary for each dataset, while $\nu_{||}$, $\nu_\perp$ and $\gamma$ were constrained to be independent of $x$. The result for the exponents $\nu_{||}$, $\nu_\perp$, and $\gamma$ is:

$$\nu_{||} = 0.667 \pm 0.011; \nu_\perp = 0.553 \pm 0.038; \gamma = 1.114 \pm 0.036$$

Using these exponents, the data in Figure 7.5 where $x>x_0$ were fitted to (7.17) $\Delta T$, $T_C$ and $T_M$ were taken from experiment. $\Delta T$ is the temperature difference between the N-Sm-A transition and the N*-Sm-A transition. $T_M$ were taken to be 15.15°C for mixture No. 5 and 15.55°C for mixture No. 6, $T_M$ for mixture No. 5 is 0.4°C smaller than the value for mixture No. 6; this is an experimental fact, which is not understood. The result of the fit is shown as the curves on Figures 7.5 & 7.6 and the fit parameters are given in Table 7.3.

Even though the expressions (7.16) & (7.17) have been derived using the theoretical prediction of a parabolic phase boundary of form (7.7), which have been found not to fit the data rigorously, the expressions (7.16) & (7.17) nevertheless accounts quantitatively for all of the striking properties of the phase-diagram. Only the nonuniversality of the fit parameters is in discrepancy with the theory. It should be noted that in the study of the 60CB-80CB mixture a similar discrepancy is found.
Table 7.3. The result of the fitting of $q_0\xi_1$, $q_0\xi_1$ and $\sigma_o$ to the theoretical prediction. The uncertainty is one standard deviation.

<table>
<thead>
<tr>
<th>MIXT.</th>
<th>$N=\text{SmA}$</th>
<th>$N^*=\text{SmA}$</th>
<th>$x &gt; x_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c/\theta_c$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_0\sqrt{M_{y,0}/a}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_0\sqrt{M_{y,0}/a}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$kT/\bar{a}T_3$</td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>MIXT.</th>
<th>$x &lt; x_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
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<tr>
<td></td>
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</tr>
<tr>
<td>26.41</td>
<td>25.41</td>
</tr>
<tr>
<td>1864±70</td>
<td>2314±100</td>
</tr>
<tr>
<td>139±16</td>
<td>164±22</td>
</tr>
<tr>
<td>4967±486</td>
<td>9615±1189</td>
</tr>
</tbody>
</table>
7.4. Conclusions

The flow studies of the mixture ascertained that the orientational order and the continuous translational symmetry along the director is restored in the reentrant nematic phase. The present study (see Figures 7.5 & 7.6) provide further evidence for the similarity of the two nematic phases. Figure 7.5 shows that the correlation lengths, characterizing the size of the smectic regions, continuously forming and disappearing in the nematic matrix, essentially display the same behaviour in the two nematic phases. There are only minor quantitative differences, as evidenced by Table 7.3, so generally this study confirms that the idea of the existence of an optimum density for smectic ordering provides a correct description of the reentrant nematic to smectic-A phase diagram. Furthermore, the whole set of correlation length-data could be fitted to the simple expressions derived by A.R. Kortan et al., thus accounting for the crossover effects and the increased bare correlation lengths.

It was found that $v_\parallel > v_\perp$, which is also seen in pure bilayer compounds. Furthermore, the numerical values are quite close to bilayer compound values. The same is not true for $\gamma$ which is lower than bilayer values, which are $\sim 1.3$.

Lastly, it is worth noting that in this ternary mixture the phase diagram is well described only locally by the parabola predicted by Pershan & Prost, whereas over the whole x-range it is described more accurately by a rotated parabola. This is different from the study performed on the mixture 60CB-80CB where the phase diagram indeed is well fitted by the predicted parabola.
REFERENCES

8. THE SMECTIC-A PHASE

As mentioned in Chapter 2, there exists no clear-cut microscopic model for the smectic-A phase which can explain the extremely weak higher-order reflections. A few attempts to explain this unusual effect\(^1,2\) are known, but none of them include the effect of the proposed Landau-Peierls state of the smectic-A phase and, furthermore, they are quite different. It is the purpose of this chapter to provide a frame for discussing different models of the smectic-A phase on the basis of generally accepted assumptions.

The experimental fact one must try to explain is that essentially all liquid crystal materials, exhibiting a smectic-A phase, display extremely weak higher-order reflections\(^3\). If \(I(00\ell)\) denotes the peak intensity of the \(\ell\)'th order reflection, then \(I(001)/I(002) \approx 10^{-4}\).

8.1. General model

In order to give an expression for \(I(00\ell)\), which can provide the basis for discussing various models of the smectic-A phase and especially the ratio \(I(001)/I(002)\), one must impose a number of assumptions. These are:

a) The smectic-A phase consists of a regular stack of layers.

b) The basic building block (B.B.B.) of the smectic-A phase is one molecule (monolayer smectic-A's) or an overlapping configuration of two molecules (bilayer smectic-A's).

c) On the average each layer contains \(N_l\) centres of gravity of B.B.B.'s, distributed randomly in the plane of the layer.

d) Any thermal motion of a B.B.B. as a whole, apart from the layer displacement \(u(z)\) introduced in Chapter 2, is neglected.
e) The layers of the smectic-A phase perform harmonic oscillations around average positions.

f) The phases of different modes of \( u(z) \) are uncorrelated.

g) The B.B.B. remains perpendicular to the layer at any point.

h) g) means that the principal axis of the B.B.B. or \( \hat{n}(\mathbf{r}) \), will not be parallel to the z-axis for a transverse undulation mode, as shown in Chapter 2 (Fig. 2.3). This effect is neglected.

The following figure plus the above-mentioned assumptions provide a general model for the smectic-A phase. Within this model it should be possible to discuss the \((00\ell)\)-line shape.

![Diagram of layering of the smectic-A phase.](image)

**Fig. 8.1.** The layering of the smectic-A phase.

The distribution of the centre positions of the B.B.B. along the z-direction will be described by the function \( P(z) \), defined by:

\[
P(z) \cdot dz = \frac{(\text{No. of B.B.B. with centre-pos. between } z \rightarrow z+dz)}{N_L}.
\]

Note that the density \( \rho(z) = N_L \cdot P(z) \).
Simple properties of \( P(z) \) are:

\[
\begin{align*}
\text{i) } & \quad \int_{-d/2}^{+d/2} P(z)dz = 1 \\
\text{ii) } & \quad \int_{-L_z/2}^{+L_z/2} P(z)dz = N_T
\end{align*}
\]

(8.2)

8.2. The scattering cross-section

With the definitions in the previous section it is possible to write down an expression for the scattered intensity at \( \hat{q}_x \):

\[
I(\hat{q}_x) = \langle n(\hat{r}) \cdot e^{i\hat{q}_x \cdot \hat{r}} \rangle^2 \quad ; \quad \hat{q}_x = (0,0,\xi \cdot q_o)
\]

(8.2)

\( n(\hat{r}) \) is the electron density ; \( q_o = \frac{2\pi}{d} \)

Inserting \( n(\hat{r}) = \sum_i n_i (\hat{r} - \hat{R}_i) \) where \( \hat{R}_i \) = pos. of atom \( i' \) and the sum is over all atoms, gives further:

\[
I(\hat{q}_x) = \langle \sum_i f_i \cdot e^{i\hat{q}_x \cdot \hat{R}_i} \rangle^2 = \langle \sum_i f_i \cdot e^{i\hat{q}_x z_i} \rangle^2
\]

where \( f_i \) is the atomic form factor, and \( z_i \) the \( z \)-position of atom \( i' \).

Inserting \( z_i = z_n + u(z_n) + z_{c,j} + z_{j,i}, \) where:

\( z_n \) = average position of the center of the \text{\!nth} layer.

\( u(z_n) \) = thermal deviation of \text{\!nth} layer from its average position.
$z_{c,j}$ = position of an appropriately defined center of the $j$'th B.B.B. relative to the layer center.

$z_{j,i}$ = position of atom $i$ relative to the above-mentioned center of the $j$'th B.B.B.

gives:

$$I(q_\parallel) = (\sum_i f_i e^{iqz_{j,i}})^2 \cdot (\sum_j e^{iqz_{c,j}})^2 \cdot \langle \sum_n e^{iqz(z_n+u(z_n))} \rangle^2$$

$$= (f(q_\parallel))^2 \cdot (O(q_\parallel))^2 \cdot (L(q_\parallel))^2$$

(8.3)

where

$$(f(q_\parallel))^2 = (\sum_i f_i e^{iqz_{j,i}})^2$$

is a molecular form factor term

sum over all atoms in one B.B.B.

or rather a B.B.B. form factor term.

$$(O(q_\parallel))^2 = (\sum_j e^{iqz_{c,j}})^2$$

is an intralayer order term.

sum over all B.B.B. in one layer

$L(q_\parallel))^2 = \langle \sum_n e^{iqz(z_n+u(z_n))} \rangle^2$ is a Landau-Peierls term.

sum over all layers
8.3. The Landau-Peierls term

\[(L(q_L))^2 \text{ has been calculated in Appendix A and the result is}
\]

\[
(L(q_L))^2 = \int e^{i\mathbf{q}_L \cdot \mathbf{r}} \cdot G(\mathbf{r}) d\mathbf{r} \quad \text{where}
\]

\[
G(\mathbf{r}) = e^{-\gamma n \left(\frac{2d}{\lambda z}\right)^2 + \left(\frac{1}{\rho}\right)^2} \cdot e^{-\frac{nE_1}{4\lambda z} \left(\frac{\rho^2}{4}\right)}
\]

\[
\rho^2 = x^2 + y^2 \quad \gamma = \text{Euler's const.} = 0.577 \quad \eta = \frac{k_B T \cdot q_0^2 g^2}{16 \pi B \lambda}
\]

8.4. The molecular form factor term

\[(f(q_L))^2 \text{ can be calculated simply by performing the summation, and it is easily done for a number of materials. I have chosen}
\]

the compounds CBOOA, 80CB, 8CB, 8S5 and 40.8, that is, 3 bilayer compounds and 2 monolayer compounds.

Apart from general assumptions a) - h), the following assumptions and/or approximations are made in the calculation.

a) The interatomic distances are the ones obtained from the crystalline phase of CBOOA.

b) The molecule is rigid. For bilayer smectic-A compounds the tail and head are at angle V with respect to each other and the tail is parallel to the z-direction in the smectic-A phase. The same is assumed for the monolayer compounds.

c) The \(z\)-coordinates of all the hydrogen atoms are set equal to those of the carbon atoms to which they are attached.

d) All the atomic form factors are set equal to the number of electrons in the atom, as the scattering angle is small \(q_0/k \approx 1/20\) for CuK\(\alpha\)-radiation.
In Figure 8.2 a CBOOA-molecule with interatomic distances and angles is given for reference.

\[
\begin{align*}
\alpha &= 1.53 \text{Å} & \beta &= 1.463 \text{Å} \\
\alpha' &= 1.436 \text{Å} & \gamma &= 1.131 \text{Å} \\
b &= 1.369 \text{Å} & \alpha' &= 38^\circ \\
c &= 1.39 \text{Å} & \alpha &= 34^\circ \\
d &= 1.424 \text{Å} & \beta &= \gamma \\
e &= 1.290 \text{Å} & \delta &= 119^\circ \\
f &= 1.468 \text{Å}
\end{align*}
\]

![Image of a CBOOA-molecule]

Fig. 8.2. CBOO\(^*\)-molecule from reference\(^4\). Average values for \(\alpha\), \(c\), \(\alpha\) and \(\gamma\) are used in the calculations, since these values deviate less than 5\% from the average value.

It is clear that \(f(q_z)\) is sensitive only to changes in the \(z\)-position of the atoms. I have assumed that the two basic mechanisms to provide this are variation of the angle \(\gamma\) and, for bilayer compounds, variation of the overlap parameter \(\delta\) as defined in Figure 8.3, where the unit cell is shown for 8CB.
Fig. 8.3. 8CB in the unit cell for $\delta = 5.5$ Å and $\delta = 6.5$ Å. The C-H-distance in the end of the tails have been set to 1 Å (from the CBOOA crystalline phase).
The symmetric structure of bilayer compounds makes it quite easy to calculate \( f(q_1) \):

\[
\begin{align*}
f(q_1) &= \sum_{i} f_{ie}^i q_{z_j,i} \\
&= \sum_{i,TAIL 1} \sum_{j} f_{ie}^i (z_{TAIL 1} + z_{j,i}) + \ldots \quad \text{(sums over other parts of molecule 1)} \\
&\quad + \sum_{i,TAIL 2} \sum_{j} f_{ie}^i (z_{TAIL 2} + z_{j,i}) + \ldots \quad \text{(sums over other parts of molecule 2)} \\
&= (z_{TAIL 2} = -z_{TAIL 1}) \\
&= \cos(q_1 \cdot z_{TAIL}) \cdot \sum_{i,TAIL} f_{ie}^i q_{z_j,i} + \ldots \quad \text{(similar terms for other parts of the molecule)}
\end{align*}
\]

\( z_{TAIL} \) is the \( z \)-position of an appropriately defined center of a tail, etc.

This means that if sums like \( \sum_{i,TAIL} f_{ie}^i q_{z_j,i} \) have been calculated once for basic constituents like \( C_8H_{17} - TAIL \), Benzene ring, N-C-links, etc., then it is quite easy to calculate \( f(q_1) \) for different bilayer compounds. For monolayer compounds this cannot be done, but in any case it is a simple procedure to write a computer program performing the full summation.

The result of the calculation is displayed in Figures 8.4, 8.5 & 8.6. As is evident from the figures, the following are the main conclusions to be drawn from the calculation:
Fig. 8.4. \( f \) versus \( q \) (units of \( \frac{2\pi}{d} \)) for the three bilayer compounds 8CB, 80CB and CBOOA and various overlap parameters. \( V = 0 \).

Fig. 8.5. \( f \) versus \( q \) (units of \( \frac{2\pi}{d} \)) for the two monolayer compounds 40.8 and 885. For 40.8 two curves are shown, one for \( V = 0 \) and one for \( V = 20 \). For 885 three curves are shown, each having a different oxygen-sulphur-distance. This distance is unknown, since it does not occur in crystalline CBOOA.
Fig. 8.6. The three bilayer compounds for one specific overlap ($\delta = 6.5$ Å) and two values of $V$. $V = 0^\circ$ and $V = 20^\circ$.

Although the general feature of the $f(q_\parallel)$-curves are rather similar, especially within the two categories of bilayer and monolayer compounds, then it is obvious that there is a pronounced $\delta$-dependence for the bilayer compounds, whereas the $V$-dependence is less marked for all compounds. As a specific example we look at 8CB and compare the $\delta = 5.5$ Å-curve with that of $\delta = 6.5$ Å. The latter corresponds to a rather large overlap.
of the benzene rings the former to a configuration, where the total length of the two overlapping molecules is equal to the d-spacing of the smectic-A phase (see Figure 8.3). To get a quantitative measure for the difference between these two curves, one can look at the ratio \( \left( \frac{f(q_1)}{f(q_2)} \right)^2 \). From the calculation one gets, for \( V = 0 \):

\[
\left[ \frac{f(q_1)}{f(q_2)} \right]^2 = 20.7 \text{ for } \delta = 5.5 \text{ Å}
\]

\[
\left[ \frac{f(q_1)}{f(q_2)} \right]^2 = 5.4 \text{ for } \delta = 6.5 \text{ Å}
\]

As can be seen from Figure 8.3, I have taken the value \( d = 31.0 \text{ Å} \) in order to compare with Ref. (1). It turned out that the value for \( \left[ \frac{f(q_1)}{f(q_2)} \right]^2 (\delta = 6.5 \text{ Å}, V = 0^\circ) \) from this reference, namely 17.54, is obtained by omitting all the hydrogen atoms, therefore yielding the difference. What is crucial to note is the rather large difference one obtains by shifting the molecules a distance as small as 1Å relative to each other.

### 8.5. The intralayer order term

The last term in the expression for \( I(q_x), (O(q_x))^2 \) is not a priori given. It is necessary to assume a particular distribution of B.B.B. along the normal layer, and one can express \( O(q_x) \) in terms of \( P(z) \) in the following way:

\[
O(q_x) \equiv \left\{ \sum_{j=1}^{N_L} e^{i q_x c_r j} \right\} = N_L \cdot \left\{ \int_{-d/2}^{d/2} e^{i q_x z} P(z) dz \right\}^{\frac{d}{2}}
\]  

(8.5)

It is in the choice of \( P(z) \), the actual modelling of the smectic-A phase takes place.

To exemplify, one can calculate \( O(q_x) \) for different \( P(z) \)'s:
1) \( P(z) = \delta(z-nd); n = 0, 1, \ldots \), corresponding to perfect line-up of all B.B.B.-centers - usual textbook picture of the smectic-A phase,

\[ O(q_z) = N_L \text{ (independent of } q_z) \]

2) \( P(z) = 1/d \); corresponds to total smearing out of B.B.B.-centers, that is in fact a nematic phase

\[ O(q_z) = 0 \text{ as expected} \]

3) Gaussian distribution of B.B.B.

\[ O(q_z) = N_L \cdot e^{-\left(q_z \langle \sigma_z \rangle \right)^2} \text{ for } \sigma_z << d \]

4) \( P(z) = \sum_{i=0}^{\infty} a_i' \cos(iq_0z); a_0' = 1/d \) \quad \text{corresponding to a Fourier expansion of the B.B.B.-density.} \]

\[ O(q_z) = N_L \cdot \frac{\langle a_z \rangle}{2} \text{ for } q_z = t \cdot q_0; t = 1, 2, \ldots \]

\( a_1 \) in Example 4 can be related to the smectic-order parameter \( \psi \), which is introduced by De Gennes (see Chapter 2). This is obvious by using that:
\[ \varrho(z) = N_L \cdot P(z) = \frac{N_L}{d} \cdot (1 + a_1 \cos(q_0 z) + \ldots + a_N \cos(Nq_0 z) + \ldots) \]

Fourier expansion of \( P(z) \), Example 4

\[ \equiv \varrho_o (1 + a_1 \cos(q_0 z) + \ldots); \quad \varrho_o \equiv \frac{N_L}{d} \]

Comparing this with \( \varrho(z) = \varrho_o \left[ 1 + \Re \left( e^{i q_0 z} \right) \right] \) from Chapter 2 yields

\[ a_1 = |\psi| \]

with \( \varrho(q_z) = N_L \langle a_1 \rangle / 2 \) it is clear that there would be no higher-order reflections if all \( a_1 \)'s; \( q = 2, \ldots \), are truly zero and only the fundamental reflection would be present with:

\[ \varrho(q_z) = N_L \frac{\langle |\psi| \rangle}{2} \]

Instead of describing the smectic-A structure via a Fourier expansion of \( P(z) \) one could more directly postulate that the smectic-A phase is obtained from the nematic phase by a specific modulation of the centres of the B.B.B. If this modulation is described by:

\[ z_j = f(z_j) \quad (8.6) \]

where \( z_j \) is the random position of the centres of the B.B.B. in the nematic phase and \( z_j \) is the position of the B.B.B. in the modulated smectic-A phase. In the nematic phase \( P_N(z) = 1/d \) (Example 2). By the modulation \( f(z_j) \) one will obtain a \( P_S(z) \), which can be found by the following argument:

The number of B.B.B. in \([z_0; z_0 + dz_0]\) in the nematic phase = \( N_L \cdot 1/d \cdot dz_0 \) will move by the modulation \( f(z_0) \) to \([z; z + dz]\); where:
This gives via the definition of $P(z)$: $P_{S}(z) = 1/d \cdot [f'(z_{0})]^{-1}$; $z_{0} = f^{-1}(z)$, which yields:

$$O(q_{z})^{2} = \langle \frac{1}{d} \int_{-d/2}^{d/2} e^{i\frac{1}{2}q_{z}} f(z_{0}) \cdot P_{S}(z) dz \rangle^{2}$$

$$= \langle \frac{1}{d} \int_{-d/2}^{d/2} e^{i\frac{1}{2}q_{z}} f(z_{0}) \cdot \frac{dz}{f'(z_{0})} \rangle^{2}$$

The simplest modulation giving a layered structure is a sinusoidal modulation:

$$z_{j}^{+} = z_{j} + A \cdot \sin(q_{0} \cdot z_{j}) ; \quad A < \frac{1}{q_{0}} \quad (8.7)$$

Yielding:

$$O(q_{z})^{2} = \langle \frac{1}{d} \int_{-d/2}^{d/2} e^{i\frac{1}{2}q_{z}} (z^{2} + A \cos(q_{0} z^{2} + z)) \cdot dz \rangle^{2} =$$

$$\frac{N_{L}^{2}[J_{x}(q_{z}A)]^{2}}{N_{L}} \quad (Hansen integral representation of the $x$'th order Bessel function $J_{x}$).

The above sinusoidal modulation approach to the smectic-A phase can of course also be described in terms of a Fourier expansion of $P(z)$ or equivalently, the density. By comparing the expression for $O(q_{z})$ in Example 4 and above, one immediately finds that the $P(z)$ describing the sinusoidally modulated structure is given by a Fourier expansion:
\[ P(z) = \frac{1}{d} \sum_{l=0}^{\infty} a_l \cdot \cos(l \cdot q_0 z) \]

where \( a_l \) is given by:

\[ a_l = 2 \cdot J_l(q_0 A) \]

and further:

\[ |\psi| = a_1 = 2 \cdot J_1(q_0 A) \equiv q_0 A \]

and

\[ a_2 = 2 \cdot J_2(2 \cdot q_0 A) \equiv (q_0 A)^2 \]

for \( q_0 A \ll 1 \) or \( T \ll T_c \)

leading to:

\[ O(q_1(=q_0)) = N_L \frac{\langle \psi \rangle}{2} \quad \text{and} \quad O(q_2(=2q_0)) = N_L \frac{\langle \psi \rangle^2}{2} \]

for \( Aq_0 \ll 1 \) or \( T \ll T_c \).

**8.6. Temperature dependence of \( I(q_1)/I(q_2) \) close to \( T_c \).**

**An example**

It is now possible to investigate the temperature dependence of \( I(q_1)/I(q_2) \) close to \( T_c \). One gets:

\[
\frac{I(q_1)}{I(q_2)} = \left( \frac{\epsilon(q_1)}{\epsilon(q_2)} \right)^2 \cdot \frac{\int e^{i \hat{q}_1 \cdot \vec{r}} G(\vec{r}) d^2 \vec{r}}{\int e^{i \hat{q}_2 \cdot \vec{r}} G(\vec{r}) d^2 \vec{r}} \cdot \frac{O(q_1)}{O(q_2)}^2
\]

(8.9)

The first term is temperature independent, but depends rather critically on the overlap parameter \( \delta \) for bilayer compounds, which is a good argument for picking a monolayer compound for an experimental study.
Fig. 8.7. \((L(q_1))^2\) and \((L(q_2))^2\) convoluted with the resolution function; \(q_1 = q_0\) and \(q_2 = 2q_0\). The difference for \(n = 0\) indicates that the resolution along \(q_0\), the longitudinal resolution, is not the same for \(q = q_1\) and \(q = q_2\). This is due to the difference in \((\Delta \lambda)/(\lambda)\)-contribution as outlined in Chapter 4. \(n_2 = 4 \cdot n_1\).

\[
(L(q_2))^2 = e^{-2\gamma n} \left(\frac{(2d)/(2\pi)}{n}\right)^{2n} \int \left(\frac{1}{\rho^2}\right)^n e^{-n \cdot E_1 \left(\frac{\rho^2}{4\lambda z}\right)} \cdot e^{i\mathbf{q}_2 \cdot \mathbf{r}} d\mathbf{r}.
\]

Three \(n_1\)-values were chosen 0.15, 0.25 and 0.35. For these values \(\lambda\) was taken from reference 5 to be 3.8, 4.5 and 8.2. The resolution functions at \(q = q_0\) and at \(q = 2q_0\) are given in Table 4.2.
The second term can be evaluated, numerically, for a specific experimental set-up. This term is temperature dependent, since $n$ grows as $T \cdot T_c^{-5}$.

The last term can be evaluated when a specific model has been chosen.

As a concrete example 80CB has been chosen. For this compound the first term is calculated and the result can be taken from Figure 8.4. The second term has been calculated for a specific resolution function. This resolution is typical for the kind of resolution function one can obtain using single crystal

![Diagram](image)

**Fig. 8.8.** Longitudinal (001)-lineshapes, convoluted the resolution function, for three $n$-values.
techniques in liquid crystal X-ray diffraction. Chapter 3 is dedicated to a description of these techniques and the resolution used here is described in detail in Chapter 4. The result for the peak value of the numerical convolution of the resolution function and \( \int e^{i \mathbf{q} \cdot \mathbf{r}} G(\mathbf{r}) \, d\mathbf{r} \) is shown in Figure 8.7 for a number of \( n \)-values in the observed range.  

In Figure 8.8 the (001)-line shape for scans along \( \mathbf{q}_0 \) is shown for different \( n \)-values. The resolution function along \( \mathbf{q}_0 \) is also shown. In Figure 8.9 the (001)- and (002)-line shapes are compared for the same value of \( \mathbf{B} \cdot \lambda \) (see Section 8.3.), corresponding to the two \( n \)-values \( n(q_1) \equiv n_1 = 0.25 \) and \( n(q_2) \equiv n_2 = 4 \cdot n_1 \).

In terms of the general Fourier expansion of \( P(z) \) in Example 4 the term \( (O(q_1)/O(q_2))^2 \) in (8.9) is:

\[
\frac{O(q_1)^2}{O(q_2)^2} = \frac{\langle \psi \rangle^2}{\langle a_2 \rangle^2} \tag{8.10}
\]

The sinusoidal modulation gives:

\[
\frac{O(q_1)^2}{O(q_2)^2} = \frac{1}{\langle |\psi| \rangle^2} = C^{-2} \cdot t^{-2 \beta} \tag{8.11}
\]

Without assuming the sinusoidal modulation McMillan's theory for the smectic-order parameter \( \langle |\psi| \rangle \) can be extended to give also \( \langle a_2 \rangle \). The result is

\[
\langle a_2 \rangle^2 = (1/2 + \gamma/\alpha) \langle \psi \rangle^2 \tag{8.12}
\]

where \( \gamma/\alpha = 0.5(a/2)^3[1-(a/2)^3] \) and \( \alpha \) is McMillan's parameter: \( \alpha = 2e^{-\pi \rho_0/\delta} \). \( \rho_0 \) denotes the length of the rigid head (or for monolayer compounds, the rigid middle section) of the constituent molecules. This gives:

\[
\frac{O(q_1)^2}{O(q_2)^2} = \frac{(1/2 + \gamma/\alpha)^2}{\langle |\psi| \rangle^2} = \frac{(1/2 + \gamma/\alpha)^2 C^{-2} \cdot t^{-2 \beta}}{\langle |\psi| \rangle^2} \tag{8.13}
\]
Fig. 8.9. Longitudinal (001)- and (002)-lineshapes, convoluted with the resolution function, for $\eta_1 = 0.25$ and the corresponding $\eta_2 = 1.0$.

The value of C can be obtained from the McMillan theory \(^1\):

$$C = \frac{1}{(1-2\gamma/a)^2} = 1.1 \text{ for } 8\text{CB}, 80\text{CB} \& \text{CBOOA}$$

Thus an extension of the McMillan theory predicts a ratio which differs from the sinusoidal modulation result by a factor $(1/2 + \gamma/a)^2$. This factor is typically $0.31^1$ for smectic-A compounds like 8CB, 80CB, and CBOOA.
8.7. Conclusion

On the basis of calculations such as the ones performed for 80CB (Figures 8.4 and 8.7), various models for $O(q)$, and an experimental study it should be possible to elucidate which mechanisms are needed to explain experimental data for a liquid crystal that displays a smectic-A phase. One needs accurate measurements of the (001)- and (002)-line shapes for a number of temperatures close to $T_c$.

An experimental study must take due account of the multiple scattering that occurs in a sample with mosaicity. The process is shown in reciprocal space in Figure 8.10. Obviously, the multiple scattering contribution depends critically on the mosaicity. To rid oneself of ambiguities, the optimal thing to do is to pick a monolayer compound with a second-order nematic-smectic-A phase transition and learn to grow smectic-A phases with a mosaicity-distribution $\ll 1^\circ$.

![Figure 8.10. Multiple scattering process in reciprocal space. $\vec{H}$ is aligning field. $|q_o| = (2\pi)/(d)$. $\vec{q}_{OUT}$. A true second order reflection is also shown.](image)
REFERENCES

1) J. Stamatoff, P.E. Cladis, D. Guillon, M.C. Cross, T. Bilash and P. Finn (1980) Phys. Rev. Lett. 44 1509. (In this letter $\delta = 6.5$ Å and all the hydrogen atoms have been omitted).


APPENDIX A

CALCULATION OF ANOMALOUS SCATTERING SINGULARITIES IN THE SMECTIC-A PHASE, USING THE HARMONIC APPROXIMATION

The model underlying the calculation is the following: The smectic-A phase is assumed to be a regular stack of layers. The layers are assumed to consist of basic building blocks (B.B.B.), which are distributed at random in the plane of the layer. The B.B.B. may be a single molecule (monolayer smectic-A's), or an overlapping configuration of two (bilayer smectic-A's).

Furthermore, the layers are assumed to perform harmonic oscillations around some average position. This oscillation can be described by the thermal average of the square of the Fourier transform of the layer displacement $\langle |u(q)|^2 \rangle$ as obtained by equipartition (Chapter 2):

$$\langle |u(q)|^2 \rangle = \frac{k_B T}{V_B (q_x^2 + \lambda^2 q_z^2)} \quad (A.1)$$

A fundamental expression for the scattering cross-section is:

$$S(\xi) = \sum_{ij} e^{i\xi \cdot (\hat{R}_i - \hat{R}_j)} \quad (A.2)$$

where $\hat{R}_i$, $\hat{R}_j$ are the positions of the $i$'th and the $j$'th layer.

Inserting $\hat{R}_i = \hat{R}_i + u(\hat{R}_i) \cdot \hat{\tau}_z$ gives:
In the harmonic approximation, one gets further:

\[ S(\kappa) = N \cdot \sum_i e^{-i \kappa \cdot R_i} \cdot e^{-1/2 \kappa^2} \cdot \langle (u(R_i) - u(0))^2 \rangle \tag{A.4} \]

On inserting the Fourier expansion of \( u(R_i) \) and assuming that the phases of the different modes of \( u(R_i) \) are uncorrelated, we obtain:

\[ S(\kappa) = N \cdot \sum_i e^{i \kappa \cdot R_i} \cdot e^{-1/2 \kappa^2} \cdot \langle |u(q)|^2 \rangle (1 - \cos(q \cdot R_i)) \]

Replacing \( \sum \) by \( \frac{V}{(2\pi)^3} \int dq \) gives:

\[ S(\kappa) = N \cdot \sum_i e^{i \kappa \cdot R_i} \cdot e^{-1/2 \kappa^2} \left[ \frac{V}{(2\pi)^3} \int |u(q)|^2 \right] (1 - \cos(q \cdot R_i)) dq \]

Shifting to the continuous variable \( \cdot \) instead of \( R_i \) gives:
\[ S(\langle \rangle) = N \cdot \int e^{i\mathbf{x} \cdot \mathbf{r}} \cdot e^{-1/2\kappa^2 \cdot I(\mathbf{r})} d\mathbf{r} \]

\[ N \cdot \int e^{i\mathbf{x} \cdot \mathbf{r}} G(\mathbf{r}) d\mathbf{r} \quad \text{(A.5)} \]

where \( I(\mathbf{r}) = \frac{V}{(2\pi)^3} \cdot \int \langle |u(\mathbf{q})|^2 \rangle \cdot (1 - \cos(q \cdot r)) dq \) and

\[ G(\mathbf{r}) = e^{-1/2\kappa^2 \cdot I(\mathbf{r})} \]

Note that the calculation so far has been exactly parallel to that of normal thermal diffuse scattering. But from now on it differs, since an expansion of the exponential term \( e^{-1/2\kappa^2 \cdot I(\mathbf{r})} \) is not justified here.

Inserting \( \langle |u(\mathbf{q})|^2 \rangle \) into \( I(\mathbf{r}) \) gives:

\[ I(\mathbf{r}) = \frac{k_B T}{B(2\pi)^3} \cdot \int \frac{1 - \cos(q \cdot r)}{q^2 + \lambda^2 q_1^4} dq_1 dq_2 dq_3 \quad \text{(A.6)} \]

\[ = \frac{k_B T}{B(2\pi)^3} \cdot \int \frac{1 - e^{iq \cdot r}}{q^2 + \lambda^2 q_1^4} dq_1 \quad \equiv A \cdot J(\mathbf{r}) \]

\[ \text{even numerator in integrand} \]

In an infinite sample the only cut-off in \( J(\mathbf{r}) \) is \( q_{1,\min} = -2\pi n/d \) and \( q_{1,\max} = 2\pi n/d \) and \( |q_{1,\max}| = 2\pi n/d \) where \( n \) is the order of the reflection.

For the \( q \)-integration \( q_{1,\max} \) can be changed to \( \infty \) and \( q_{1,\min} \) to \( -\infty \). The \( q \)-integration can then be done by a residue-calculation. The \( q \)-integral is:
Performing the contour integral along the curve $C$ shown beneath gives:

$$\int = 2\pi i \sum \text{resid} = \int_{C_R}^{+R} \int_{-R}^{+R} \int_{C_R} J^+(r)$$

For $R \to \infty$, $\int_{C_R} \to 0$ and $\int_{-\infty}^{+\infty} = 2\pi i \sum \text{resid} = 2\pi \cdot \frac{1-e^{-\lambda q_1^2 + i\delta \cdot q_{\perp}}}{2\lambda q_1^2}$ and one gets:

$$J^+(r) = \pi \cdot \frac{1-e^{-\lambda q_1^2 + i\delta \cdot q_{\perp}}}{\lambda q_1^2}$$ (A.8)
Inserting \( dq_{1,1} \cdot dq_{1,2} = q_1 d\theta dq_1 \) and using the Hansen integral expression for \( J_0 \) (the zero'th Bessel function):

\[
J_0(x) = \frac{1}{2\pi} \cdot \int_0^{2\pi} e^{ix\cos \theta} d\theta
\]

gives, when integrating over \( \theta \):

\[
J(r) = \frac{2\pi^2}{\lambda} \int_0^{q_{1,\text{max}}} \frac{q_1}{q_1} \left( 1 - e^{-z\lambda q_1^2} J_0(q_1^2) \right) dq_1
\]

\[
= \frac{2\pi^2}{\lambda} \cdot \left[ 1 - \frac{e^{-z\lambda q_1^2}}{q_1} \right] \cdot \sum_{n=0}^{\infty} \frac{(-1)^n q_{1,\text{max}}^2 n}{(n!)^2} \left[ \frac{q_{1,\text{max}}^2}{4} \right] dq_1
\]

The power series expansion of \( J_0(q_{1,\rho}) \)

\[
= \frac{2\pi^2}{\lambda} \cdot \left[ 1 - \frac{e^{-z\lambda q_1^2}}{q_1} \right] \cdot \sum_{n=1}^{\infty} \frac{(-1)^n q_{1,\text{max}}^2 n}{(n!)^2} \left[ \frac{q_{1,\text{max}}^2}{4} \right] dq_1
\]

The last integral is known and is given by:

\[
\int_{q_{1,\text{max}}}^{q_{1,\text{max}}} x^{n-1} e^{-z\lambda x} dx = \left[ e^{-z\lambda x} \cdot \sum_{i=0}^{n-1} \frac{(n-1)! x^{n-1-i}}{(n-1-i)! (-z\lambda)^i} \right]_{q_{1,\text{max}}}^{q_{1,\text{max}}}
\]

\[
= \frac{(n-1)!}{(\lambda a)^n} \left[ 1 - e^{-z\lambda q_{1,\text{max}}^2} \right] \cdot \frac{1}{(n-1)! (-z\lambda)^i+1} \left[ \frac{q_{1,\text{max}}^2}{4} \right]_{q_{1,\text{max}}}^{q_{1,\text{max}}}
\]

for \( z\lambda q_{1,\text{max}}^2 \gg 1 \).
Inserting this limit yields:

\[ J^* = \frac{2\pi^2}{\lambda} \int_0^{q_{1,\max}} \frac{(1-e^{\lambda q_1^2})}{q_1} dq_1 - \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left( \frac{\rho^2}{4} \right)^n \frac{1}{(2\lambda)^n} \]

\[ = \frac{\pi^2}{\lambda} \left[ 2 \int_0^{q_{1,\max}} \frac{(1-e^{\lambda q_1^2})}{q_1} dq_1 + \gamma + \ln \left( \frac{\rho^2}{4\lambda} \right) + E_1 \left( \frac{\rho^2}{4\lambda} \right) \right] \]

The power series expansion of the exponential integral \( E_1(x) \) is:

\[ E_1(x) = -\int \frac{e^{-t}}{x} \frac{dt}{t} \quad \text{(A.9)} \]

\( \gamma \equiv \text{Euler const.} \). The last integral can be evaluated in the following way:

\[ 2 \int_0^{q_{1,\max}} \frac{(1-e^{\lambda q_1^2})}{q_1^2} dq_1 \]

\[ = \left[ \ln(\lambda q_{1,\max}^2) + \gamma + E_1(\lambda q_{1,\max}^2) \right] \quad \text{(A.10)} \]

"Handbook of mathematical functions" ed. by Abramowitz & Segun p. 230,

which finally gives (\( E_1(x) \to 0 \) for \( x \gg 1 \)) for \( \lambda q_{1,\max}^2 \gg 1 \):

\[ J^* = \frac{\pi}{\lambda} \left[ \ln(\lambda q_{1,\max}^2) + 2\gamma + E_1 \left( \frac{\rho^2}{4\lambda} \right) + \ln \left( \frac{\rho^2}{4\lambda} \right) \right] \quad \text{(A.11)} \]

\[ = \frac{\pi^2}{\lambda} \left[ 2\gamma + \ln \left( \frac{\rho^2 q_{1,\max}^2}{4} \right) + E_1 \left( \frac{\rho^2}{4\lambda} \right) \right] \]
Inserting $J(r)$ into $I(r)$ (A.6) and thereafter $I(r)$ into $G(r)$ (A.5) gives:

$$G(r) = \left( \frac{\rho \cdot q_{1,\text{max}}}{2} \right)^{-2 \cdot \eta} \cdot e^{-\eta \cdot E_1 \left( \frac{\rho^2}{4 \lambda z} \right)}$$  \hspace{1cm} (A.12)

where

$$\eta = \frac{k B T \pi^2}{2 \pi (2 \pi)^3 \cdot 2 \lambda} = \frac{k B T \cdot \kappa_z^2}{16 \pi B \lambda}$$  \hspace{1cm} (A.13)

Inserting

$$\kappa_z = n \Delta = \frac{2 \pi}{d}$$ and $q_{1,\text{max}} = \frac{2 \pi n}{d}$ finally gives, for $z \gg \frac{d}{4 \pi^2 n^2 \lambda}$:

$$G(r) = e^{-\gamma \eta} \cdot \left( \frac{2 \cdot d}{2 \pi n \cdot \rho} \right) \cdot e^{-\eta E_1 \left( \frac{\rho^2}{4 \lambda z} \right)}$$  \hspace{1cm} (A.14)

where $\eta = \frac{k B T \cdot q_o^2 n^2}{16 \pi B \lambda}$

For $\rho \ll z$ one gets:

$$G(r) = e^{-\gamma \eta} \cdot \left( \frac{d^2}{4 \pi^2 n^2 \lambda z} \right)^\eta$$  \hspace{1cm} (A.15)

and for $z \ll \rho$ one gets

$$G(r) = e^{-2 \gamma \eta} \cdot \left( \frac{2d}{2 \pi \rho \cdot \rho} \right)^{2 \eta}$$  \hspace{1cm} (A.16)

which yields the postulated $S(\kappa)$ in Chapter 2.
APPENDIX B

CONSTRUCTION OF CONJUGATE DIAMETERS. TRANSFORMATION FROM ONE SET TO ANOTHER

The transformation from one set of conjugate diameters to another, where the direction of one of the new diameters is given (the y-axis on the figure), is given by the following formulae (Variables relate to the figure. On the same figure the construction of a set of conjugate diameters from perpendicular diameters in a circle with the same diameter as the long axes of the ellipse is shown):

\[ Y_1 = \frac{X_1 \cdot X_2 \cdot \sin \phi}{w_x} \; ; \; w_x^2 = A_x^2 + B_x^2 \]

\[ \tan \alpha = -\frac{w_x}{A_x A_y + B_x B_y} \; ; \; Y_2 = \frac{w_x}{\sin \alpha} \]

\[ A_x = \text{x-component of } X_1 \]
\[ A_y = \text{y-component of } X_1 \]
\[ B_x = \text{x-component of } X_2 \]
\[ B_y = \text{y-component of } X_2 \]
Fig. B. Geometric construction of conjugate diameters
APPENDIX C

NUMERICAL DECONVOLUTION PROCEDURE USED TO OBTAIN CRITICAL DATA FOR THE MONOLAYER LIQ. X-TAL 8S5 AND THE MIXTURE 5CT:9:7CBx:80CB91-x

The experiments reported on in this thesis, are high-resolution X-ray diffraction experiments in the critical region of the nematic to smectic-A phase transition. The perfect crystals, described in Chapter 3, have made it possible to measure the diverging correlation lengths as close as 10^{-5}-10^{-4} in reduced temp. Correlation lengths as large as 10,000 Å can be measured, but in order to obtain these data it is necessary to deconvolute the raw data. For this purpose it is essential to know what the resolution of the spectrometer is. Chapter 4 is dedicated to a discussion of the resolution function when the spectrometer operates in the horizontal triple-axis mode. The numerical deconvolution procedure used to deconvolute the data is a slightly modified version of a procedure developed at M.I.T. by M. Kaplan and coworkers. This appendix will describe this procedure. It is assumed that the resolution function is a given function. In the 8S5 and the mixture experiments the resolution function has two components, the in-plane resolution, and out-of-plane resolution \delta_{T}(q_{T}) \cdot R_{\ast}(q_{\ast}) and R_{\nu}(q_{\nu}) respectively, where R_{\ast} and R_{\nu} are assumed to be Gaussians with the measured and/or calculated FWHM.

Once the resolution function is known, the basic problem is to fit the experimental data, that is, longitudinal and transverse scans, to the scattering cross-section convoluted with the resolution function and, if necessary, convoluted with the mosaicity distribution.

Formally the scattered intensity is given by:
\[ I(q) = \int S_N(q-q') \cdot R(q') dq' \quad (C.1) \]

where:

\[ S_N(q-q') = \int M(q'^*) \cdot S(q-q'-q'^*) dq'^* ; \]

\[ M(q'^*) \] is the mosaicity distribution and

\[ S(q) = \frac{a \cdot r^2}{1 + (q \cdot q_0)^2 \cdot [(q - q_0)/q_0]^2 + (q_1/q_0)^2 \cdot (q_1/q_0)^2} \quad (C.2) \]

\[ q_z = q_z ; \quad q_1^2 = q_x^2 + q_y^2 \]

The essential steps in the numerical deconvolution are the following:

1) Conversion of intensity versus motor positions to intensity versus coordinates in reciprocal space.
2) Assuming no resolution correction a first guess on the parameters in (C.2) is obtained.
3) The data from 1) are least-squares fitted to a numerical convolution of \( S(q) \) with the resolution function, using the parameters from 2) as a first guess.

C.1. Conversion from motor position to reciprocal space

Since the \( k \)-vector of the radiation is \( \sim 20 \cdot q_0 \) it is simple to perform longitudinal and transverse scans. A longitudinal scan is made merely by rotating the analyzer crystal (A.R.) or rotating the sample arm (S.A.); similarly, a transverse scan can be made by rotating the sample (S.R.) (See the figures of the experimental setup in Chapter 3). This means that performing, either a longitudinal or transverse scan involves stepping only one motor; thus, it is quite convenient to operate the spectro-
meter in terms of motor positions, especially at the synchrotron where the data accumulation rate is very high. In principle, the spectrometer could be operated in reciprocal space coordinates. This would be a matter of merely using a different subroutine package for the remote computer control of the spectrometer.
The motor positions have to be converted to reciprocal space coordinates to put the data on a proper scale. This is easily done. In Figure C.1 the connection between angles (motor positions) and reciprocal space coordinates is displayed for either type of scan.

C.2. No resolution correction

There are essentially three physical parameters in (C.2) which can be deduced from the experimental data:

i) The longitudinal correlation length $\xi_\parallel(t)$
ii) The transverse correlation length $\xi_\perp(t)$
iii) The susceptibility $\chi^2(t)$

If there are no resolution corrections, these parameters can be readily deduced from a longitudinal and transverse scan.

Longitudinal: $q_\perp = 0 \Rightarrow S(q_\perp = 0, q_\parallel) = \frac{a \cdot \xi_\parallel^2}{1 + (\xi q_\parallel)^2 \cdot [(q_\parallel - q_0)/q_0]^2}

\Rightarrow \text{HWHM (Half Width at Half Maximum)} = \frac{1}{\xi_\parallel q_0}

Transverse: $q_\parallel = 0 \Rightarrow S(q_\parallel, 0) = \frac{a \cdot \xi_\parallel^2}{1 + (\xi q_\parallel)^2 \cdot q_\parallel/q_0)^2}

\Rightarrow \text{HWHM} = \frac{1}{\xi_\parallel q_0}

$\chi$ can then obviously be obtained from the peak intensity.

The parameters thus obtained can then be used as a first guess when convoluting $S(\mathbf{q})$ with the resolution function.
C.3. Least-squares fit

The least-square fitting was done using a standard fitting routine. This requires a convolution of $S(q)$ with the resolution function for all points in the longitudinal and transverse scans, typically 30–70 points, and for each set of parameters specified by the fitting routine. This two-dimensional integration, which has to be done many times in one fit, is rather time-consuming, and it is essential to find an integration procedure that is accurate and fast. The functions to be convoluted are

$$S(q) = \frac{P(1) \cdot (P(2))^2}{1 + [P(2)]^2 \left[ \left( q_\|/q_0 - P(4) \right)^2 + [P(3)]^2 \cdot \left( q_\perp/q_0 - P(5) \right)^2 \right]};$$

$$q_\|= q_z \quad ; \quad q_\|^2 = q_x^2 + q_y^2$$

(C.3)

and

$$R(q') = e^{-\frac{q_y^2}{2\sigma_y}} \cdot e^{-\frac{q_z^2}{2\sigma_z}} \cdot \delta(q_x)$$

(C.4)

where $P(1) + P(5)$ are the fitting parameters. Note that $P(2) = q_0 \cdot \xi_\|; P(3) = q_0 \cdot \xi_\perp; a = P(1)/q_0^2$.

The parameters $P(4)$ and $P(5)$ have been included to deal with the possibility that the longitudinal scan was not made exactly at $q_\|= 0$, and similarly for the transverse scan.

The two-dimensional integration procedure is one out of a number of integration procedures described by A.H. Stroud\(^1\) which performs the integrations by intelligently picking out a number (N) of points in the plane and for each point specifying a corresponding weight factor. The convolution integral is thus calculated by the sum:

$$\sum_{i=1}^{N} B_i \cdot S(q_i) \cdot R(q_i)$$

(C.5)
In Reference 1) the points and weight factors $B_i$; $i=1, \ldots, N$ are specified for $N = 12, 13, 16, 20, 21, 25, 28, 37, 44, 48$. The points are defined for an integration over a $-1, +1$-quadrant in the plane. Therefore, scaling is necessary when applying the method to integration in the $q_y'$-$q_z'$ plane, but since $R(q')$ is only significantly different from zero within a few FWHM in the $q_y$-direction and a few FWHM in the $q_z$-direction, the integration range was chosen to be $2 \cdot \text{FWHM of } R_y$ in the $q_y$-direction and $2 \cdot \text{FWHM of } R_z$ in the $q_z$-direction.

**SCALING:**

$$\{q_{y,i}', q_{z,i}'\} = \{\alpha_y + \Delta_y \cdot y_i, x_z + \Delta_z \cdot x_i\}$$

Fig. C.2. Area of integration - scaling.
This area is shown in Figure C.2. When performing the integration, this area could, optionally, be subdivided into smaller squares, thus increasing the accuracy of the integration. The points in the -1, +1-quadrant from 1) were scaled to each square (see Figure C.2). A fast and accurate procedure could be obtained with N=28 and four boxes in the q<sub>y</sub>-direction and two in the q<sub>z</sub>-direction. The analysis was done on a P.D.P.-11-computer with floating point processor and a complete fit could be done in approximately 5 minutes.

If pretransitional mosaicity is an essential feature of the nematic to smectic-A phase transition, the resolution function must be modified by inclusion of the mosaicity, as outlined in Chapter 4. Since the out-of-plane resolution R<sub>v</sub>(q<sub>y</sub>) in any case was much broader than the mosaicity, the only correction to R(q') is in the q<sub>x</sub>-direction. The inclusion of mosaicity in the fit was made simply by convoluting S(q) with M(q<sub>x</sub>) before convolution with R(q'). The convolution of M(q<sub>x</sub>) and S(q) was made by a simple equidistant summation along q<sub>x</sub>:

\[ S_M(q_x,q_y,q_z) = \sum_i M(q_x',i) \cdot S(q_x - q_x', i, q_y, q_z) \]

where M(q<sub>x</sub>',i) was obtained from transverse scans at or just below T<sub>c</sub>.

The only correction to the intensity was a volume correction. The sample geometry is shown in Figure C.3. From this figure it is clear that the beam attenuation goes like:

\[ e^{-t/cos\phi} \]

and that the illuminated volume is proportional to 1/cos\phi. This gives the following gain factor to the intensity:

\[ e^{-t/cos\phi} \cdot \frac{1}{cos\phi} \quad (C.6) \]

All measured intensities have thus been divided by this factor.
Fig. C.3. Sample geometry - transmission geometry.

REFERENCES

APPENDIX D

COMBINATION OF THE TWO RESOLUTION ELLIPSES

In order to be able to combine the two ellipses to a final resolution function it is useful to transform the $\check{x}_1, \check{x}_2$-set of conjugate diameters to a new set with $\check{x}_2' \perp \check{k}_1$. This is done by using the formulas of Appendix B, and the result is that:

$$
x_1'^2 = \frac{(x_{0,1}^2 + x_{0,2}^2) \cdot \cot^2 \theta_M}{\sin^2 \alpha_M}; \quad x_2'^2 = \frac{(x_{0,3}^2 + x_{0,4}^2) \cdot \cot^2 \theta_M}{\sin^2 \alpha_A};
$$

$$
x_3'^2 = \frac{x_{0,1}^2 \cdot x_{0,2}^2}{x_{0,1}^2 + x_{0,2}^2}; \quad x_4'^2 = \frac{x_{0,3}^2 \cdot x_{0,4}^2}{x_{0,3}^2 + x_{0,4}^2},
$$

$$
\tan \alpha_M = -\frac{x_{0,1}^2 + x_{0,2}^2}{x_{0,1}^2 \cdot \tan \theta_M}; \quad \tan \alpha_A = -\frac{x_{0,3}^2 + x_{0,4}^2}{x_{0,3}^2 \cdot \tan \theta_M}
$$

where $x_{0,1} = Ck_o$ and $x_{0,2} = Ck_D$; $C = \sqrt{2\ln 2}$ and $\alpha_M$ is the angle between $x_1'$ and $x_2'$. Similarly $\alpha_A$ is the angle between $x_3'$ and $x_4'$.

From Chapter 4 one has:

$$
x_3' = x_3 = "\alpha"; \quad x_4' = x_{0,2}; \quad \alpha_A = 90 - \theta_M
$$

The set-up in Figure 3.1 in Chapter 3 corresponds to configuration 2) in Figure 4.3 in Chapter 4. In Figure D.1 this set-up is shown together with the resolution ellipses and conjugate diameters $x_1, x_2, x_1', x_2'$ and $x_3, x_4, x_3', x_4'$. 
Fig. D.1. The two resolution ellipses tied to the monochromator and the analyzer, respectively. Note that $\hat{X}_1 \parallel M$ and $\hat{X}_3 \parallel A$.

It is now straightforward to combine the resolution ellipses, since deviations of $k$ along $\hat{X}_2$ or $\hat{X}_4$ automatically fulfills the condition of elastic scattering. These two conjugate diameters will thus contribute to $R_i$ by the half-contour ellipse shown in Figure D.2a, where it is assumed that $\sigma_0^2 \gg \sigma_k^2$, leading to the relation $X_2' = X_4'$. 
In the same figure D.2b a transformation of the $X_2^*, X_4^*$-set of conjugate diameters is shown. The formulae for $Y_1''$, $Y_2''$ and $\alpha''$ are:

$$Y_1''^2 = \frac{4X_4''^2 X_2''^2 \cos^2 \theta_s \sin^2 \theta_s}{X_4'^2 \sin^2(\delta - \theta_s) + X_2'^2 \sin^2(\delta - \theta_s)}$$

$$\tan \alpha'' = -\frac{X_4'^2 \sin^2(\delta - \theta_s) + X_2'^2 \sin^2(\delta + \theta_s)}{X_4'^2 \sin(\delta - \theta_s) \cos(\delta - \theta_s) + X_2'^2 \sin(\delta + \theta_s) \cos(\delta + \theta_s)}$$

$$Y_2''^2 = \frac{X_4'^2 \sin^2(\delta - \theta_s) + X_2'^2 \sin^2(\delta + \theta_s)}{\sin^2 \alpha''}$$
In the above formulae it is assumed that $90 - \theta_S > \delta > \theta_S$. It is straightforward to construct the transformation in other regions for $\delta$ using Appendix B.

Note that the contribution from $X_2'$ and $X_4'$ to the in-plane resolution is independent of the spectrometer configuration. Furthermore it is salient to notice that for, $\theta_S = 0$ and $a_M^2 \gg a_B^2$, this contribution degenerates to a line along $q_0$ of length $\gamma_2^2 = 2 \cdot x_0^2$, which is simply a convolution of the

![Diagram](image)

**Fig. D.3.** The combination of $X_1'$ and $X_3'$. 
Darwin-reflectivity with itself = the direct beam profile!
Similarly, if $\theta_s = 0$ and $\eta_D^2 >> \alpha_M^2$ the contribution from $X_2'$ and $X_4'$ degenerates to a line along $q_0$ of length $X_2^2 = X_0^2, z$.

The remaining contribution to $R_1$ comes from $X_1'$ and $X_3'$. These two must be combined under the condition of elastic scattering. The contribution to $R_1$ depends on the spectrometer configuration and the contribution is derived in Figure D.3 for one of the two analogous non-dispersive set-ups (configurations 1 & 2 in Figure 4.3 in Chapter 4).

The half-value $\ell$ of the line contribution in Figure 3 can be found by looking at the probability for a scattering process like the one in Figure D.3. Generally, such a scattering process can be designated by the coordinates $(X_M, X_A)$, where $X_M$ is the coordinate along $X_1'$ and $X_A$ is the coordinate along $X_3'$; the following relation then holds between $X_M$ and $X_A$:

$$|X_A| = |X_M| \cdot \frac{\sin \alpha_M}{\cos \alpha_M}$$

The relation is imposed because the scattering is elastic. The probability for the scattering process $(X_M, X_A)$ is:

$$P(X_M, X_A) = e^{-1/2} \left( \frac{X_M^2}{X_1^2} \right) \cdot e^{-1/2} \left( \frac{X_A^2}{X_3^2} \right)$$

$$= e^{-1/2} X^2 \left( \frac{1}{X_1^2} + \frac{\sin \alpha_M^2}{X_3^2 \cos \alpha_M} \right)$$

$$= e^{-1/2} \left( \frac{X_M^2}{\sigma_\ell} \right)$$
where

\[
\frac{1}{\sigma_L^2} = \left( \frac{1}{X_1^2} \right) + \left( \frac{\sin \alpha_M}{X_3 \cos \alpha_M} \right) = \left( \frac{1}{X_1^2} \right)
\]

and \( t \) can be found by setting \( X_M = 2\sqrt{2\tau_2^2 \cdot \sigma_L} \) as done in Figure D.3.

Once the angle between \( \ell \) and \( a \) in the triangle \( a, b, \ell = \delta' \) is determined it is straightforward to find the angle between \( \ell_0 \) and \( \ell = \delta \) for the specific set-up and if \( t \) has been found, the line contribution to the resolution function, originating from \( X_1' \) and \( X_3' \), can be combined with the ellipse determined by \( X_2' \) and \( X_4' \). In Figure D.2 there is prepared for it and the final resolution ellipse is given by the conjugate diameters \( \gamma_1, \gamma_2 \) and the angle between them \( \alpha \), and the angle \( \delta \), where:

\[
\begin{align*}
Y_1^2 &= \ell^2 + \ell''^2 \\
Y_2^2 &= \gamma_2^2 \\
\alpha &= \alpha''
\end{align*}
\]

The rule of sum-of-squares has been used for conjugate diameters along the same direction (Reference 2 in Chapter 4; see Figures D.2b) and D.2c).

Looking at the triangle \( a, b, \ell \) in Figure D.3 the following general expressions are valid for \( t \) and \( \delta' \):

\[
\ell^2 = a^2 + b^2 - 2ab \cos \gamma = X_1'^2 \cdot \frac{\sin^2 \alpha_M}{\cos^2 \alpha_M} + 1 - 2 \cdot \frac{\sin \alpha_M}{\cos \alpha_M} \cdot \cos \gamma = X_1'^2 \cdot f^2
\]
and

\[
\cos \delta' = \frac{a^2 + t^2 - b^2}{2at} = \frac{f^2 + \frac{\sin \alpha_M}{\cos^2 \theta_M} - 1}{2 \cdot \frac{\sin \alpha_M}{\cos \theta_M} f}
\]

(D.5)

\( \alpha_M \) is given by the formula in the beginning of the appendix.

\( \phi \) is the angle between \( a \) and \( b \) in triangle \( a, b, \ell \) and is given by the following table for the four different configurations.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ - - ~ 1</td>
<td>(</td>
</tr>
<tr>
<td>+ + - ~ 2</td>
<td>(</td>
</tr>
<tr>
<td>+ - + ~ 3</td>
<td>(</td>
</tr>
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APPENDIX E

THE EFFECT OF MOSAICITY IN THE SAMPL

The resolution is modified by the mosaicity of the sample and
for some experiments mosaicity may be the factor which limits
the resolution; therefore it is worth looking at the effect of
mosaicity in the sample. The argument \( \hat{q}_0 \) will be dropped in \( R \)
in the following. If the mosaicity is described by

\[
M(q_1^0) = M_T(q_T^0) \cdot M_V(q_v^0); \quad \hat{q}_1^0 = q_T^0 \cdot \hat{1}_T + q_v^0 \cdot \hat{1}_v
\]

where \( M(q_1^0) dq_T dq_v \) is the fraction of "mosaic blocks" with normal
vector in the solid angle \( \delta \Omega \) shown in the figure, then the ex­
pression (*) in Chapter 4 must be modified in the following way:

\[
I(q) = \int S_M(q-q') R(q') dq'
\]

where

\[
S_M(q-q') = \int M(q_1^0) \cdot S(q-q'-q_1^0) dq_1^0
\]

\[
= \int M(q_1-q_1-q_1^0) \cdot S(q_1^0, q_1-q_1^0) dq_1^0
\]

(see the figure).
Inserting $S_M(\tilde{q}-\tilde{q}')$ into the expression for $I(\tilde{q})$ gives:

\[
I(\tilde{q}_1,q_z) = \int ... \int M_T(q_T-q_T'-q_T) \cdot M_V(q_V-q_V'-q_V) \cdot S(q_T',q_V',q_*-q_*)
\]

\[
dq_Tdq_V \cdot R_T(q_T') \cdot R_V(q_V') \cdot R_n(q_n')dq_Tdq_Vdq_n =
\]

\[
\int \left[ [M_T(q_T'-q_T-q_T') \cdot R_T(q_T')dq_T]\right].
\]

\[
\int [M_V(q_V'-q_V-q_V') \cdot R_V(q_V')dq_V] \cdot S(q_T',q_V',q_*-q_*)
\]

\[
\cdot R_n(q_n') \cdot dq_Tdq_Vdq_n
\]

\[
= \int a_T(q_T'-q_T) \cdot a_V(q_V'-q_V) \cdot R_n(q_n') \cdot S(q_T',q_V',q_*-q_*)dq_Tdq_Vdq_n'
\]

where

\[
a_{T,V}(q_T',q_V'-q_T',q_V') \equiv \int M_{T,V}(q_T'-q_T'-q_T',q_V'-q_T',q_V') \cdot R_{T,V}(q_T',q_V')dq_T'
\]

Using the $\alpha$-notation one gets further:

\[
I(\tilde{q}) = \int a_T(q_T'-q_T) \cdot a_V(q_V'-q_V) \cdot R_n(q_n'-q_n
\]

\[
\cdot S(q_T',q_V',q_n')dq_Tdq_Vdq_n
\]

where $q_n' = q_n-q_*$. 

This gives:

\[ I(\hat{q}) = \int R_c(\hat{q} - \hat{q}^\prime) S(\hat{q}^\prime) d\hat{q}^\prime \]

with \( R_c = \omega_T \omega_V R \).

Thus the usual expression for \( I(\hat{q}) \) is obtained except \( R + R_c \), which means that the corrected resolution function \( R_c \neq R \) if the mosaicity-FWHM >> FWHM of either \( R_T \) or \( R_V \).