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## Liquid Crystals

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### Plenary Lecture. Smectic liquid crystals. A historical review

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# Plenary Lecture

## Smectic liquid crystals

### A historical review

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This paper is intended to reflect the development of liquid crystal research, rather than to present a detailed historical survey. The author has been involved in this field for some 30 years as a member of the Halle Liquid Crystal Group. There has been a remarkable continuity in liquid-crystal research at the University in Halle—almost from the beginning of scientific investigation of liquid crystals about a century ago. This continuity has been maintained by fruitful collaboration between teachers and students as well as by the accumulation of past experience, but all of this activity can be connected with one man—Daniel Vorländer (1867–1941), Professor of Chemistry and Director of the Chemical Institute of Halle University from 1908 to 1935. Vorländer and his co-workers published their first results on liquid crystals in 1902.

#### 1. The first period: from 1888 to 1910

Three monographs focus on the research in this early period:

Lehmann, O. *Flüssige Kristalle sowie Plastizität von Kristallen im Allgemeinen. Molekulare Umwandlungen und Aggregatzustandsänderungen*  
(Leipzig, 1904);

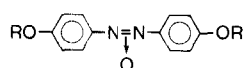
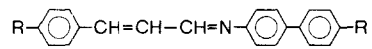
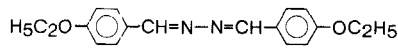
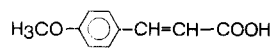
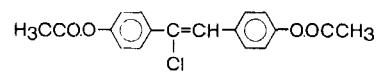
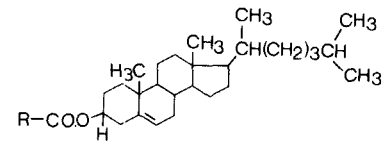

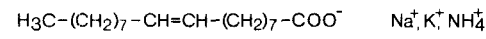
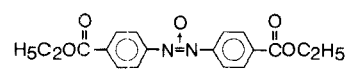
Schenck, R. *Kristallinische Flüssigkeiten und flüssige Kristalle*  
(Leipzig, 1905);

Vorländer, D. *Kristallinisch-flüssige Substanzen*  
(Stuttgart, 1908).

In the extensive work of Lehmann (1855–1922) we find described a collection of liquid-crystalline substances, whose behaviour he studied by microscopical investigation in polarized light on a heating stage. He developed this method in a number of variations. For the most part, the discoverers of substances with liquid crystal phases sent him samples for further investigation, as, for example, did Reinitzer.

This collection of compounds is listed in table 1—classified using modern nomenclature. Already during the earliest period, smectic types occurred. Lehmann summarized the phases of cholesteric and smectic types as 'flowing crystals' and the nematic phases as 'liquid crystals'. This division was primarily determined by the microscopic appearance of the phases as spherical or rod-like forms or as droplets respectively. Lehmann's photographs demonstrate the behaviour of Vorländer's ester of azoxybenzoic acid. The smectic rods are growing (see figure 1) and the fully developed texture can be seen in a polygonal variation (see figure 2). Figures 3 and 4 present

Table 1. Compounds investigated by Lehmann.

Nematic phases	
	Gattermann (1890)
R = CH <sub>3</sub> -; C <sub>2</sub> H <sub>5</sub> -	
	Gattermann (1906, 1904)
R = H-; CH <sub>3</sub> -	
	
	van Romburgh (1901)
	Münch (1903)
Cholesteric phases	
	
R = CH <sub>3</sub> -; 	Reinitzer (1888/89)
R = C <sub>2</sub> H <sub>5</sub> -; C <sub>3</sub> H <sub>7</sub> -	Jaeger (1906)
R = CH <sub>3</sub> --(CH <sub>2</sub> ) <sub>7</sub> --CH=CH--(CH <sub>2</sub> ) <sub>7</sub> --	
Smectic phases	
	Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>
	Lehmann (1895)
(S <sub>A</sub> )	Vorländer, Meyer (1902)

nematic droplets and the nematic schlieren texture exhibited by Gattermann's 4,4'-di-*n*-alkoxyazobenzene. The total syntheses of the substances prepared by Gattermann, Vorländer and others (see table 1) were of special importance at that time. The derivatives of cholesterol were not completely synthetic products, and the chemical constitution of cholesterol was not fully established. The oleic acids used for the synthesis of the corresponding derivatives were often products of dubious chemical purity. The purity of the synthetic compounds was an argument against those people who did not accept the reality of liquid crystals as new states of matter. They explained the new phenomena by the heterogeneity or impurity of the particular compounds.

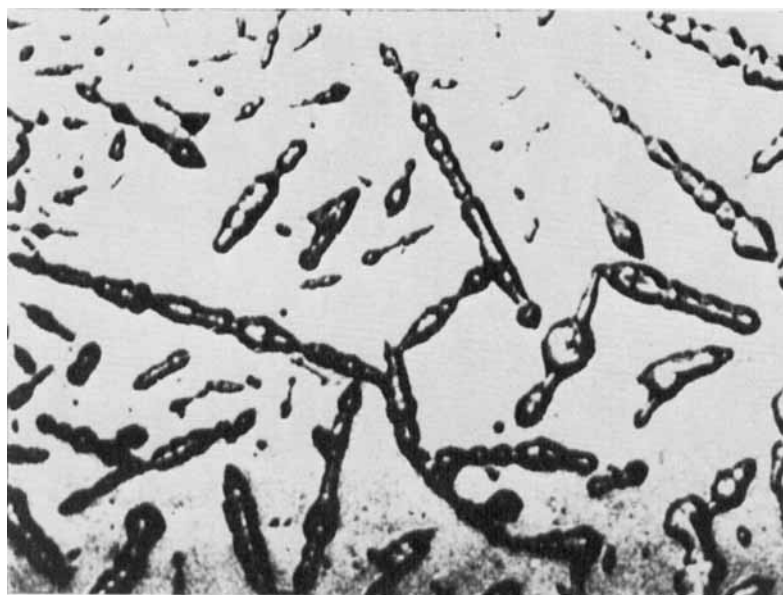


Figure 1. Growing smectic rods (Lehmann 1904).

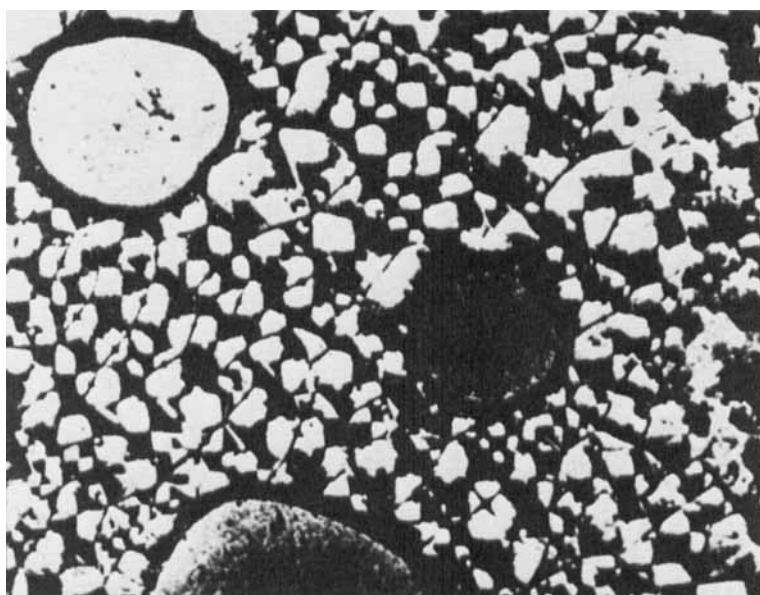


Figure 2. A polygonal texture (Lehmann 1904).

The first physico-chemical measurements are summarized in Schenck's monograph. These properties include density, dependence of transition temperatures on pressure, depression of clearing points in solutions, phase diagrams for two-component mixtures, viscosity, surface tension and dielectric properties. These investigations strengthened the assumption that liquid crystals were new phases.

Vorländer's monograph presents the results of extensive studies on substances forming liquid crystals. He and his co-workers studied the influence of molecular

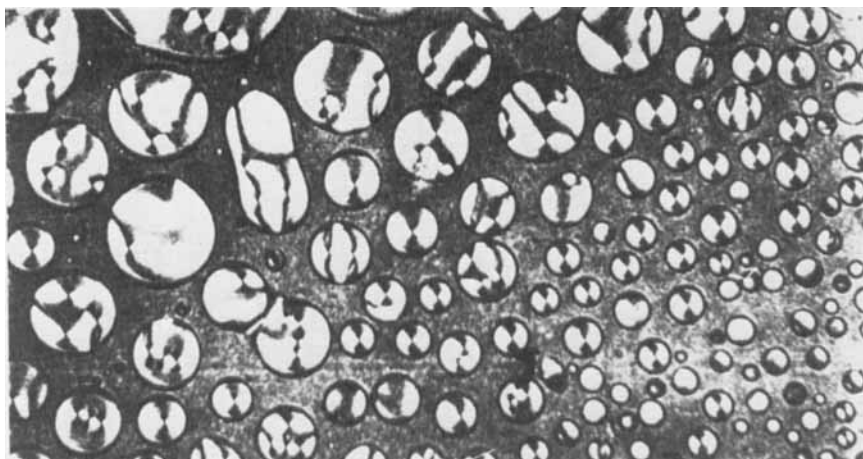


Figure 3. Growing nematic drops (Lehmann 1904).

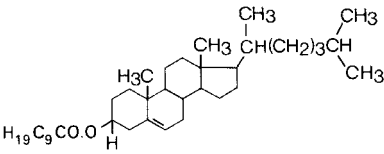
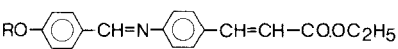


Figure 4. The schlieren texture (Lehmann 1904).

structure on the appearance of liquid-crystalline phases by synthesizing new substances. They recognized molecular linearity as the essential feature of liquid crystals. Vorländer pointed out that ‘the anisotropy of liquids is illustrated to a certain degree by the chemical structure of the crystalline liquid substances’. Along with this work on the synthesis of liquid crystals, numerous investigations of the optical behaviour, transition temperatures etc. were carried out and compared.

The observation of two liquid-crystalline phases in one compound produced by changing the temperature unified the picture of liquid-crystalline phases (cholesteric and smectic—nematic and smectic in modern nomenclature). This dimorphism was first found by Lehmann in a cholesteric compound synthesized by Jaeger (see table 2).

Table 2. First polymorphic compounds.

Dimorphism	
 <p> <math>\text{H}_{19}\text{C}_9\text{CO}_2\text{O}</math>  <math>\text{H}</math> </p>	
$\text{kr.fest} \xrightleftharpoons{82.2^\circ\text{C}} \text{kr.fl.I} \xrightleftharpoons{90.6^\circ\text{C}} \text{am.fl.}$ $\text{Kr.fl.II (S}_A\text{)} \xrightleftharpoons{77.4^\circ\text{C}} \text{kr.fl.I (Ch)}$	Jaeger, Lehmann (1907)
 <p> <math>\text{RO-}</math>  <math>\text{R} = \text{CH}_3</math> </p>	
$\text{kr.fest} \xrightleftharpoons{108^\circ\text{C}} \text{kr.fl.II (S}_A\text{)} \xrightleftharpoons{117^\circ\text{C}} \text{kr.fl.I (N)} \xrightleftharpoons{136^\circ\text{C}} \text{am.fl. (I)}$	Vorländer, Wilke (1906)
Trimorphism	
$\text{R} = \text{C}_2\text{H}_5-$	
$\text{kr.fest} \xrightleftharpoons{69^\circ\text{C}} \text{kr.fl.III (S}_B\text{)} \xrightleftharpoons{113^\circ\text{C}} \text{kr.fl.II (S}_A\text{)} \xrightleftharpoons{152^\circ\text{C}} \text{kr.fl.I (N)} \xrightleftharpoons{159^\circ\text{C}} \text{am.fl. (I)}$	Vorländer, Wilke (1908)

The smectic phase is monotropic. Numerous analogous findings by Vorländer and co-workers followed. The phases in table 2 are enantiotropic. In addition, some compounds with a higher polymorphism were discovered, as can be seen from table 2. This extension of compounds, phases and polymorphic variants confirmed the existence of liquid crystals as objects of general significance.

This first period is not separated from the next by a discontinuous change in the interpretations and conceptions. In summary, it can be said that the century of liquid crystal research was initiated by Lehmann and advanced in a decisive way by Vorländer. Qualitative knowledge was increasingly corroborated by physical investigations. I have mentioned Schenck. But already Lehmann had investigated double refraction, optical rotation and other physical properties. The dimorphism encouraged comparative physical investigations of the two phases. For example, E. Dorn, Professor of Physics in Halle, published exact results on double refraction. In figure 5 the first values for a dimorphic substance can be seen (the phases are N and  $\text{S}_A$ ).

With respect to polymorphism, several types of liquid crystal are known. Non-chiral and chiral phases are distinguished by their different double refraction, by the optical rotation of the latter and by the pleochroic phenomena characterizing these phases. Chiral and non-chiral compounds sometimes possess liquid-crystalline dimorphism. Some substances with a higher polymorphism were discovered. Molecular linearity was associated with the known physical properties and led to the first structural concepts. In a more or less clear way these contained some idea of the role of the parallel molecular alignment and indeed of other structural elements within the phases and their torsion within the chiral phase.

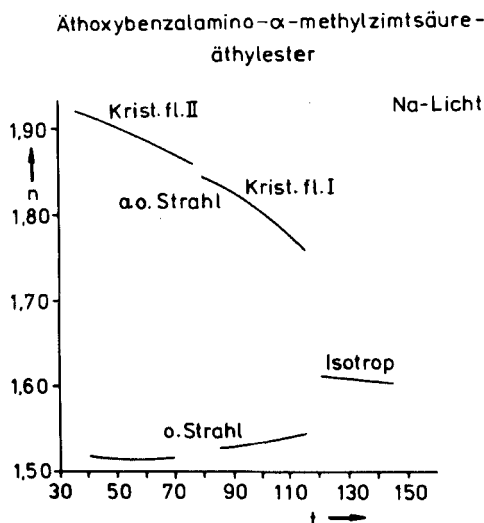


Figure 5. The temperature dependence of the refractive indices ( $n_o$  and  $n_e$ ) of double refraction in a smectic A-nematic dimorphic compound (Dorn and Lohmann, Dorn, Hatz [1]).

## 2. The second period: from 1910 to the 1940s

The second period is characterized by the expansion of methods and theories following the trends of rapidly increasing knowledge, especially in the physical sciences. H. Kelker has given a survey in his well-known article in *Molecular Crystals and Liquid Crystals* [2].

An outstanding work in the early years was published by Georges Friedel (1865–1933):

Les états mésomorphes de la matière, *Annales de Physique, Paris*, **18**, 273–474 (1922).

In this monograph peculiarities of the microscopical textures of liquid crystals are mainly summarized, ordered, substantially deepened by his own observations, and interpreted. This work began about 1910 (in part with Grandjean). As a highlight, he analysed the focal-conic textures of smectic liquid crystals, such as the polygonal texture (see figure 2) and the fan-shaped texture (see figure 6). The optical discontinuities were explained as resulting from an interplay of strata. These layers are arranged in Dupin cyclides as basic arrangements. The cyclides are the most frequent defects in smectic phases of the  $S_A$  type. The interpretation of the defect structures (in terms of modern solid state physics) was clear proof of the existence of a layer structure in smectic liquid crystals.

G. Friedel ended his monograph with a remark on a classification of the compounds investigated, which can be seen in table 3. In this connection, Friedel's work has a second aspect concerning the definition, significance and use of terms. Because of the extraordinary character of liquid crystals, he wanted to avoid the words 'liquid' and 'solid'. He saw the pair solid-liquid as an inaccurate description, whereas the pair crystalline-amorphous describes the structural situation exactly. Therefore the word '(isotropic) liquid' is replaced by 'amorphous'. Liquid crystals are new states of matter, which he named mesomorphic states. He distinguished two liquid-crystalline states by the words 'nematic', following the Greek word  $\nu\eta\mu\alpha$ , meaning thread,

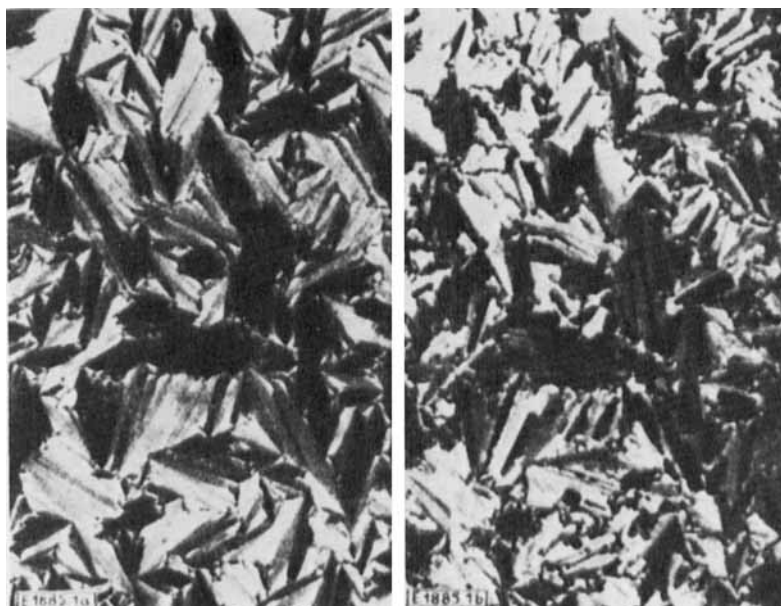
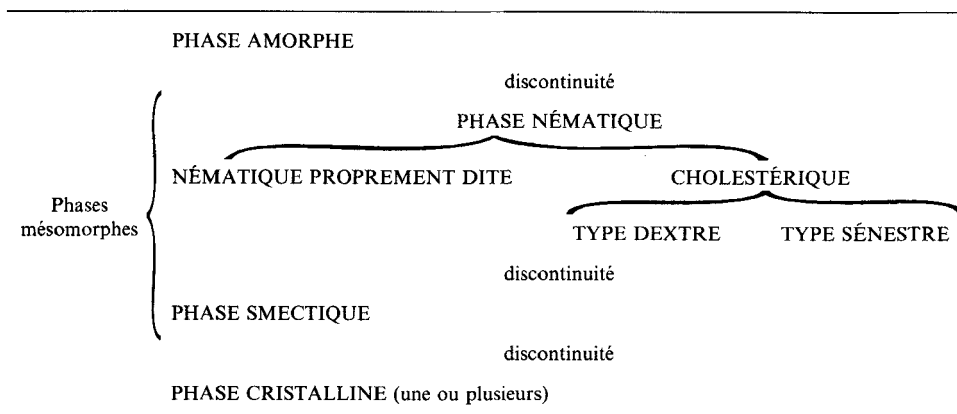


Figure 6. Fan-shaped and broken fan-shaped textures in  $S_A$  and  $S_C$  phases [12].

Table 3. Liquid-crystalline phases according to Friedel.



according to the thread-like discontinuities in nematic textures, and smectic (Greek *σμήγμα* meaning soap), using soaps as a paradigm for a phase with conic textures having a layered structure. Higher polymorphism (see table 1) was not taken into account. Friedel was not convinced of the existence of more than one smectic phase.

In 1923 M. de Broglie and E. Friedel (the son of Georges) proved the existence of a layer structure in liquid-crystalline phases by using X-rays for the first time in a system of sodium oleate containing water [3]. In 1925 E. Friedel included more defined organic compounds; among others was the smectic phase of Vorländer's standard, the ethyl ester of azoxybenzoic acid (see table 1) [4].

In 1924 D. Vorländer published a short monograph

*Chemische Kristallographie der Flüssigkeiten* (Leipzig, 1924).



with the subtitle 'a short guidance for synthesis and investigation of polymorphic and crystalline liquid substances'. We find a summary of the principles of the synthesis of liquid crystals and a table with standard compounds suitable for good observation of polymorphism in optically active and non-active compounds in research and academic education, together with examples with more than two liquid-crystalline phases. The existence of more than two liquid-crystalline forms awakened further interest. On the basis of the equidistant layers, E. Alexander and K. Herrmann, in 1928, considered arrangements of the molecular rods in some of the 80 two dimensional space groups [5]. C. Hermann (1931) widened this concept by defining all of the geometrical structures conceivable between an irregular molecular assembly and the three dimensional space group [6].

In 1932–35 K. Herrmann, together with A. K. Krummacker, took a decisive step by performing X-ray investigations of Vorländer's polymorphic phases [7]. The transition from one to the other smectic modification was accompanied by a change of the broad ring to a sharp one at wide angles. They interpreted this as a transition from a statistical molecular order in the layers to an ordered (hexagonal) one. Tilted structures were also envisaged for phases of sodium and thallium salts of stearic acid (K. Hermann in 1933 [8]; A. Brettville and J. W. McBain in 1943 [9]). This marked approximately the end of what we have termed the second period.

I should like to make a remark on an interesting 'conference by correspondence'. In 1931 the *Zeitschrift für Kristallographie* organized a series of articles [10]. Some authors wrote summaries, which were discussed in letters, which themselves were then answered by the original authors. The publication gives an interesting survey of the problems, questions, and controversies concerning the whole field of liquid crystal research at that time. We also note a tendency to see the problems of liquid crystals in connection with other mesophases such as colloidal systems. Wolfgang Ostwald reported on 'mesomorphic and colloidal systems'. G. and E. Friedel sought sharp and clear-cut definitions of terms such as structure or texture, and they defined a new word 'stase'. But in the place of the old ambiguities new ones arose.

The editor P. P. Ewald concluded this interesting project with the following remarks (my shortened and free translation): 'The termination of the discussion has external causes and does not mean that the participating scientists agree'—and furthermore—'besides really new results in theories and experiments, the document gives a cross-section of the concepts of scientists, who will be considered by future generations as pioneers in a field that cannot even be given a name without sharp contradictions by one or the other side' (the term 'liquid crystal' was opposed by Friedel, and 'mesophase' by Vorländer).

### 3. The beginning of the recent period [11]

After the Second World War, research on liquid crystals began only slowly in Europe.

In the 1950s we find the beginning of new synthetic work, especially in England by G. W. Gray and in Germany by H. Schubert. There was an enormous increase in new groups of substances with liquid-crystalline phases. Synthesis advanced in the direction of liquid crystals made to measure for various uses in science and soon in applied research. With respect to smectics, new compounds with higher phase polymorphism—up to six phases in one compound—came to light. The existence of distinct regions on the temperature scale indicated a corresponding number of different structures.

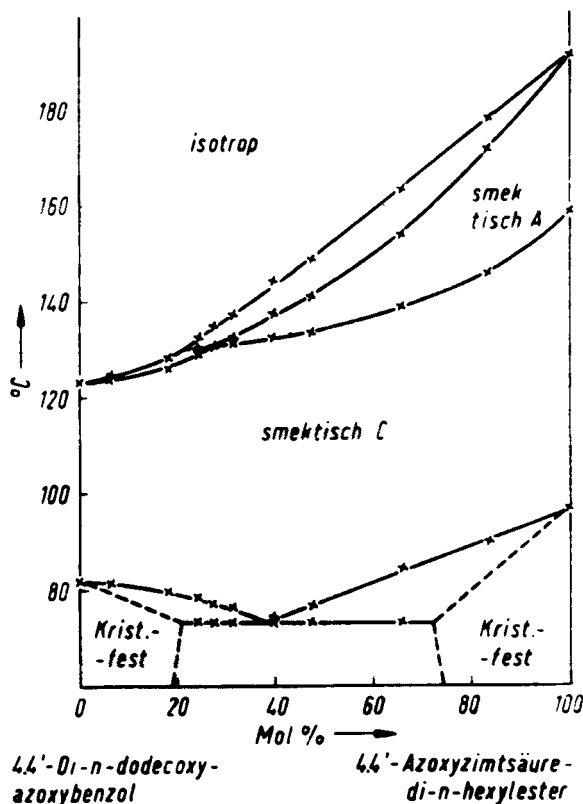


Figure 7. Miscibility in the binary mixture III-I.

Table 4. Smectic phases used for miscibility studies [12].

I	Dihexyl-4,4'-azoxycinnamate (Vorländer, 1927)	C-S <sub>II</sub> -S <sub>I</sub> -I S <sub>C</sub> S <sub>A</sub>
II	Diethyl-4,4'-azoxybenzoate (Vorländer, 1902)	C-S <sub>I</sub> -I S <sub>A</sub>
III	4,4'-Bis-n-dodecyloxyazoxybenzene (Gabler, 1939)	C-S <sub>I</sub> -I S <sub>C</sub>

This increasing number of liquid-crystalline phases in monomorphic as well as in polymorphic systems required a proof of their relationships. In order to do this, the Halle Liquid Crystal Group started investigations on the miscibility of phases in binary mixtures. Miscibility is a thermodynamic criterion. In the case of constant pressure, homogeneous regions within the temperature-concentration plane are separated by phase-transition lines or points according to Gibbs phase rule. We have investigated these phase diagrams by noting the different textures of the phases and their changes on a heating stage.

In general, nematic phases were always distinguished from other phases by their characteristic textures. The nematic phases of two substances in most cases showed complete miscibility. In polymorphic compounds the nematic phases were always the high temperature phases in accord with the well-known earlier observations. But the

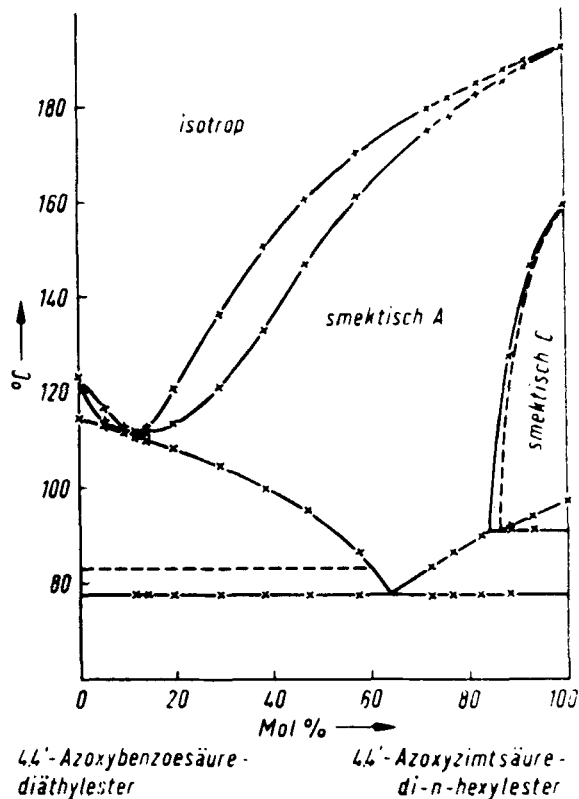


Figure 8. Miscibility in the binary mixture II-I.

non-nematic phases, which we all named smectics initially, showed a selective miscibility behaviour.

Two examples are selected here from one of the first reports on miscibility in binary systems [12]. In table 4 the compounds and the polymorphism can be seen. We see a smectic (no nematic phases) dimorphism in compound I and smectic monomorphism in compounds II and III. All of the smectic phases had fan-shaped textures, although there are unambiguous, small differences. In figure 6 the two textures are to be seen. On the left-hand side we see the normal fan-shaped texture of the high temperature smectic phase of I; this is the normal texture. On the right-hand side we see the texture of the low temperature phase of I. We named this texture a broken fan-shaped texture.

The phase diagram (see figure 7) shows complete miscibility between the smectic phase of III and the *low* temperature phase of I. In figure 8 we see complete miscibility between the smectic phase of II and the *high* temperature phase of I. This points to a special relationship between the high-temperature phase of compound I and the smectic phase of compound II, as well as between the low temperature phase of compound I and the smectic phase of compound III. This is in accord with the textures in figure 6. We expressed these relationships by the different letters A and C for the smectic phases.

According to the miscibility criterion, Vorländer's substances, investigated by X-ray diffraction (Herrmann, Krummacher) showed a phase  $S_A$  and a new phase,

Table 5. Polymorphic variants [11].

Monomorphic	Dimorphic	Trimorphic
N	S <sub>A</sub> N	S <sub>B</sub> S <sub>A</sub> N
S <sub>A</sub>	S <sub>B</sub> N	S <sub>C</sub> S <sub>A</sub> N
S <sub>B</sub>	S <sub>C</sub> N	S <sub>G</sub> S <sub>A</sub> N
S <sub>C</sub>	S <sub>G</sub> N	S <sub>E</sub> S <sub>A</sub> N
S <sub>E</sub>	S <sub>B</sub> S <sub>A</sub>	S <sub>G</sub> S <sub>B</sub> N
S <sub>I</sub>	S <sub>C</sub> S <sub>A</sub>	S <sub>I</sub> S <sub>C</sub> N
	S <sub>E</sub> S <sub>A</sub>	S <sub>E</sub> S <sub>B</sub> S <sub>A</sub>
	S <sub>G</sub> S <sub>C</sub>	S <sub>B</sub> S <sub>C</sub> S <sub>A</sub>
	S <sub>I</sub> S <sub>C</sub>	S <sub>E</sub> S <sub>C</sub> S <sub>A</sub>
	S <sub>E</sub> S <sub>B</sub>	S <sub>I</sub> S <sub>C</sub> S <sub>A</sub>
	S <sub>G</sub> S <sub>I</sub>	S <sub>G</sub> S <sub>C</sub> S <sub>A</sub>
	S <sub>G</sub> S <sub>F</sub>	S <sub>G</sub> S <sub>B</sub> S <sub>A</sub>
		S <sub>G</sub> S <sub>F</sub> S <sub>A</sub>
		S <sub>F</sub> S <sub>I</sub> S <sub>C</sub>
		S <sub>G</sub> S <sub>I</sub> S <sub>C</sub>
Tetramorphic	Pentamorphic	Hexamorphic
S <sub>G</sub> S <sub>B</sub> S <sub>A</sub> N	S <sub>G</sub> S <sub>B</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>G</sub> S <sub>F</sub> S <sub>B</sub> S <sub>C</sub> S <sub>A</sub> N
S <sub>E</sub> S <sub>B</sub> S <sub>A</sub> N	S <sub>H</sub> S <sub>G</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>G</sub> S <sub>F</sub> S <sub>I</sub> S <sub>C</sub> S <sub>A</sub> N
S <sub>B</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>G</sub> S <sub>I</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>K</sub> S <sub>I</sub> S <sub>I</sub> S <sub>C</sub> S <sub>A</sub> N
S <sub>G</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>G</sub> S <sub>F</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>H</sub> S <sub>G</sub> S <sub>F</sub> S <sub>C</sub> S <sub>A</sub> N
S <sub>I</sub> S <sub>C</sub> S <sub>A</sub> N	S <sub>K</sub> S <sub>I</sub> S <sub>I</sub> S <sub>C</sub> N	
S <sub>H</sub> S <sub>G</sub> S <sub>C</sub> N	S <sub>G</sub> S <sub>F</sub> S <sub>I</sub> S <sub>C</sub> S <sub>A</sub>	
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S <sub>G</sub> S <sub>B</sub> S <sub>C</sub> S <sub>A</sub>		
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S <sub>G</sub> S <sub>I</sub> S <sub>C</sub> S <sub>A</sub>		
S <sub>K</sub> S <sub>I</sub> S <sub>C</sub> N		
<hr/> Temperature $\rightarrow$ <hr/>		

named smectic B. More and more compounds (Vorländer's and new ones) were tested by this miscibility criterion. The existence of complete miscibility between phases is a suitable criterion for an ordering of liquid-crystalline phases in types according to the miscibility rule. All liquid-crystalline phases that exhibit complete miscibility in binary mixtures (temperature–concentration) can be denoted by the same symbol without contradiction; that is, those liquid-crystalline phases denoted by the same symbol in no case exhibit complete miscibility with the liquid-crystalline phases denoted by another symbol.

In the course of time, many compounds with one, two and up to six liquid-crystalline phases were tested on the temperature scale. The results are summarized in the list shown in table 5. The smectic phases designated by letters are written from left to right in the sequence of their appearance with increasing temperature. All individual compounds investigated belong to one of these variants. The phases appearing in a wide range of compounds can be reduced by the miscibility criterion to eleven phase types, denoted with letter symbols. Furthermore, we find a temperature sequence for the polymorphic phases. Nematic phases exist in the highest temperature region. The S<sub>A</sub> and S<sub>C</sub> phases follow. S<sub>B</sub> and the other phases are low temperature forms in

SMECTIC LAYER STRUCTURES

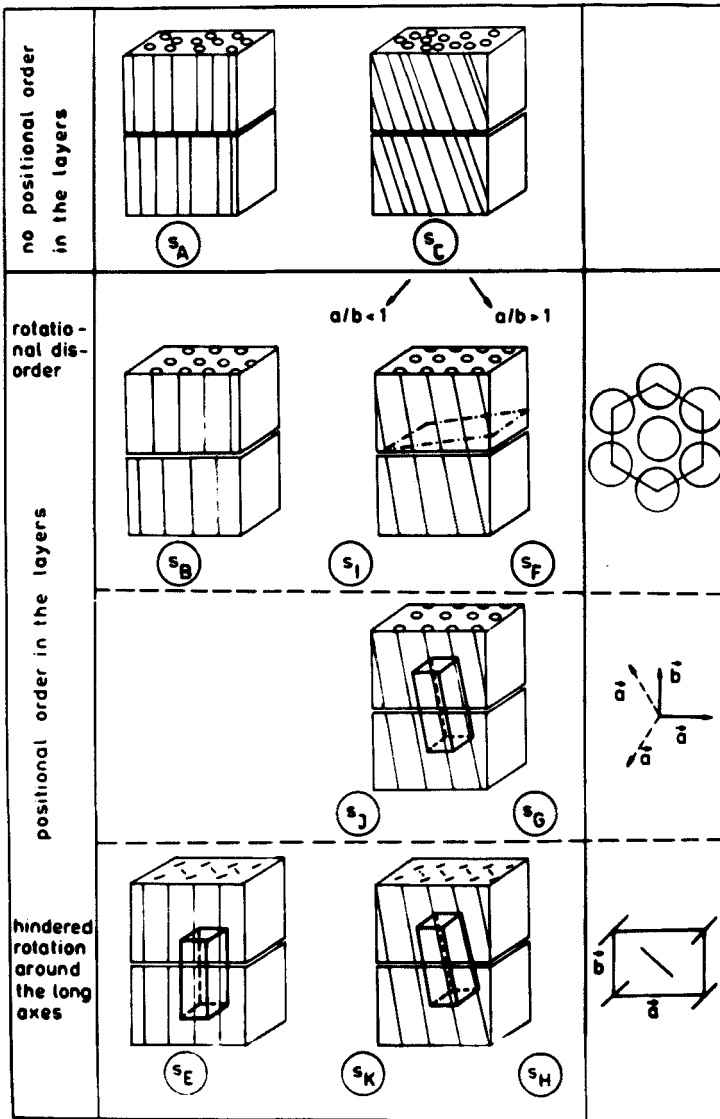


Figure 9. Smectic layer structures.

polymorphism with  $S_A$  and  $S_C$ , and further sequences for the low temperature phases can be seen.

During the development of this system of phase types, the structures of these phases were increasingly examined by X-ray diffraction. A. de Vries, S. Diele, and especially A. M. Levelut in France and A. J. Leadbetter in England may be mentioned here as representative of important groups who accompanied and influenced this development over a long time. As can be seen in figure 9, the system of phase types has become a system of structures. The smectic phase without order in the layers named the  $S_A$  phase is the smectic phase that was analysed by G. Friedel. The tilted variant is the  $S_C$  phase. These phases without order are followed by phases with order

in the layers with orthogonal and tilted orientation of the long molecular axes. They are ordered in different hexagonal arrangements—tilted phases ( $S_I$ ,  $S_F$ ,  $S_G$ ,  $S_J$ ) as well as non-tilted phases ( $S_B$ ). Restricted rotation about the long axes causes a herring-bone arrangement of the molecules in the layers in tilted ( $S_H$ ,  $S_K$ ) and non-tilted ( $S_E$ ) variants. The sequence of liquid-crystalline phases on the temperature scale in table 5 reflects the decrease in structural order with increasing temperature.

In some compounds cubic phases were found in polymorphic variants with layer phases; they have been termed 'smectic D', previously, but they do not belong to this structure system. According to this, the classification 'smectic' is reserved for liquid crystals having layer structures.

These remarks on the system of smectic phase types and structures should terminate what I have called the beginning of the recent period. Especially in the past 15 years, the system of smectic phases and our understanding of the behaviour of these phases have been enlarged continuously, differentiated and deepened not least by a variation of the molecular species [11]. I may mention the twisted smectic C phases and other twisted smectic phases in chiral substances. To the pair nematic-cholesteric the pairs tilted-twisted smectics have to be added. Furthermore, I should mention the smectic A and C phase systems in polar compounds, the reentrant phase phenomena and the problem of phase transitions. I should also point to our increasing understanding of the order in and between the layers, of layer stackings, of correlated and uncorrelated smectics and their dynamics etc., and not least to the progress that has been made in theoretical treatment.

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