Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

History of Liquid Crystals

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To cite this article: H. Kelker (1973): History of Liquid Crystals, Molecular Crystals and Liquid Crystals, 21:1-2, 1-48

To link to this article: http://dx.doi.org/10.1080/15421407308083312

Molecular Crystals and Liquid Crystals. 1973. Vol. 21, pp. 1–48

History of Liquid Crystals†‡

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Received November 10, 1972

Abstract—The history of our field of interest is more clearly discernible when time periods are chosen which are covered by characteristic summarizing papers. Such papers can serve as the landmarks when a rather complex development is to be described briefly. So I shall report on the following periods:

First period, was from the middle of the 19th century until 1908, comprising the discovery of liquid crystals, and work of predominantly descriptive character. Monographs, covering this period, are those of *Lehmann*⁽¹⁾ (1904), *Schenck*⁽²⁾ 1905, and *Vorländer*⁽³⁾ (1908).

The originals of all the older monographs are presented and held available for inspection.

Second period, was from 1908 to 1922.

This is the time of the first theoretical work and the foundation of systematology of liquid crystals. We must name E. Bose,⁽⁴⁾ M. Born,⁽⁵⁾ F. Stumpf⁽⁶⁾ (1918), G. Friedel⁽⁷⁾ (1922), and again D. Vorländer⁽⁸⁾ (1924) and O. Lehmann⁽⁹⁾ (1922).

Third period, was from 1922 to 1933.

This was perhaps the most fruitful period before the climax in the sixties. We note the development of quantitative theory and the investigation of the effects of outer forces and fields on liquid crystals. In 1929 a monograph was published by *Oseen*,⁽¹⁰⁾ " Liquid crystals, facts and theories ". The work of *Ornstein*, *Kast*, and *Zocher* will be dealt with later. Further chemical work was done predominantly at Halle (*Vorländer*), physical experimental work at Utrecht (*Ornstein*), at Leningrad (*Frẽedericks*, later *Zwetkoff*) and in Poland (*Jeżewsky*).

As a summary, a written discussion has been organized by *P. P. Ewald* in the Z. für Kristallographie 1930/31.⁽¹¹⁾ In 1933 the Faraday Society Meeting at London under *Sir William Bragg* took place.⁽¹²⁾

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† Plenary Lecture presented at the Fourth International Liquid Conference, Kent, Ohio, U.S.A., August 21–25, 1972.

‡ Herrn Professor Dr. Werner Fischer zum 70.Geburtstag (21.8.1972) gewidmet.

Fourth period, was from 1933 to 1945.

This period brought new experimental work and some extension of basic theories, the foundation of later work. The Bunsen Discussion Meeting(13) in 1938 was the last one before the war. Severe interruption and even complete collapse of international communication continued until the end of the war. The last work, comprehensive with respect to chemistry and morphology of liquid crystals was written in 1941 by *Weygand*.(14)

During the last period, beginning soon after 1945, we observe a strong revival which lasts until today. The activity in the sixties and seventies is beyond the scope of this historical review. In view of this fact, my review should be closed with the year 1945, and it will be biassed with respect to the early works.

First Period

Let us return to the last century. Scientific interest in liquid crystals is first encountered around the middle of the century, and was concerned with organic materials or products produced from them, for example soap. The first report about anisotropic liquids I could find comes from an author, Edgar Allan Poe,(15) who liked to embellish his stories with excursions into natural and technical science. In 1837 he describes in his *Narrative of Arthur Gordon Pym* an anisotropic phase. I cite some passages:

> I am at a loss to give a distinct idea of the nature of this liquid, and cannot do so without many words. Although it flowed with rapidity in all declivities where common water would do so, yet never, except when falling in a cascade, had it the customary appearance of limpidity. It was, nevertheless, in point of fact, as perfectly limpid as any limestone water in existence, the difference being only in appearance. At first sight, and especially in cases where little declivity was found, it bore resemblance, as regards consistency, to a thick infusion of gum arabic in common water. But this was only the least remarkable of its extraordinary qualities. It was not colorless, nor was it of any one uniform color—presenting to the eye, as it flowed, every possible shade of purple, like the hues of a changeable silk. This variation in shade was produced in a manner which excited as profound astonishment in the minds of our party as the mirror had done in the case of Too-Wit. Upon collecting a basinful, and allowing it to settle thoroughly, we perceived that the whole mass of liquid was made

> up of a number of distinct veins, each of a distinct hue; that these veins did not commingle; and that their cohesion was perfect in regard to their own particles among themselves, and imperfect in regard to neighboring veins. Upon passing the blade of a knife athwart the veins, the water closed over it immediately, as with us, and also, in withdrawing it, all traces of the passage of the knife were instantly obliterated. If, however, the blade was passed down accurately between the two veins, a perfect separation was effected, which the power of cohesion did not immediately rectify. The phenomena of this water formed the first definite link in that vast chain of apparent miracles....

Poe's vision has been interpreted: it concerns BLOOD; Dr. Dintenfass will hopefully appreciate the example and *Arno Schmidt's* interpretation!

Apart from soap, *Virchow's* myelin, first described in 1854,⁽¹⁶⁾ is the longest known and over the years has been an intensively investigated liquid crystal. *Mettenheimer* (1875)⁽¹⁷⁾ first described its double refraction. The myelin forms are shown in Fig. 1. They emerge from the withdrawing of nerve core into water; lecithin, protagon, choline and ammonium oleate behave similarly. The first monograph on the polarization microscopy of organic material was written by *Valentin* (Leipzig 1861).⁽¹⁸⁾

At that time people were engaged in the detailed study of many

Aufmerkſam auf dieſen Zuſammenhang wurde ich durch eine Publikation des engliſchen Pathologen Charles Powell White in Mancheſter (Medical

Fig. 1

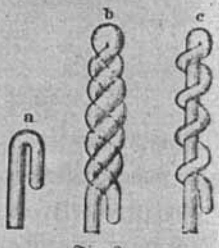


Fig. 2

Chronicle, März 1908) über die von R. Virchow (1854) entdeckten und ſeit dem ſehr vielfach unterſuchten Myelinformen, an deren Bildung meinen Beobachtungen zufolge flüſſige Kriſtalle ebenfalls beteiligt ſein mußten.

Figure 1. Myelin forms.

colloid chemical problems, i.e., with the formation of emulsions and with the morphology and formation of diffusion precipitation membranes. Here an important role was played by *G. Quincke*,(19) who, later in the nineties would not believe that crystalline liquids exist.

Let us stay for a moment in the years preceding the discovery of the cholesteric phase. A name now to be mentioned respectfully is Otto Lehmann, born on January 13, 1855 at Konstanz. His father was a teacher at Freiburg from whom Lehmann learnt much about natural philosophy. Lehmann's dissertation " Über Physikalische Isomerie " appeared in 1877. It dealt with the phenomena of enantiotropy and monotropy. From then on Otto Lehmann pursued microscopic crystal analysis. In 1889 the 2-volume monograph " Molecular physics " appeared(20) He described, repeatedly and gladly, among other things the so-called " TRICHITES " (Fig. 2).

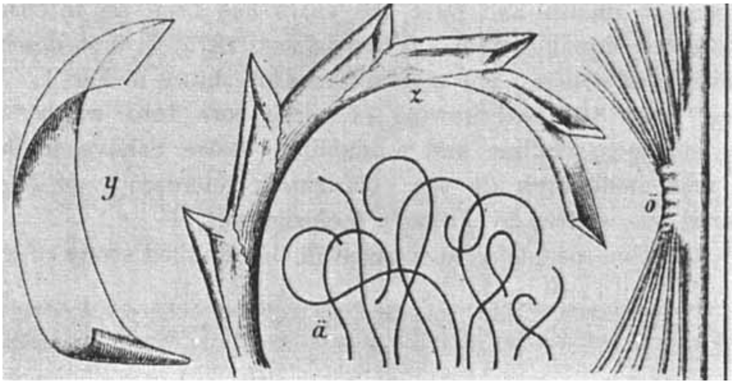


Figure 2. Trichites.

These are twisted, bent and partly branched shapes. In 1888 Lehmann was Professor at the technical college of Aachen and from 1889 he was in Karlsruhe.

The next picture (Fig. 3) shows O. Lehmann (from an old photograph).

Through what, one wonders, did O. Lehmann become known in these years? It must have been above all for the work on crystal analysis, as well as for a large technical skill in the construction of microscopes

Figure 3. Otto Lehmann (1855–1922); see *Physikal. Zs. 24*, 289 (1923), the obituary note by A. Schleiermacher and R. Schachenmeier.

with a hot-stage and projection apparatus. The beautiful lithograph from Lehmann's dissertation(21) (Fig. 4) clearly showed which direction Lehmann's work would follow: CRYSTALLIZATION-MICROSCOPE became a symbol of his further works.

A quotation from the year 1884 may demonstrate how close O. Lehmann came in his studies to the model concepts on phase changes and " liquid crystals ", so that only a spark was needed to bring these concepts into being.

Citation from Lehmann:

This liquid contains already dissolved in it the solid (or gaseous)

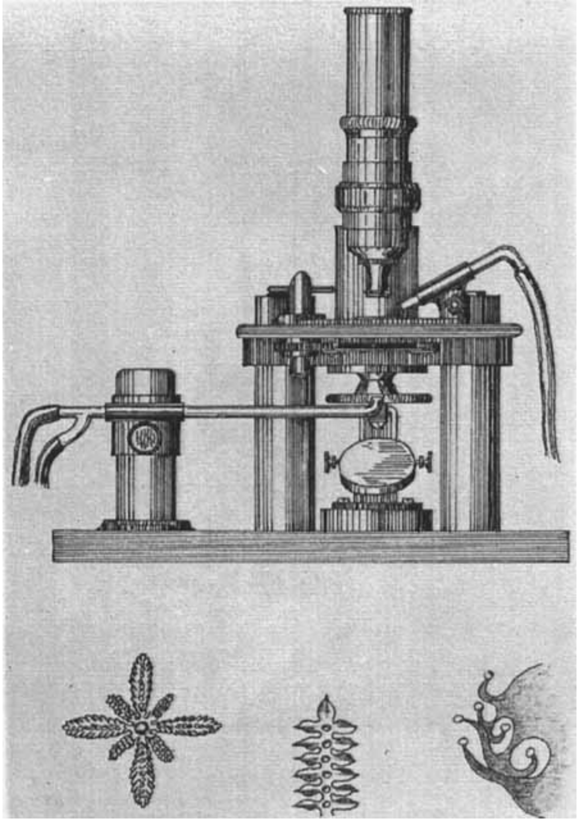


Figure 4. Lehmann's crystallization microscope and three examples of obserrated crystalline forms (drawn from the original).

> modifications when the liquid is in the proximity of its freezing (or boiling) point,... The ratio of both modifications is determined in a similar way as is the dissociation of compounds of different components, as well as by the rate and by the *viscosity* of the compound

(please compare this with J. I. Frenkels heterophase fluctuations theory).

Lehmann writes further:

> Occasionally the actual freezing point is not reached because the mixture gradually changes into an amorphous form.... The

> amorphous solid is favoured by the addition of *thickening agents* (such as colophony, rubber!!).

The same substances are later used to produce " liquid crystals ".

A striking colour phenomenon of the cholesteryl esters—of which the composition was not known at this time—was reported by several chemists, by *Planer*⁽²²⁾ and *Löbisch*⁽²³⁾. The remarkable iridescent colours caused by the cooling of cholesteryl esters were reported by *Raymann.*⁽²⁴⁾

Reinitzer (Fig. 5) was however the first to give a detailed description of this phenomenon.⁽²⁵⁾ In 1888 he observed that the effect is connected with double refraction, optical activity and occurs in the " liquid " state. He also recognized the connection with Lehmann's previous works, and he sent Lehmann his preparations in order to obtain his opinion of them.

Citation (Reinitzer to Lehmann):

> Encouraged by Dr. V. Zepharowich (Prof. of mineralogy at Vienna), I venture to ask you to investigate somewhat closer the physical isomerism of the two enclosed substances. Both substances show such striking and beautiful phenomena that I can hopefully expect that they will also interest you to a high degree.... The substance has two melting points, if it can be expressed in such a manner. At 145.5 °C it melts to a cloudy, but fully liquid melt which at 178.5 °C suddenly becomes completely clear. On cooling a violet and blue colour phenomenon appears, which then quickly disappears leaving the substance cloudy but still liquid. On further cooling the violet and blue colouration appears again and immediately afterwards the substance solidifies to a white, crystalline mass. The cloudiness on cooling is caused by the star shaped aggregate. On melting of the solid the cloudiness is caused not by crystals but by a liquid which forms *oily streaks* in the melt.

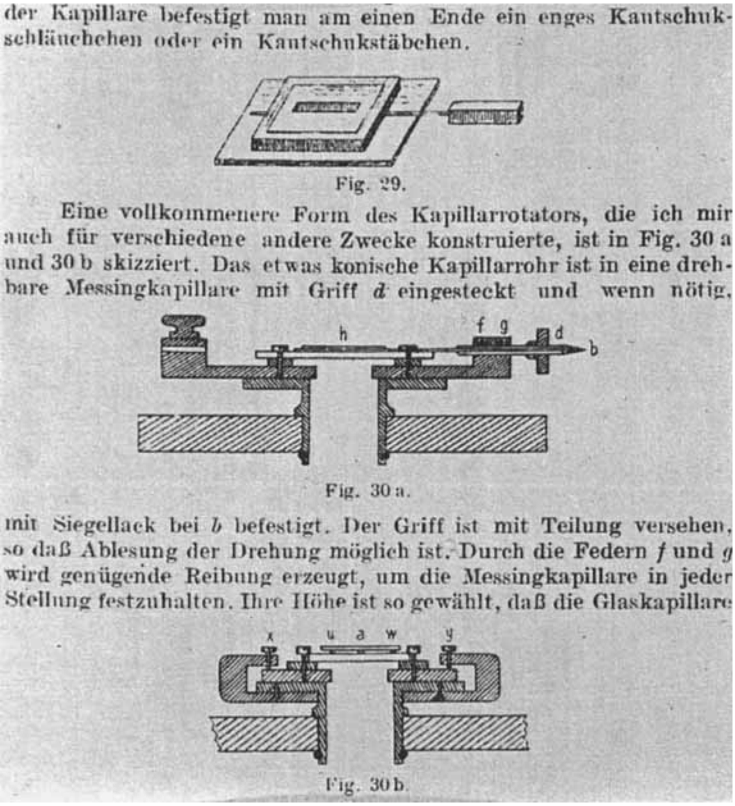
In the following years Lehmann came gradually to the opinion that a chemically uniform substance had been discovered. From now on things became more and more interesting for the chemists. In the following year (1889) *Gattermann* and *Ritschke*⁽²⁶⁾ observed the liquid crystalline phase of *p*-azoxyanisole, which was then described by Lehmann in 1890.⁽²⁷⁾ Lehmann differentiated consistently

Figure 5. F. Reinitzer.

throughout between the spherical droplet forming " fluid " crystals (like for ex. PAA) and the " elongated, angular, edged " crystal shapes forming " flowing " crystals. Many years passed, however, after Reinitzer's letter to Lehmann before the range of the discovery was recognizable. Lehmann gradually discovered the plastic and later the aqueous systems and the dispute with *Tammann*,(28,29) *Nernst*, *Quincke*, *Rotarski* carried on to the turn of the century.

It is curious to observe how many definitions were invented by Lehmann. Still it can be agreed that it was a matter of expression and these terms were always contained in the generic terms " flowing " = high viscosity, and " fluid " = low viscosity, that means in effect " smectic " and " nematic ". When the question arises of when and where the terms " flowing, fluid, viscous etc. " first became used with the term crystal, then the importance of Reinitzer's discovery is immediately recognizable. The term " flowing crystals " was used for the first time by Lehmann in 1889, " crystalline liquid " 1890 and " liquid crystal " appeared first in 1900.(30)

To-day it is hard to imagine how difficult it was in former times to produce a liquid crystalline preparation. It was necessary to heat with gas and to use blast air to cool. Lehmann had even placed



der Kapillare befestigt man am einen Ende ein enges Kautschukschläuchchen oder ein Kautschukstäbchen.

Fig. 29.

Eine vollkommenere Form des Kapillarrotators, die ich mir auch für verschiedene andere Zwecke konstruierte, ist in Fig. 30 a und 30 b skizziert. Das etwas konische Kapillarrohr ist in eine drehbare Messingkapillare mit Griff *d* eingesteckt und wenn nötig,

Fig. 30 a.

mit Siegellack bei *b* befestigt. Der Griff ist mit Teilung versehen, so daß Ablesung der Drehung möglich ist. Durch die Federn *f* und *g* wird genügende Reibung erzeugt, um die Messingkapillare in jeder Stellung festzuhalten. Ihre Höhe ist so gewählt, daß die Glaskapillare

Fig. 30 b.

Figure 6. Capillary rotator (Lehmann).

the whole object lens together with the object table in an oil bath, and used a pump to circulate the hot oil. The " capillary rotator "—a typical laboratory aid of Lehmann—is shown in Fig. 6.

Under all the circumstances Lehmann remained with the concept of "liquid (mono-)crystals ". The following pictures make clear why he did this. Figure 7 shows the " octahedrons ", which are symmetrical under rotation, which also appear adorned with " pearls " (Fig. 7: pictures 33–36).

The working with " solvents ": such as olive oil, colophony, monobromonaphthalene amongst others served only to generate the

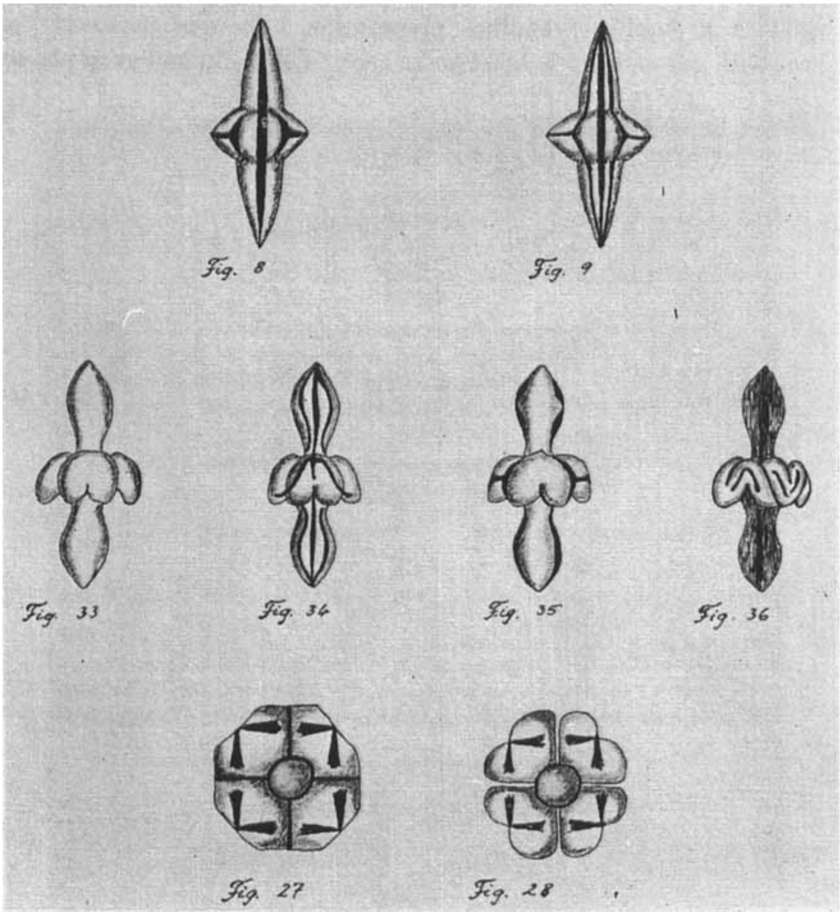


Figure 7. Liquid monocrystals as described by Lehmann.

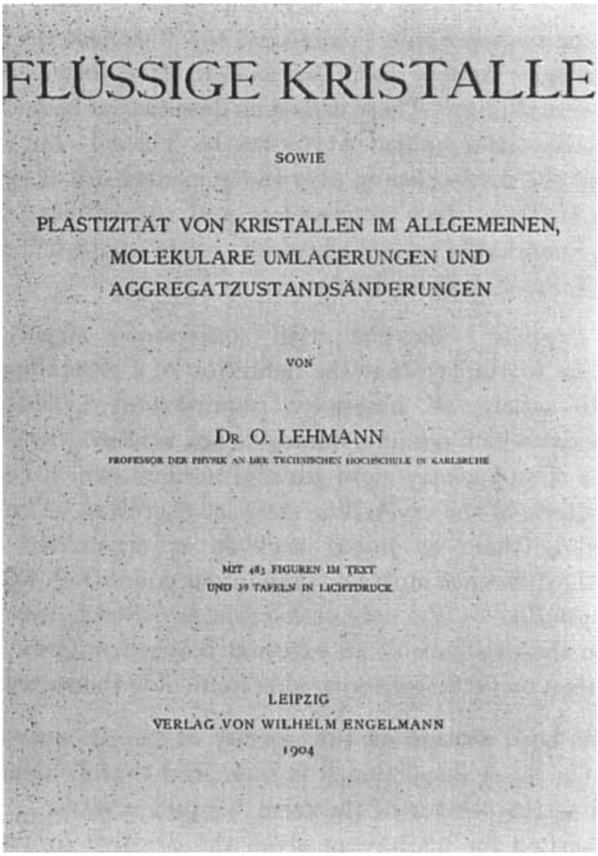
" TRICHITEN ", CRYSTALS i.e., MONOCRYSTALS. Using colophony or other non-mesomorphic substances, the " cholesteric infection " was discovered. Texture disturbances were interpretted as twinning, or as polycrystallinity. There can be no doubts that he had produced monocrystals—latter named BÂTONETS by Friedel—but it is also certain that the whole dispute over the nomenclature of crystals was looked on in those days as senseless and superfluous. *Woldemar Voigt*, the remarkable crystal-physicist, wrote about it⁽³¹⁾ (*Lehrbuch der Kristallphysik*, Leipzig 1910):

> *Liquid Crystals.* Material with constrained structures. We should like to observe that the definition of a crystalline material seems to satisfy all necessary requirements. Thus when... liquids exist which adopt a homogeneous texture when under the influence of sufficiently close parallel borders, which corresponds to the criteria of the crystalline state, so there can be no objection to labelling them as liquid crystals *or* crystalline liquids... though the difference must be taken into account that the substance being *crystalline or also only aeolotropic*, is called however crystallize from the existence of an external polyhedric form. The first term is then on further viewing able to include the second term....

Much has been written on the priority of the discovery of liquid crystals. On closer inspection it is soon seen that Lehmann can be recognized as the creator of the term " liquid crystals ". *Reinitzer* must be merited for his having given the decisive contribution to the discovery of the cholesteryl substances. (" Two melting points.")

Virchow and later *Mettenheimer* have described the birefringent liquid myelin and thus indeed the *first liquid crystal*. *Ambronn*,⁽³²⁾ a name which should not be forgotten in the history of polarization microscopy and liquid crystals, has revealed the connection between myelin, i.e., lyotropic, amphiphilic substances, and " Lehmann's substances ". Gattermann has discovered the first nematogenic fully synthetical substance. In 1904 Otto Lehmann published a large paper, the first monograph⁽¹⁾ on liquid crystals. The title is reproduced in Fig. 8.

Lehmann had in 1890, when *Gattermann* had sent him the azoxyethers, found in them an induced optical activity, when rather thick preparations of *p*-azoxyanisole were " displaced ".



FLÜSSIGE KRISTALLE

SOWIE

PLASTIZITÄT VON KRISTALLEN IM ALLGEMEINEN,
MOLEKULARE UMLAGERUNGEN UND
AGGREGATZUSTANDSÄNDERUNGEN

VON

DR. O. LEHMANN
PROFESSOR DER PHYSIK AN DER TECHNISCHEN HOCHSCHULE IN KARLSRUHE

MIT 483 FIGUREN IM TEXT
UND 39 TAFELN IN LICHTDRUCK

LEIPZIG
VERLAG VON WILHELM ENGELMANN
1904

Figure 8. O. Lehmann's great monograph.

Elliptically polarized light resulted from such a texture disturbance.

Dichroism studies on coloured crystals supplemented the picture, and they would be revived 30 years later by *Zocher* and *Dreyer*.

" Contact movements " remained one of Lehmann's favourite themes; it means material-exchange and the current caused by the strong difference between surface tension between phases with a common interface. Lehmann's imagination was soon at work with the construction of a motor which would work on this principle.

In *Flüssige Kristalle und die Theorien des Lebens*(33) he wrote:

> ... it would perhaps be successful in the production of an extremely light weight and yet productive motor, the lack of which has

> hindred the so ardently, but vainly hoped for development of aeronautics.

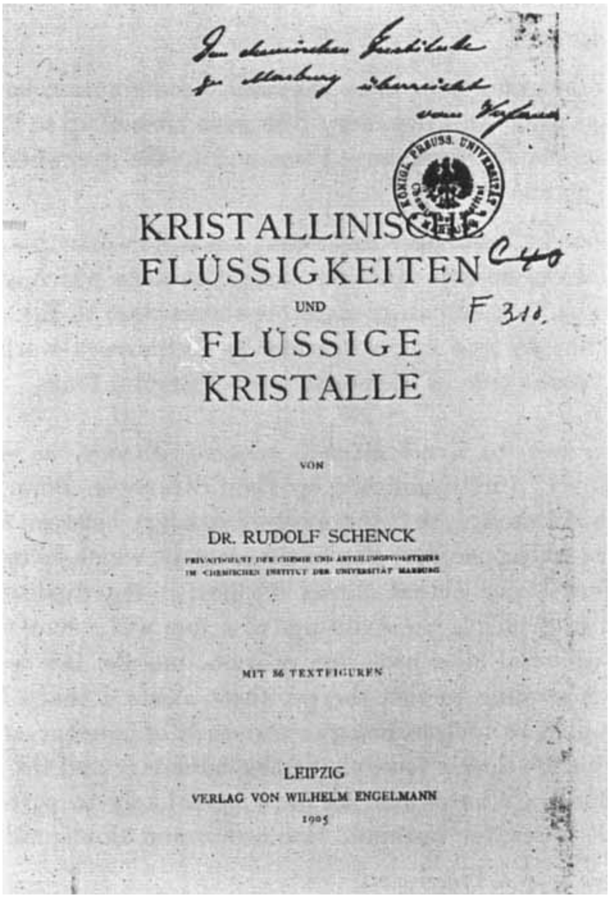
It would be unfair to belittle Lehmann's contribution just because at this stage after " his discovery " he gave himself up to the defense and propagation of his strange ideas and to the overwhelming production of publications:

> In addition to Lehmann's important scientific works, his appealing popular works deserve mention; for it was these which earned him wide recognition and an honourable status close to Ernst Häckel. Häckel himself was much touched by Lehmann's work, as it is proved by the title of his latest work " Crystal Souls " (Kristallseelen).
>
> In contrast (to Ernst Häckels monistic theory, as set out in " Welträtsel " [first published by Emil Strauss in Bonn in 1899], in which it stated... that there is no boundary between the lowest life forms and apparently like liquid crystals, which he regarded as themselves being actual forms of life,... the dualistic theory assumes in principle the existence of a free will; since it regards this as essential as a basis for religion, morals, law and public order. According to this theory, there exists a sharp boundary between physics and physiology; the study of liquid crystals would be suitable for clearly recognizing this boundary and the functions of the mind. What would he have been likely to write, had he been able to see, for instance, Robinson's and Bouligand's works?

Wallerant writes (1907):(34)

> La découverte de M. Lehmann est certainement un des plus importantes du siècle dernier; ses consequences sont nombreuses et de premier ordre et elles permettent en particulier de préciser nos connaissances sur la structure des corps cristallisés.

The contemporaries of Lehmann, who contributed important experimental and theoretical knowledge, should be remembered. First, *Rud. Schenck* will be mentioned. The conclusion of his papers on liquid crystals were published in the prominent work:(2) *Liquid Crystals and Crystalline Liquids* (1905) (Fig. 9). It goes back to his dissertation and includes also work of his students: (1) *Schönbeck*, Marb. 1900; (2) *Eichwald*, Marb. 1904; (3) *Bühner*, Marb. 1906.



Dem chemischen Institute
zu Marburg überreicht
vom Verfasser

KRISTALLINISCHE
FLÜSSIGKEITEN
UND
FLÜSSIGE
KRISTALLE

VON

DR. RUDOLF SCHENCK

MIT 86 TEXTFIGUREN

LEIPZIG
VERLAG VON WILHELM ENGELMANN
1905

Figure 9

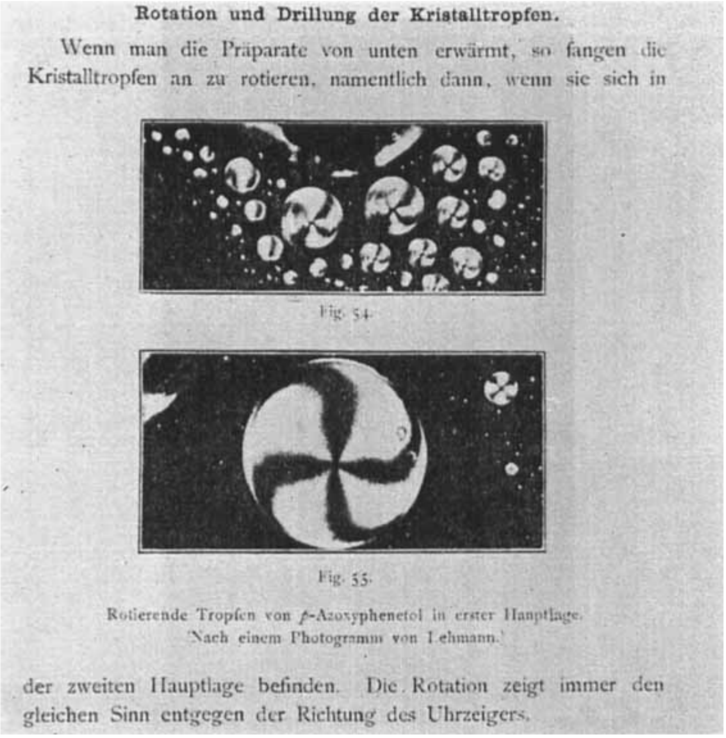
Schenck clarified the nature of the liquid crystalline state in the sense of homogeneous phases. *Nernst*, *Tammann* and *Quincke* now had to revise their objections. The following results of Schenck gave evidence for:

(1) *Discontinuities in the flow properties at phase transitions*
(2) *Determination of surface energy and molecular weights* (*Eötvös' constant*)
(3) *Measurement of dielectric constants*
(4) *Heat of transition.*

Schenck described also the optical activity (which later would be reported in detail by *Mauguin* as follows:

> Drops in the second principal position rotate when heated from below, always in the same sense of rotation. Drops in the first principal position under the same conditions show a spiral cross (Fig. 10).

The so-called SCHLIEREN pattern was investigated as well as the behaviour in a magnetic field.



Rotation und Drillung der Kristalltropfen.

Wenn man die Präparate von unten erwärmt, so fangen die Kristalltropfen an zu rotieren, namentlich dann, wenn sie sich in

Fig. 54.

Fig. 55.

Rotierende Tropfen von *p*-Azoxyphenetol in erster Hauptlage.
(Nach einem Photogramm von Lehmann.)

der zweiten Hauptlage befinden. Die Rotation zeigt immer den gleichen Sinn entgegen der Richtung des Uhrzeigers.

Figure 10. Nematic " Schlieren " texture (Schenck).

Mixtures of cholesteryl benzoate and Gattermann's *p*-azoxyphenetol formed the " layer crystals " with " Schraffierung " as described by Lehmann (today known as " Grandjean planes with large pitch "). All in all this was an outstanding experimental result.

The next worker in the organic chemistry aspect—and for a long time the only one—was *Daniel Vorländer* in Halle (Fig. 11). Complete information on the first publications of Vorländer is given in the small book: *Kristallinisch flüssige Substanzen* (Enke, 1908).⁽³⁾

The first and at that time, the most important feat was the synthesis of (as would later be called) the first smectic phase, i.e., *p,p'*-azoxybenzoic acid-ethylester (1902, by *F. Meyer* and *Dahlem*,(35) students of Vorländer); but Vorländer himself did not appear in this work. A further highlight of Vorländer's " school " was the discovery of polymorphism within the liquid crystalline state. The papers from Halle (mostly dissertations) began to increase rapidly.

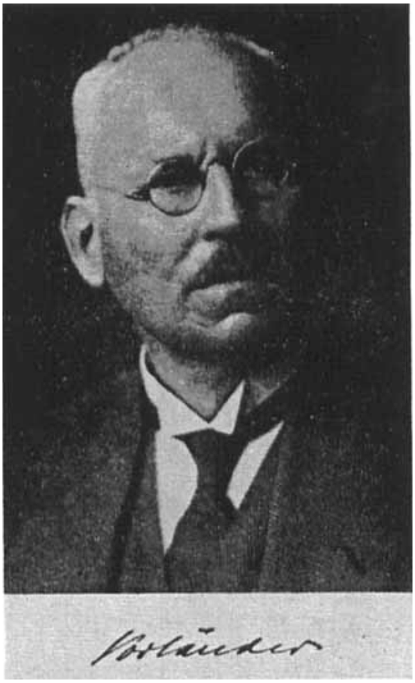


Figure 11. Prof. Daniel Vorländer, Halle.

Dissertations from Halle University are: *John* (1901), *Meyer* (1902), *Dahlem* (1903), *Schröter* (1904), *Lungwitz* (1905), *Hansen* (1906), *Siebert* (1906) and *Hulme* (1907).

It is remarkable that, in the 20 years from Reinitzer's discovery, the characteristics of the cholesterinic phase were hardly noticed. Lehmann gave only two pages in the *Flüssige Kristalle* (1904) for the cholesteric phase. Observed phenomena were interpreted in the sense of a model of superimposed mica-plates with an angular displacement. In 1884 a reference to the " Christiansen effect " appeared.(36) Later on, by use of the Christiansen effect one can eliminate Form-double-refraction to observe Eigen-double-refraction.

Second Period

Now we enter the second period. Frans Maurits *Jäger* in the Netherlands,(37) *Vorländer* and *Dorn* in Halle, *Wallerant* in Paris, *Stumpf* in Kiel and *Friedel* at Strasburg (St. Etienne) would soon report more and more about the nature of the cholesteric phase.

It should be mentioned that Bakhuis *Roozeboom* in Amsterdam had his interest in liquid crystals aroused by a correspondence with Lehmann.(38) His death stopped important work on phase theory, but there was, apart from those of Ornstein, about whom much remains to be said, highly significant Dutch publications. They include publications by Ada *Prins*,(39) van *Romburgh*,(40) and de *Kock*.(41) Much later, this work was continued by *Dave*(42) and extensively by *Sackmann*(43) at Halle.

France was at this moment in the calm before the storm. *Wallerant* was highly interested and had carried out his own investigations on cholesteryl esters since 1906. *Otto Wiener*(44) (1904) developed the optical theory of double refraction of lamellar and rod-like particles. In the years from 1906–8 the young physicist Emil *Bose*(4) (Fig. 12) worked intensively on a theory of the liquid crystalline phase. " For and against the nature of emulsions " he made experiments with magnetic fields. His " swarm " theory would be the starting point for a long list of experimental and theoretical work that would start 15 years later in Holland.

The year 1922 saw the appearance of *G. Friedel's* great work, the fiftieth anniversary of which we could celebrate this year. We appreciate the significance of this lucid and valid work. *Grandjean* reported in the obituary in memory of Friedel (Fig. 13):

> Nous commencâmes en 1909, Friedel et moi à observer les liquides anisotropiques de O. Lehmann.

The flow of publications by Lehmann ended with the summary in *Abderhalden's Handbook* of biological methods. This publication concluded his life's work. Lehmann died in Karlsruhe on June 17, 1922. During the last phase of his life (from 1908 to 1922) he

Figure 12. Emil Bose, gest. 25 May 1911 in La Plata.

introduced the study of liquid crystals outside Germany. Friedel's work (1922) shows how fruitful was the encounter between our " Privy Councillors " imaginative spirit of ideas, partly confused by speculation though they were, and the ésprit of *Wallerant, Friedel, Mauguin, Grandjean* and *Gaubert*. It is not improbable that Lehmann himself provided the incentive for intensive work on the subject in France, namely through the conference on " Les Cristaux Liquides " in Paris 1909, repeated in Genf on May 22, 1909.(45,46) (Mauguin 1911 made a return visit to Lehmann.(47))

> Cette Conférence était illustrée par 114 projections, dont un cinématographique. On avait aussi exposé 64 photographies (19 × 28) et 124 positifs sur verre (13 × 13) fixant les resultats décrits. Les expériments elles-mêmes ont été répetées par un grand nombre des membres de la societé, aux séances de manipulations faites à la Sorbonne après.

Figure 13. Georges Friedel (1865–1933).

It was during the war that the theoretical concept by *Max Born* appeared in Berlin continuing the work by *E. Bose.* Unfortunately, Vorländer resisted new ideas and probably to some extent also the entry of theoretical physicists into " his " sphere of work. Nevertheless he continued work as an outstanding experimenter and chemist. The physicist *Dorn*(48) was his coworker in the field of experimental optics.

The opportunity provided by Friedel's publications will now be taken to expound on individual topics in this field of research, since such topics are arising with increasing clarity.

These topics are the following:

Morphologically distinguishable conditions of crystalline liquids
Structural analysis by means of X-rays
Theory of the liquid-crystalline phase from intermolecular actions
Elasticity and viscosity

Influence of fields
Light scattering of nematic and smectic phases
Theory of the twisted and the cholesteric phase.

MORPHOLOGY

As long ago as 1906, *Fred. Wallerant* in France and Lehmann described " pseudo-isotropy " or " forced homeotropy ". Wallerant in particular explained the " undisordered " cholesteric phase.(49) He established that this texture does not display any coloured reflection. He also described the changes to " liquide homogène ", which occurs as a result of slight pressure. Unfortunately, he did not indicate the character of the birefringence in this context. Mauguin picked up the problem again, when in 1911 he described the twisted phases.(50) He had recognized in the azoxyanisole spirals that the molecules lie with their longitudinal axis parallel to the interface. The fact that Wallerant's " erected phase " had negative birefringence and that the analogy to Mauguin's spirals went further than Mauguin himself realized at that time was first recognized by Friedel in collaboration with Grandjean. On the other side Lehmann is completely justified in his observation relating to nematic phases (1906):(51)

> Pseudo-isotropy can be caused by the adsorbtive (!) action of the glass; the optical axis is everywhere perpendicular to the surface.

Furthermore, Lehmann stated:

> Thin layers absorbed on the glass govern the orientation of the remaining molecules. They can be altered to such a degree like soft crystals by means of rubbing, that the entire mass obtains a uniform structure. The transformation temperature of the layers adsorbed by the glass is raised, so that they are maintained even when heated considerably to above the clarification point.

All these observations are indeed correct, but still as late as 1922 the significant difference between optically positive and optically negative layers was not represented with complete clarity. On the other hand, Lehmann 1922 interpreted correctly(9) the vertical position of lecithin molecules on a glass surface and measured the interference strips. Also, the tilt of the molecules on cleavage planes of crystals was very familiar to him as " liquid-layer crystals ". Mention should be made in this connexion of the pictorial atlas entitled *Achsenbilder Flüssiger Kristalle*, published by *Vorländer* and *Hauswaldt*.(52) It was here that orientation differences perpendicular to the layer were investigated experimentally for the first time. It is, incidentally, to *Stumpf*, who wrote the fine summary in 1918,(6) that we are indebted for the identification of Z direction changes and for the knowledge that the phenomena resemble the *Brezina* double plates. Stumpf came from Göttingen, where in 1911 he graduated with a thesis on the rotatory power of *Vorländer* and *Dorn's* cyanobenzylidine amino cinnammic acid amyl ester. Quite early the term " conical texture " occurred in Lehmann's work. He reported this in about 1906, as shown in Figs. 14a, b.

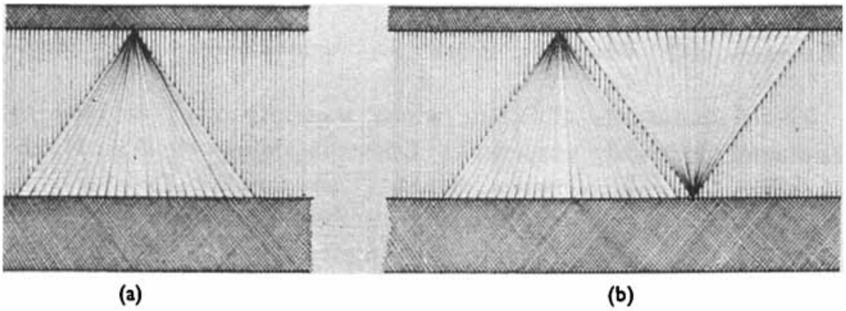


Figure 14a, b

Lehmann classified this type of disorder as the " glutinous-liquid " crystal phase (in other words, smectic phases). When, in 1920–22, figures like the following (Fig. 15) were seen in Lehmann's work,(53) this was at once reminiscent of the work done by *Friedel*(7) (Fig. 16).

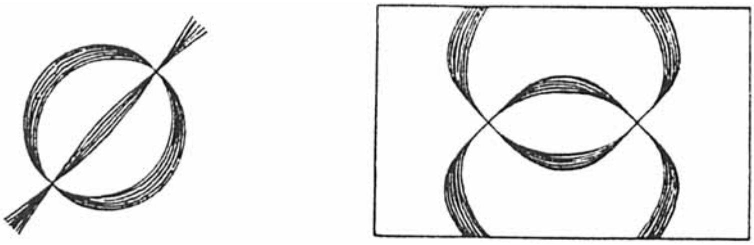


Figure 15

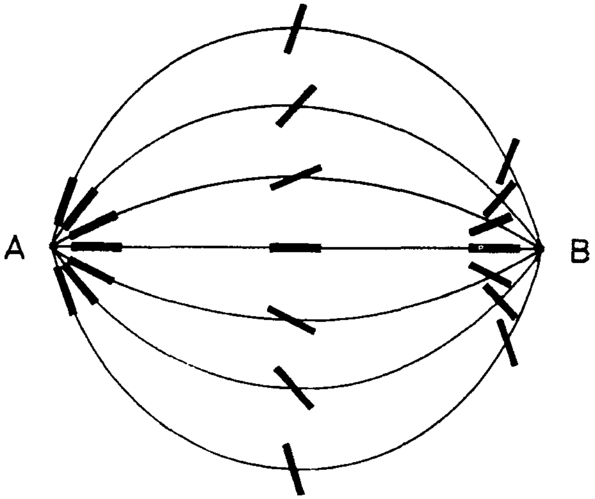


Figure 16. (A) " Kernpunkt " (fixed); (B) " Konvergenzpunkt " (rotating).

The Schlieren classification, which was originated in 1904 by Lehmann is purely empirical. Lehmann defines⁽⁵⁴⁾ (Fig. 17a, b) and (Fig. 18c, d) his views as follows: " The number of convergence points is always one fewer than the number of nucleus points."

Today, such series of points of symmetry (Fig. 19) are designated disinclination walls, and it has been confirmed by Saupe and Nehring⁽⁵⁵⁾ that $\Sigma s = 0$.

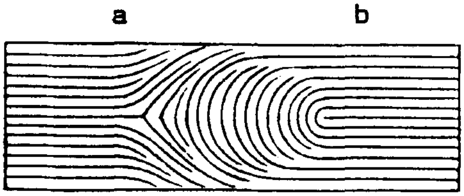


Figure 17. (a) a half convergence point; (b) a half nucleus point.

Lehmann unfortunately did not venture to investigate layers systematically; but he found that crystalline growth occurs in the Z-direction. This directional growth displays the corresponding arrangements in superimposed layers giving a nematic thread (Fig. 20). Threads of different morphology (with or without a shadow (" Hof ")) have been briefly described (Fig. 21).

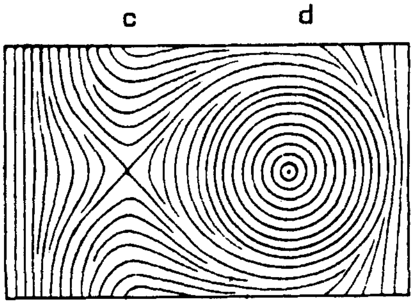


Figure 18. (c) a whole convergence point; (d) a whole nucleus point.

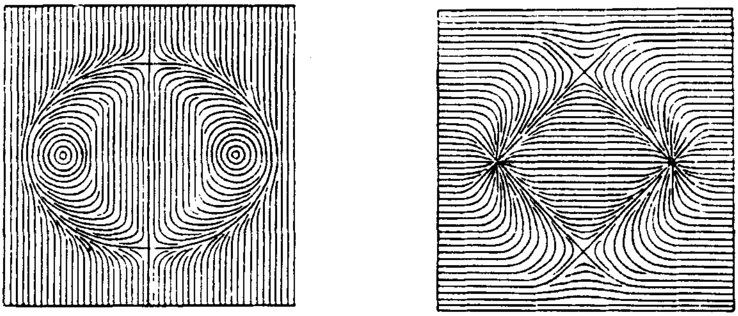


Figure 19. Disinclination walls (Lehmann).

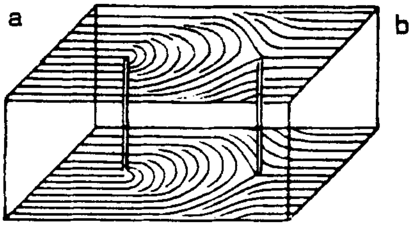
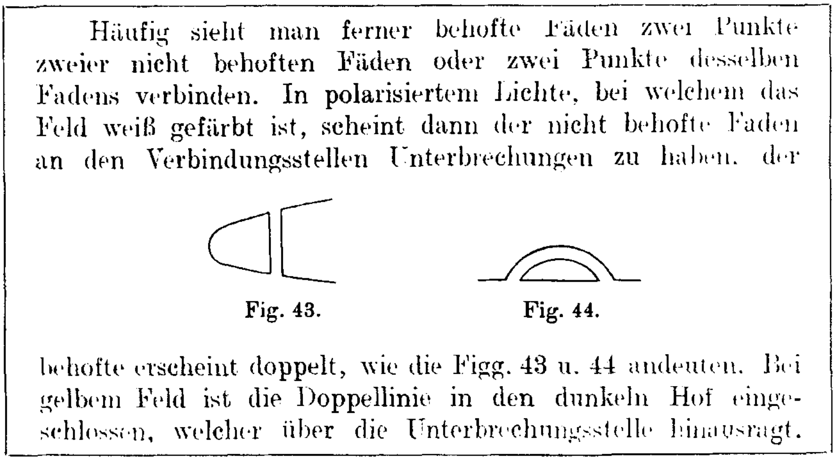


Figure 20. Nematic threads (scheme).

Mauguin and especially *Grandjean* also investigated the orientation of liquid crystals on cleavage surfaces of crystals. A typical difference in the epitaxy behaviour of the smectic phase as compared with the nematic phase is recognized. In close connexion with this are Grandjean's free " graded droplets " (Fig. 22) which were obtained by him with azoxybenzoic acid ethyl ester on arsenic sesquisulphide, talc, pyrophyllite, or rock salt. The melting crystal



Häufig sieht man ferner behofte Fäden zwei Punkte zweier nicht behoften Fäden oder zwei Punkte desselben Fadens verbinden. In polarisiertem Lichte, bei welchem das Feld weiß gefärbt ist, scheint dann der nicht behofte Faden an den Verbindungsstellen Unterbrechungen zu haben, der

Fig. 43. Fig. 44.

behofte erscheint doppelt, wie die Figg. 43 u. 44 andeuten. Bei gelbem Feld ist die Doppellinie in den dunkeln Hof eingeschlossen, welcher über die Unterbrechungsstelle hinausragt.

Figure 21

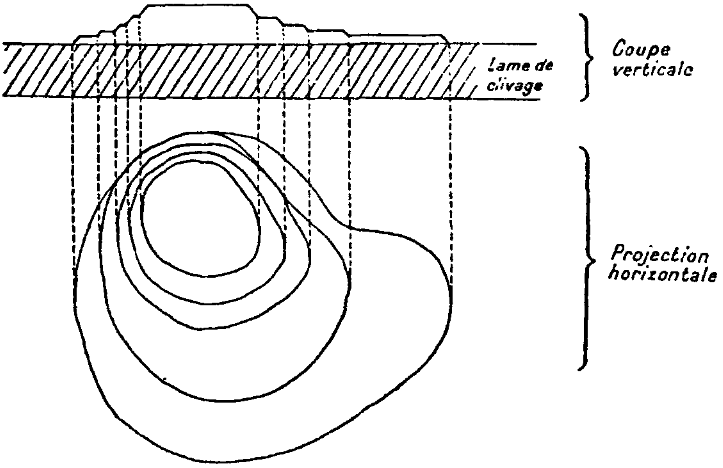


Fig. 1. — Goutte en *gradins* reposant sur une lame de clivage.

Figure 22. Stepped droplet (Friedel, Grandjean).

expands in a band or as a symmetrical figure (Fig. 23) with straight edges in parallel pairs on the cleavage surface of the crystal, and in conjunction with this a parallel-striped pattern also forms, this depending on the system and the symmetry of the surface. *Grandjean* alone investigated 80 instances of such epitaxy. The graded droplet had nothing to do with Grandjean's texture of the cholesteric phase which is created between mica cleavage surfaces and whose

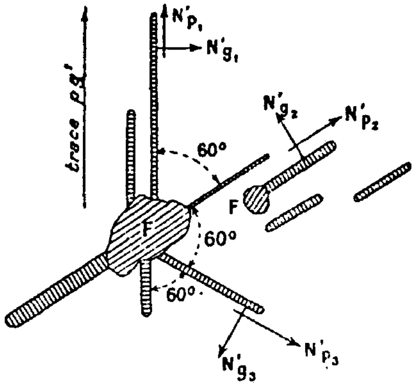


Fig. 17. — *Talc* et *azoxycinnamate d'éthyle*. Formation de gouttes rectilignes allongées suivant *g'* et suivant des directions à 60° de *g'*.

Figure 23. " Epitaxy " on a crystal surface.

graded edges were explained by *Friedel* in the sense of linear disinclinations.

Another point of interest is the use of *Beckes line* for identifying contiguous regions of varying orientation. In connexion with these delimiting lines, Friedel wrote:⁽⁵⁶⁾

> There can therefore be no doubt that this limit, which could be regarded as a plane surface, . . . is the contact line of two orientations of the same phase.

THEORY

With regard to the theory of intermolecular forces it should be stated that the relevant conception of dispersion interaction did not exist until 10 years later (*London*). Thus, at first there was no alternative but to use starting points deriving from a molecular dipole moment, as, for instance, *Max Born* did. The fact that the expected confirmation of the theory—the existence of ferroelectric properties of nematic phases—was not forthcoming caused the theoretical starting points unjustifiably to fall into oblivion.

Without exactly defining the nature of the intermolecular action, *Oseen* (Fig. 24) was to produce a successful synthesis of molecular statistics in conjunction with symmetry observations, thereby clearly defining the six elastical constants for the first time and

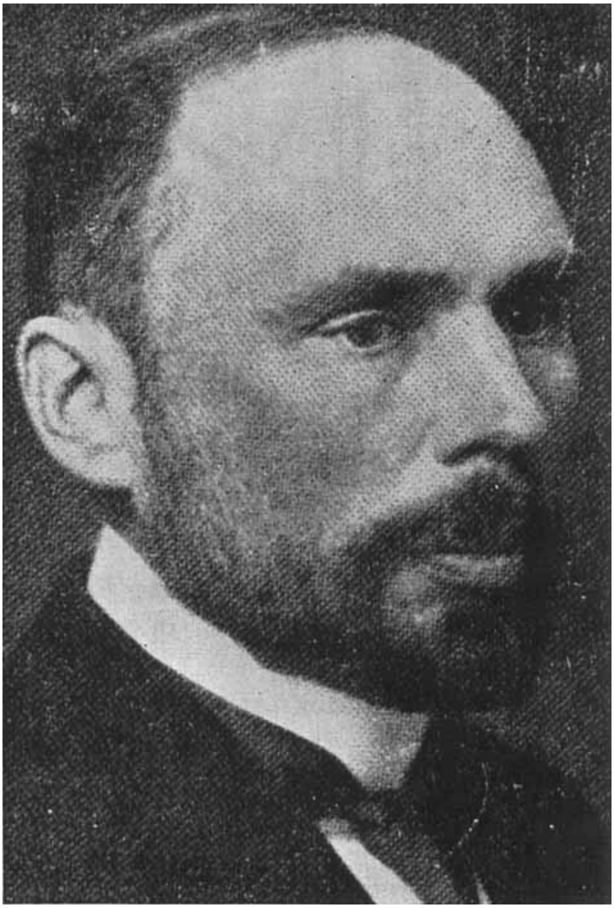
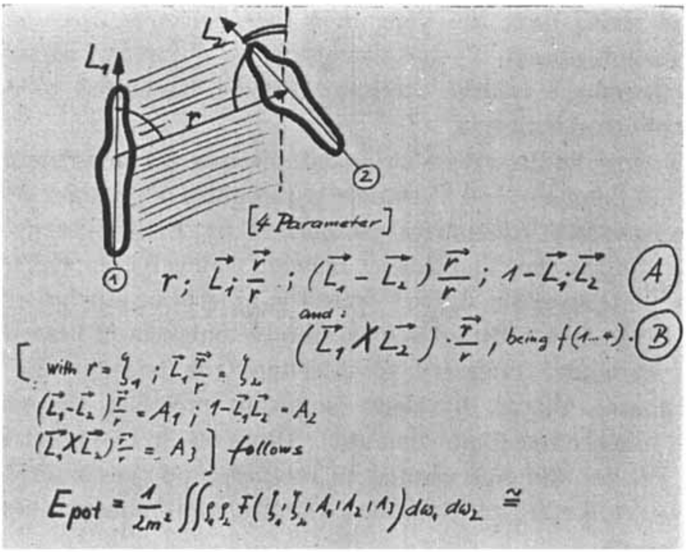


Figure 24. Carl Wilhelm Oseen (1879–1944).

adding to the theory some formulations that are still valid now in essentially an unchanged state (Figs. 25, 26).

The concept of the molecular structure of the material especially of liquids, was of theoretical importance. A distinction was drawn for a long time between "chemical" and "physical" molecules. The latter were said to be very large in the case of liquid crystals. Later these latter units were to be named "swarms". Various modifications of a material would be attributed either to differences in the *structure of lattice* or to differences in the *structure*



① r; $\vec{L}_i \cdot \frac{\vec{r}}{r}$; $(\vec{L}_1 - \vec{L}_2)\frac{\vec{r}}{r}$; $1-\vec{L}_1\cdot\vec{L}_2$ Ⓐ

and :

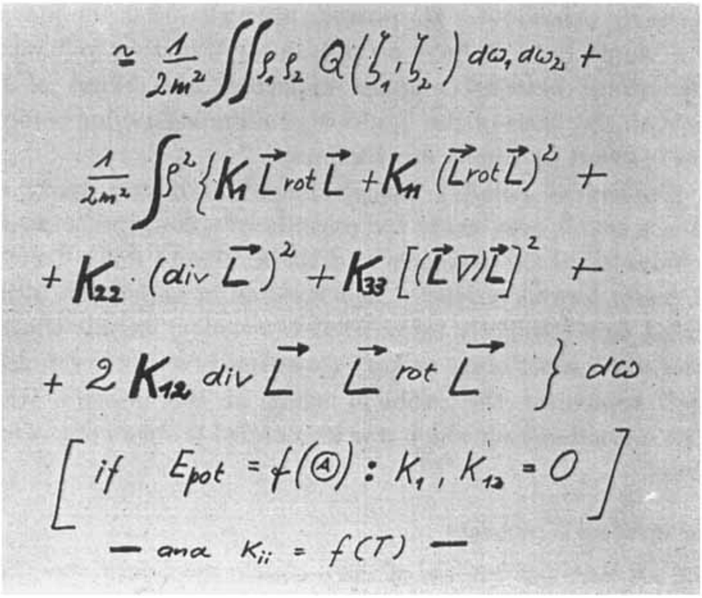
$(\vec{L}_1 \times \vec{L}_2)\cdot\frac{\vec{r}}{r}$, being $f(1\ldots 4)$ · Ⓑ

[with $r = \zeta_1$; $\vec{L}_1 \frac{\vec{r}}{r} = \zeta_2$

$(\vec{L}_1 - \vec{L}_2)\frac{\vec{r}}{r} = A_1$; $1-\vec{L}_1\vec{L}_2 = A_2$

$(\vec{L}_1 \times \vec{L}_2)\frac{\vec{r}}{r} = A_3$] follows

$$E_{pot} = \frac{1}{2m^2}\iint \rho_1\rho_2 F(\zeta_1,\zeta_2,A_1,A_2,A_3)\,d\omega_1\,d\omega_2 \cong$$



$$\cong \frac{1}{2m^2}\iint \rho_1\rho_2\, Q(\zeta_1,\zeta_2)\,d\omega_1\,d\omega_2 +$$

$$\frac{1}{2m^2}\int \rho^2\Big\{K_1\,\vec{L}\,\mathrm{rot}\,\vec{L} + K_{11}\,(\vec{L}\,\mathrm{rot}\,\vec{L})^2 +$$

$$+K_{22}\cdot(\mathrm{div}\,\vec{L})^2 + K_{33}\,[(\vec{L}\nabla)\vec{L}]^2 +$$

$$+\,2K_{12}\,\mathrm{div}\,\vec{L}\cdot\vec{L}\,\mathrm{rot}\,\vec{L}\Big\}\,d\omega$$

[if $E_{pot} = f(\text{Ⓐ})$: $K_1, K_{12} = 0$]

— and $K_{ii} = f(T)$ —

Figures 25 and 26. Potential energy in a liquid crystal as formulated by C. W. Oseen.[10]

of the molecules. The much discussed *identity theory*, which was to be accepted soon, took the view that the molecules were *identical* in the various phases. " Gestaltungskraft " (" force of figuration ") was to become a central concept. Friedel attempted to develop clearer physical concepts.

What must be described as lamentable was the unwillingness on the part of Lehmann and Vorländer to recognize or consider critically the characteristic differences established by Friedel between the nematic and the smectic phases. Instead, claims for the existence of further " intermediate states " were the objects of much confusion. Liquid crystalline substances even became subjects of heated argument; Vorländer preferred to introduce the terms† " Bz " and " Pl " phases, though by these he meant precisely the same as Friedel, namely smectic or nematic. However, in one point he was right: Friedel had not wanted to recognize polymesomorphism—which was, according to Vorländer, a typical and frequently observed phenomenon.

Vorländer succeeded in ascertaining experimentally the essential characteristics of molecular constitution which are the prerequisites for mesogenic behaviour. He proved, inter alia, that the individual molecule would have to have a rigid, linear structure and was able to differentiate between angular molecules and those of linear structure on the basis of the liquid-crystalline behaviour before this had been proved by dipole measurement.

The problem of polarity was evidenced at a very early stage, wherever a search was made for possible relationships between the polar character of the molecule and the ability to form " erected " phases, or for ferroelectricity. This resulted in important, although not at that time explicitly formulated knowledge, namely the apolar character of a " short range group " consisting of only a few molecules. We shall encounter the problem again in the interpretation of dielectric measurements which was the central problem of the following period.

ELASTICITY AND VISCOSITY

In 1922, all that was known of visco-elastic behaviour was the fact that it was an additional criterion for differentiation between nematic

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† Bz: smectic, Pl: nematic.

and smectic phases, and that pretransformation ranges are observable. We found an early description by *Bose* where he clearly describes the principal possibilities related with phase changes (Fig. 27).

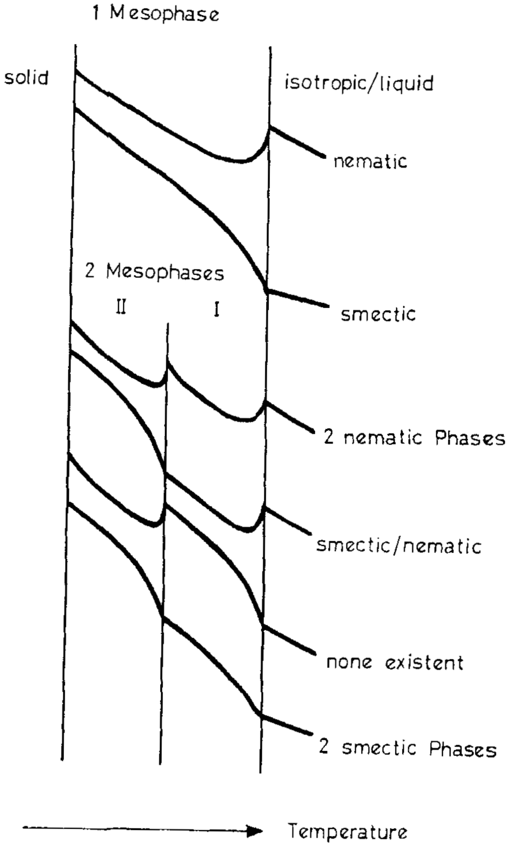

Figure 27. Viscosity of crystalline liquids, as discussed by Bose.(4)

INFLUENCE OF FIELDS

The following quotation should show how *Friedel's* ideas on the action of the electric field were already clear by 1922:

> The electric field, likewise without any effect on the smectic substances, orientates the nematic liquids (PAA!) in doing which it attempts to align the optical axes in a plane perpendicular to the lines of force. Since the optical axis remains free to align itself

in any direction within this plane, the electric field, unlike the magnetic field, initiates the creation not of a homogeneous structure but of a threadlike structure, in that the threads adopt a parallel to //**E** orientation as axes of the alignment (in accordance with Björnstahl's observation).

It is particularly evident from this example that there was a great risk of arriving at conclusions on the general principle from observations on one particular group of substances. Apart from this, it is repeatedly apparent how readily credence was given to the chemist's assertion that a mesogenic substance is homogeneous in its composition.

In 1922 the physicist, *P. Weiss*, worked at Strassburg, in other words: in Friedel's immediate vicinity. His theory of ferromagnetism found widespread recognition and the suggestion was advanced by Friedel, for instance, that Weiss's concept should be applied also to liquid crystals. The effects of the interaction of electric and magnetic fields on isotropic materials, and the Cotton-Muoton, the Faraday, and the Kerr effects were all familiar.

Light Scattering

By 1922, only a little was known about light scattering of nematic and smectic perceptible and the " flicker phenomenon " (Mauguin). Most interest was now centered on the cholesteric phases (*Stumpf, Dorn, Vorländer, Mauguin* and *Friedel*). The optics of the twisted phases could be approached by means of models, using the *Poincaré*-sphère. It is important to realize the advanced level that theoretical optics and general crystal physics had reached at that time. The only feature still lacking was the " molecular basis ". At Upsala, *T. Svedberg*(56) was at work, investigating anisotropic reaction behaviour and conductivity with and without a magnetic field. Nearby, *Björnstahl* and *Oseen*(10) started working in a very general way, concerning theory and reactions with respect to outer fields. In Amsterdam, *van de Waals* was lecturing (identity theory coming up!). *Ornstein* (Fig. 28), a pupil of H. *Lorentz*, was at that time a lecturer in theoretical physics at Groningen, and from 1915 onwards was Professor of mathematical physics at Utrecht.

By about 1924 he had published fundamental works on statistical

Figure 28. L. S. Ornstein (born 1888).

thermodynamics, statistical mechanics, density fluctuations, crystalline phenomena, light quanta and the Zeemann effect. His encounter with liquid crystals, became the base for *Ornsteins* theory.(57)

Kast's doctoral(58) thesis in 1922 was to provide a significant new starting point for liquid crystal theory. Four years later, *Kast* (Fig. 29) worked as a Rockefeller fellow in Ornstein's Institute, this being one of the most remarkable steps in further development of liquid crystal research.

Figure 29. Wilhelm Kast.

Third Period (up to 1930–33)

The geographical table (Table 1) shows where research on liquid crystals was undertaken. Most of the names should be so well known that a more detailed description would be superfluous at this time. So we will now continue with the theme of the preceding chapter. This period is summarized by *Oseen*,(10) in the *Ewald*-Discussion,(11) and in the Faraday Society Transaction 1933.(12)

TABLE I

IOWA	UPSALA	LENINGRAD		
G.W. STEWART	SVEDBERG SANDQUIST BJÖRNSTAHL OSEEN FAHREUS ANZELIUS	FREEDERICKSZ ZOLINA, REPIEWA PUSHIN, GREBENSHIKOW (TSVETKOV ab 1934)		
CALIF. (STANFORD)				
J.W. Mc BAIN (später VOLD & VOLD)				
CAMBRIDGE	BRISTOL	LONDON	KRAKAU	
BERNAL, FOWLER CROWFOOD A.S.C. LAWRENCE RAWLINS	T. MALKIN	W. BRAGG N.K. ADAM	M. JEZEWSKI 1923 1929...	
STRASSBURG	PARIS	NANCY	BESANÇON	
G. FOËX ROYER P. WEISZ G.+E. FRIEDEL	J.J. TRILLAT P. GAUBERT F. GRANDJEAN	MAUGUIN	J.J. TRILLAT	
UTRECHT	DELFT	AMSTERDAM	BRÜSSEL	
ORNSTEIN ZERNICKE (W.KAST 1932-33) v. WIJK, MOLL, RIWLIN		ADA PRINS de KOCK JÄGER ↔ (ROOZEBOOM)	ERRERA	
FREIBURG	STUTTGART	BERLIN	HALLE	LEIPZIG
W. KAST 1933 F. RINNE † 1933	C. HERMANN	(BOSE) (BORN)→ Gottingen ZOCHER bis 1931 KWI HERRMANN KRUMMACHER	VORLÄNDER et. al. KAST	Wo. OSTWALD C. WEYGAND (1933-35 Ankara) ab 1936
KARLSRUHE		PRAG		INDIEN
LEHMANN, K. L. WOLFF		ZOCHER ab 1931		KRISHNAMURI

MORPHOLOGY

The system of *Lehmann* and *Friedel* for the disinclination centres, lines and surfaces, needed hardly any refinement. In *Zocher's* continuum model the directional changes in the Z-axis were emphasized. He introduced the P-N-P etc. layers. Basically at this time no fundamental changes or enlargements were necessary to

Oseen's theory. Oseen's theory is valid for areas where the direction of the molecules is a constant function of the coordinate of the centre of gravity. What *Zocher*† mainly contributed was a substantial expansion of experience with directed adsorption and the inclusion of colloidal systems (as also *Wo. Ostwald* did) into the group of " lyotropic " mesophases, Salvarsan, azo-dyes and many more.

Friedrich Rinne, Freiburg, had earned equal merit on this question. In Freiburg there were his colleagues, *Staudinger* (a student of

Figure 30. Wilhelm Maier.

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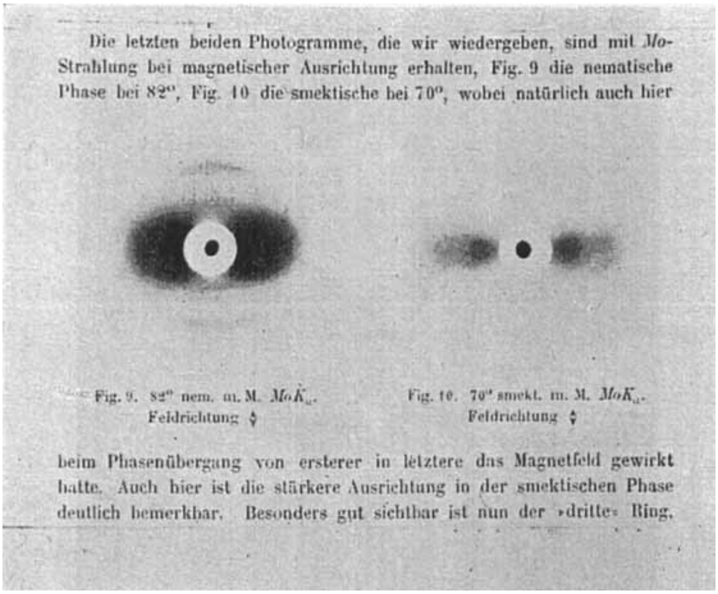
† A portrait of Zocher is given in the proceedings of the Third Liquid Crystal Conference.

Vorländer) and *Kast;* later Kast's students, *Wilhelm Maier* (Fig. 30) and *Alfred Saupe*. The town of *Freiburg* from that time on would remain linked with research into macromolecules and liquid crystals.

It is understandable that *Oseen's* line of thought soon developed into the " continuum theory ", which contained only macroscopic parameters in the simplest form with three independent elasticity constants. This development was advanced strongly by *Zocher*, and later on intensively by *Frank*. Of course, the aim must have been a uniform theory which underpinned the macroscopic-elastomechanic theory and took thermodynamics into account. This target was reached by the next generation when the flow properties and the interaction with fields had also to be included. In this connection the astounding intensity and continuity of research in the *Fréedericksz* school in Leningrad must be mentioned. Through the works of Zwettkoff this research reached a new peak. Their works remain undiminished up to the present day. We will come back to them in in the next section.



Die letzten beiden Photogramme, die wir wiedergeben, sind mit *Mo*-Strahlung bei magnetischer Ausrichtung erhalten, Fig. 9 die nematische Phase bei 82°, Fig. 10 die smektische bei 70°, wobei natürlich auch hier

Fig. 9. 82° nem. m. M. MoK_α.
Feldrichtung ↕

Fig. 10. 70° smekt. m. M. MoK_α.
Feldrichtung ↕

beim Phasenübergang von ersterer in letztere das Magnetfeld gewirkt hatte. Auch hier ist die stärkere Ausrichtung in der smektischen Phase deutlich bemerkbar. Besonders gut sichtbar ist nun der »dritte« Ring.

Figure 31

STRUCTURE ANALYSIS

The first positive results were obtained by *W. Kast* and *Edmond Friedel* (the son of *George Friedel*) from the investigation of nematic phases orientated in a magnetic field and from smectic phases. Figure 31 shows one of the first X-ray photographs which indicates an ordering larger than the usual liquid structure. That was the breakthrough. *Herrmann* and *Krummacher* reported at some length on X-ray studies, and *Bernal* and coworkers demonstrated the analogies between nematogenic crystals and fibre structure. *Friedrich Rinne* (Fig. 32) coined the term *paracrystals.* X-ray structure analysis would later be investigated in much greater scope.

The dissertation by *Hermann* (Karlsruhe) is a very important

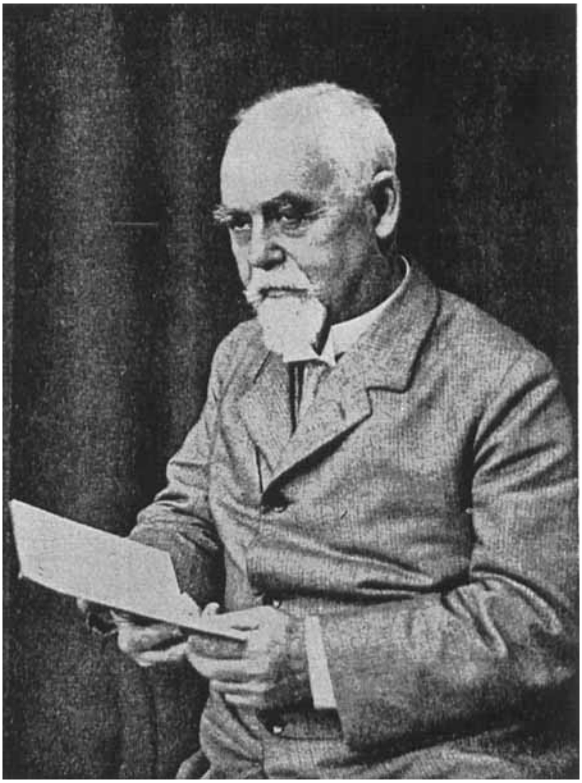


Figure 32. Friedrich Rinne.

theoretical contribution, which reached far into the future and is appreciated and referred to in current literature.

THEORY

Although *Oseen* had drawn up a comprehensive theory, the argument between the " swarm " and the " continuum " was the main discussion point. *Ornstein* started from the " infinite thick " layer; experimentally he used layers which were many millimeters thick. *Zocher* was right as long as he considered the mechanical disturbance of a constantly oriented, thin layer, i.e., a " macro-swarm " which is identical with the whole preparation. Much later it would be shown how important this difference was for the practical application of liquid crystalline preparations. How exactly this problem was recognized is shown by the experiments performed, in particular those from *Fréedericksz.*

FIELD EFFECTS

It was generally accepted that diamagnetism of the molecules and not the magnetical swarm moment was the cause of the alignment. The theory of this directional effect came from *Szivessy*, *Debye*, *Jeżewski* and *Kast* through the dependence of dc on the orientation of a liquid crystalline phase by a magnetic field. *Fréedericksz* and *Repiewa*, as well as the diamagnetic measurements of *Foex* and *Royer*, finally proved the " diamagnetic " interpretation. At that time *Ornstein* described quantitatively the directional effect of the magnetic field in which the value of v (called swarm-volume) is obtained from the concept of the magnetic energy of a " swarm ":

$$E_H = -H^2 \cos^2 \phi \cdot (\mu_1 - \mu_2) \cdot v$$

ϕ : angle to the magnetic field $\mathbf{H}$

μ_1 = longitudinal permeability

μ_2 = transversal permeability

E_H is the typical energy value for a Boltzmann's distribution. In order to be able to follow the dependence of the directional effect of $\mathbf{H}$ the dielectric constant ϵ_H was measured with increasing magnetic field. We cannot go into details here.

E_H is a function of the dc-anisotropy, of the magnetic energy (see above) and of the temperature. To prove the theory, $\Delta\epsilon = \epsilon_H - \epsilon_0$ (ϵ_0: no field) versus variable **H** was measured and calculated until saturated. Then the value of $v \cdot (\mu_1 - \mu_2)/kT$ is available. When $\Delta\mu$ is known, then v can be obtained. It was found that

$$v \cong 40 \cdot 10^{-18}\ \text{cm}^3.$$

The large problem in the interpretation of the results was that whilst the coordination of the μ's to a stretched, symmetrical molecule could be easily, conceived in a sense of its structure, this was not true of the electrical anisotropy because the state of the molecular electrical moment was not known. The most interesting experiments are those which aimed at finding a correlation between molecular electric moment and the dc-anisotropy i.e., the directing effect of an electric field at low frequency. From the experiments of *Lehmann*, *Friedel*, *Kast*, *Zocher* and *Fréedericksz* come the connection between positive and negative dc-anisotropy and the symmetry and polarity of single molecules (*Zocher's rule*). *W. Kast* showed that there are molecules which arrange themselves parallel to the direction of the electric field, but we must still be careful not to identify the dc-anisotropy immediately and simply with the molecular dipole moment. The matter became yet more complicated when the electric field was also used for orientation. The competition between the directing influences of electric fields on the dc, formed for years to come the object of investigation. To this came a third, the electrolytic conductance. This was investigated by *Kast*⁽⁵⁸⁾ and by *Svedberg.*⁽⁵⁶⁾ Svedberg found a connection between the conductivity κ in the direction α with respect to the magnetic fields direction:

$$\frac{\kappa^2\alpha \cdot \cos^2\alpha}{\kappa^2 0^\circ} + \frac{\kappa^2\alpha \cdot \sin^2\alpha}{\kappa^2 90^\circ} = 1$$

$$\kappa 0^\circ > \kappa 90^\circ.$$

The relationship between field H, temperature ϑ and conductivity κ is given in Fig. 33.

That however is not enough; the directing influence of the wall must also be mentioned. *Ornstein,*⁽⁵⁹⁾ *R. Riwlin,*⁽⁶⁰⁾ *van Wijk*⁽⁶¹⁾ and *Fréedericksz*⁽⁶²⁾ have investigated this effect closely and have determined quantitatively that the dependency of the wall-oriented zone on magnetic field strength is such that the thickness of the zone

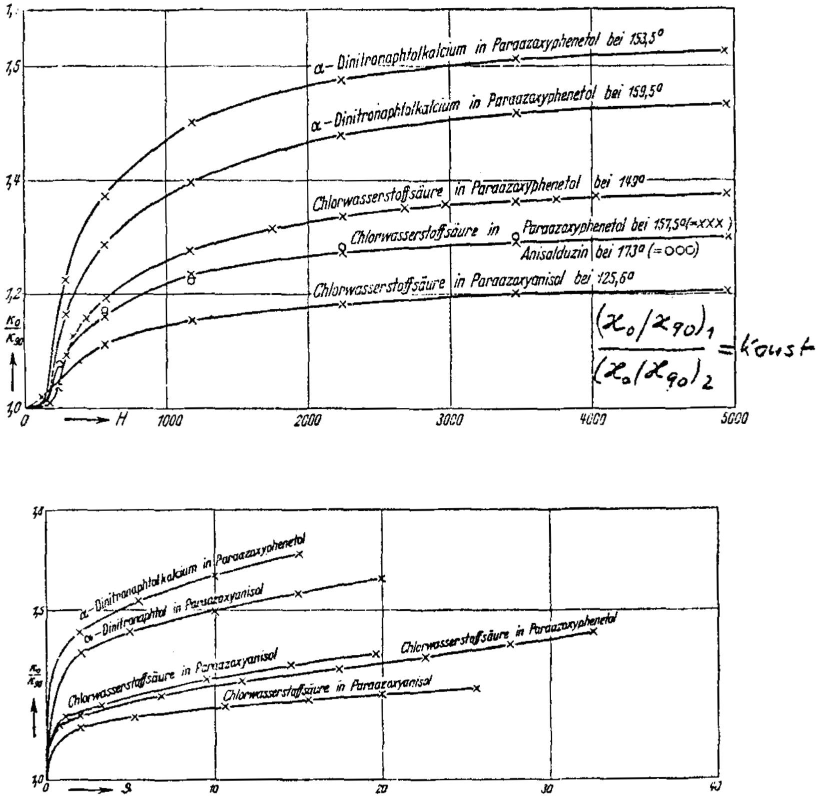


Figure 33. Dependence of conductivity κ with respect to magnetic field H and temperature.

decreases with increasing field strength (Fig. 34). It is thus understandable that depending on the interference given by the thickness of the " wall " zone to monochromatic light, only *periodic* brightness is obtained and so the assumption is based on the observation of an interference figure. In the observations made, only the measurement of light scattering (or as then called " extinction ") was missing in connection with the fields. This can be supplemented by reference to the work of *Björnstahl*⁽⁶²⁾ and *R. Riwlin.*⁽⁶⁰⁾ The measured trend of the extinction against E (from Björnstahl⁽⁶²⁾) should not be completely unknown (Fig. 35).

It must be admitted that in this period of time not all the points between static and dynamic field effects were yet differentiated, and

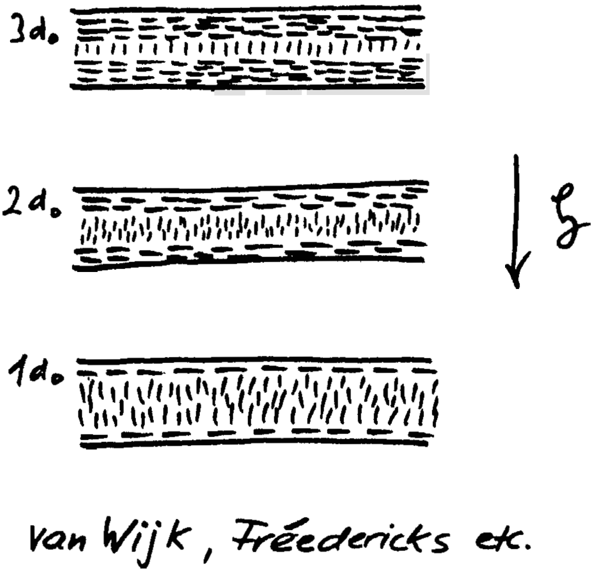
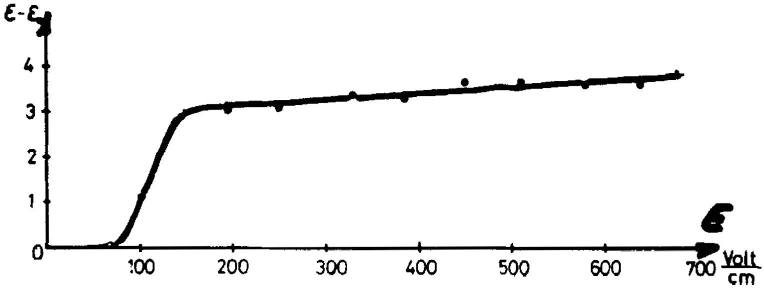


Figure 34. Interferences with twin-layers, formed by magnetic field.



Lichtabsorption durch Streuung in
Abhängigkeit von der Feldstärke
(nemat. Phase)

Figure 35. Extinction by light scattering with respect to field E.

also frequency dependency would be investigated a few years later. An important influence can also be exerted by the forces caused by the imperfect homogeneity of the applied fields. *Zwettkoff* would later engage himself again with the problem.

Meanwhile about 80 dissertations on liquid crystals were completed in Halle in Vorländer's institute with the result, that " one can prepare as many liquid crystals as one wants to have ". See Table 2 for " Dissertations from Vorländer's school ".

TABLE 2. Dissertations from Vorländer's school (Halle)

- A. Apel 1932
- S. Baentsch 1931
- C. Bästlein 1912
- F. Bättenhausen 1925
- K. Bergt 1925
- V. Bertleff 1908
- W. Böhme 1924[a]
- H. Boysen 1925
- H. Brandt 1922
- J. Brauer 1924[a]
- J. Bremer 1924
- W. Dahlem 1903
- E. Däumer 1912
- F. Dickenschied 1908
- H. Dietze 1922[a]
- K. Eulner 1930
- H. Filss 1926
- E. Fischer 1922
- H. Franke 1912
- E. Froelich 1910
- A. Gahren 1908
- K. Gieseler 1927
- E. Günther 1922
- U. Haberland 1924
- P. Hansen 1907 (1906!?)
- W. Harz 1917
- H. Hempel 1926
- W. Hennicke 1924
- F. Hentze 1925
- H. Hoffmann 1923
- P. Horbach 1922[a]
- J. E. Hulme 1907
- M. E. Huth 1909
- F. Janecke 1910
- John 1901
- K. Karg 1934
- W. Kasten 1909
- W. Knudsen 1924
- K. Kohlhardt 1921[a]
- V. Kosanke 1924
- G. Kreiss 1925
- A. H. Krummacher 1929
- R. Kühnemann 1922
- C. Kuhrmann 1927
- B. Lenk 1913
- W. Lützkendorf 1922
- Lungwitz 1905
- E. Mauerhoff 1922
- O. Meissner 1922
- O. Meye 1908
- F. Meyer 1902
- W. Naucke 1922
- L. Oberlaender 1914
- K. Ost 1938[a] (?)
- H. Ottensmeyer 1924
- W. Rasche 1921
- C. Reichardt 1909
- K. Reinknecht 1924[a]
- O. Ritter 1928
- E. Rolle 1921
- H. Schade 1933
- E. Schaefer 1911
- K. Schoenemann 1922
- E. Schroedter 1925
- R. Schroeter 1923
- Schröter 1904
- E. Schröter 1927
- R. Schulze 1937[a]
- H. Schuster 1933
- Siebert 1906
- B. Specht 1908
- M. Steineck 1924
- H. Stoltzenberg 1911
- C. Sultze 1908
- W. Täglich 1923
- C. Thinius 1928
- R. Urban 1921
- W. Vaupel 1911
- G. Vieth 1910
- L. W. Wasum 1928
- F. H. Weber 1914
- W. Weisswange 1925[a]
- R. Wilke 1909
- E. Wolferts 1909[a]
- W. Zeh 1926

[a] Dissertations lost during the war, up to now not found again.

Fourth Period (1933–1945)

In 1933 *Kast* had to break off his activities with Ornstein; he returned to Freiburg and took up work on field behaviour and heats of transition of liquid crystals. In 1937 he went to Halle, where he remained working on the same subject until the end of the war.

Here *W. Maier* began his extensive research(64) into dielectric constant measurement which would lead to his well known publications from Freiburg. After his return from Ankara (1935), *Conrad Weygand* (Leipzig) worked under Vorländer's direction with great success, his theme was " constitution and liquid crystalline properties ".(14) He discovered among other general rules the characteristic (alternating) thermic and caloric properties within a mesogenic homologous series. Many parallels to steric properties and melting point behavior of non-mesomorphic systems (e.g., fatty acids) should arise. (Only one typical example shall be given. It concerns the relations between structure and molecular volumes (" Raumchemie ") as worked out by *W. Biltz, W. Fischer* et al.65).

Weygand died as a storm-trooper in the last days of the war. *Zocher* found himself in Prague in 1937 (Diss. Tropper) and wrote, partly together with *Ungar* and in discussion with his Prague colleagues *Fürth* and *Sitte,* the compact and elegant interpretation of the continuum theory in the sense of *Oseen* and *Fréedericksz.*

Lawrence,(66) *McBain*(67) and *Vold*(68) continued their studies of lyotropic systems. Thus *Zocher* gave also the quantitative analysis of *Lehmann–Hauswald's* pictures in light of *Oseen's* theory (Fig. 36).

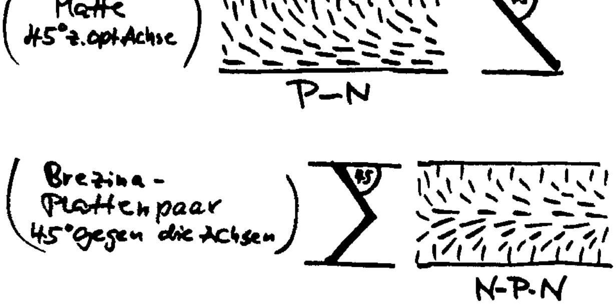


Figure 36. N, P-N, and N-P-N layer as described by Zocher.

One development that should be referred to is the continuation of *Fréedericksz's* tradition by *V. Zwetkoff* and coworkers (i.e., *Michailow, Marinin, Beneschevitsch*) in Leningrad(69,70,71) who worked further on the theory of the anisotropic phases and investigated their elastochemical and field properties. *Björnstahl*(72) investigated the light absorption and light-scattering in longitudinal and transversal magnetic fields. The most important, and at the time most surprising, finding was that despite the " perfect " orientation in both cases, the transmission took place but, in the longitudinal field the expected increase in light transmission was observed. Thus here the influence of the depolarization by the ordered phase was clear. Châtelain(73) would soon report more about this, leading up to a new era of research in France which is still growing. Also, the work of *Naggiar*(74) should not be forgotten(!).

Since 1929, *Fréedericksz, Zwetkoff* and *Zolina* have investigated the elastic properties of oriented layers and the influence of fields. They have obtained many important results. These results may be outlined as follows:

(1) An experiment with an anisotropic liquid layer of variable thickness showed that in the low frequency electric field the liquid shows an intensive movement which increases with increasing field intensity.

(2) When the orienting effect of a magnetic field is used, as a result of the turbulent movement, a disorientation of the molecules takes place. However, a degree of order still remains—a certain parallelity of molecular axes to the lines of force and to the current.

(3) Every field intensity E implies a "critical thickness" Z_0 which forms a sharp border between the moving and the still parts: $Z_0 \cdot E = \text{const.}$

(4) p-Ethoxyanisole, p-acetoxybenzalazine follow " Zocher's rule " (asymm $\perp$, symm $\|\mathbf{E}$), but not so dibenzalbenzidine ($\|\mathbf{E}$) and anisilidenbenzidine ($\perp\mathbf{E}$), the last differing only by the p,p'-ether-dipoles.

(5) The orientation effect in the electric field is proportional to E^2, i.e., dependent on dielectric anisotropy (Kast had also detected this).

(6) The magnetic field can counter-balance the **E**-field, thus $\Delta\kappa$ can be determined from known values of ϵ.

(7) At high frequency ($> 3 \cdot 10^5$ Hz) the same effect is obtained as by low frequencies only that no current occurs.

(8) The determination of $\Delta\kappa$ allows the determination of the elastic constant for the lateral deflection

$$A = \frac{K_0}{\pi^2}\kappa_1 - \kappa$$

(9) The elastic constants for deflection and torsion were determined in relationship to temperature.(75,76)

(10) Magnetic, dielectric and optical properties agree with the theory of cooperative phenomena (*Bragg* and *Williams*) and, as in the " Orientierungsschmelzen " (*Frenkel*), can be expressed in terms of the DEGREE OF ORDER, introducing the to-day well known definition

$$S = \tfrac{1}{2}(3\cos^2\vartheta - 1).$$

The degree of long range order and the energy of orientation are obtained as functions of temperature, and a first quantitative theory of the phase change nematic/isotropic is given.

In the years that followed, a uniform theory of dielectric behavior was developed (especially by *W. Maier*) followed by the molecular structure of the nematic phase including an expansion of *Zwetkoff's* theoretical work (*Maier*, *Saupe*, *Weber*). The results are so well known today, that they need not to be mentioned here.

Fifth Period

The period from 1945 until to-day brings many breakthroughs in different directions. The first international meeting after the war was the Faraday discussion (1958)(76); then a well-known article of *Brown* and *Shaw*(77) was published in *Chemical Reviews*. *Kast's* tables(78) in *Landolt–Börnstein* and papers by *Chistiakoff*(79) followed. *G. W. Gray's* great systematic work and his book *Molecular structure and the properties of liquid crystals*(80) followed soon after.

Profound theoretical work in the U.S.A., France and Russia followed an old tradition. Continuation of work at Halle and Freiburg (*Maier*, *Saupe*, *G. Meier*), publication of the Journal *Molecular Crystals and Liquid Crystals*, regular repetition of Liquid Crystal Conferences under the auspices of *Glenn Brown*, *Porter*, *Johnson* in the United States, of *Châtelain* and *de Genne* in France, of the Faraday

Society in London (1971), and at Freiburg (G. Meier) have stimulated research in the field.

The activity increases beyond the scope of an historical synopsis. In view of this fact, our review must close now. Most of you have a personal contact with events and with people representive of the last period. So my report could be biassed giving more accent to the earlier work, work which is originally written in the French or German languages. I am sorry that so many names must remain unmentioned; but they can be considered as well known. It is superfluous to talk about the development of technical and scientific work in the U.S.A. at this time. The papers presented at this meeting will speak for themselves.

Acknowledgements

I should like to thank Mr. Edwards of the translation department, Hoechst U.K. Ltd., Dr. R. Hatz, Farbwerke Hoechst, and Mr. Shepherd of Loughborough University for their valuable help in preparing the English version of this article.

REFERENCES

1. Lehmann, O., *Flüssige Kristalle, sowie Plastizität von Kristallen im Allgemeinen, molekulare Umlagerungen und Aggregatzustandsänderungen*, Engelmann, Leipzig, 1904; 264 pp.
2. Schenck, R., *Kristallinische Flüssigkeiten und flüssige Kristalle*, Engelmann, Leipzig, 1905; 159 pp.
3. Vorländer, D., *Kristallinisch flüssige Substanzen*, Enke, Stuttgart, 1908.
4. Bose, E., *Phys. Zeitschr.* **8**, 513 (1907); **9**, 708 (1908); **10**, 230 (1909).

4a. Bose, E. and Conrad, F., *Phys. Zeitschr.* **9**, 196 (1908).

5. Born, M., *Sitzungsber. Preuss. Ak. d. Wissensch., phys. math. Klasse v. 25.5.1916*, **XXX**, 614 (1916).

5a. Born, M. and Stumpf, F., *ibid.* **XL**, 1043 (1916).

6. Stumpf, F., Doppelbrechung und optische Aktivität flüssigkristalliner Substanzen, *Jahrb. Radioakt. Elektronik* **15**, 1 (1918).
7. Friedel, G., Les états mésomorphes de la matière, *Ann. Phys.* **18**, 273 (1922).
8. Vorländer, D., *Chemische Krystallographie der Flüssigkeiten*, Akadem. Verlagsanstalt, Leipzig, 1924; 90 pp.
9. Lehmann, O., " Methoden zur Darstellung und Untersuchung flüssiger Kristalle ", in E. Abderhalden's *Handbuch der biologischen Arbeitsmethoden*, Abt. III, Teil A, Heft 2, Berlin—Wien 1922; 123–352 pp.

10. Oseen, C. W., *Flüssige Kristalle, Tatsachen und Theorien*, Fortschr. d. Chemie, Eucken, A., Ed., Vol. 20, Heft 2 (Serie B), Bornträger, Berlin, 1929.
11. *Zeitschr. f. Kristallographie* (special issue), Bd. 79, Heft 1/4, Akad. Verlagsanstalt, Leipzig (1931).
12. Liquid crystals and anisotropic melts, *Trans. Faraday Soc.* (special issue) **29,** 881–1085 (1933).
13. *Zs. f. Elektrochemie* **45,** 126–226 (1939).
14. Weygand, C., Chemische Morphologie der Flüssigkeiten und Kristalle, *Hand- und Jahrb. der chem. Physik*, Eucken, A. and Wolf, K. L., Eds., Vol.2, Abschnitt IIIC.
15. Poe, E. A., *Narrative of Arthur Gordon Pym* (Ed. Doubleday, 1966), Chapt. 18, p. 706.
16. Virchow, R., *Virchows Archiv* **6,** 571 (1854).
17. Mettenheimer, C., *Corr.-Blatt d. Vereins f. gem. Arbeit z. Förd. d. wissensch. Heilkunde* No. 24, p. 331 (1857).
18. Valentin, G., *Die Untersuchung der Pflanzen–und der Tiergewebe im polarisierten Lichte*, Leipzig, 1861; 312 pp.

8a. Valentin, G., Beitrag zur Mikroskopie IV, *Arch. f. mikr. Anatomie* **XI,** 661 (1875).

19. Quincke, G., *Pogg. Annalen* **139,** 58 (1870); *Wied. Annalen* **53,** 613 (1894).
20. Lehmann, O., *Molekularphysic*, Vol. I u. II; cf. Vol. II, 221 (1889), Engelmann, Leipzig.
21. Lehmann, O., Über physikalische Isomerie, Diss. Strassburg, 1877.
22. Planer, Pr., *Ann.* **118,** 25 (1861).
23. Löbisch, W., *Ber.* **5,** 513 (1872).
24. Raymann, B., *Bull. Soc. Chim.* Paris **47,** 898 (1887).
25. Reinitzer, F., *Monatsh.* **9,** 421 (1888).
26. Gattermann, L. and Ritschke, A., *Ber. deutsch. chem. Ges.* **23,** 1738 (1890).
27. Lehmann, O., *Zs. phys. Chem.* **V** (5), 427 (1890).
28. Lehmann, O., *Ann. Phys.* 4. Folge, **8,** 908 (1902).
29. Lehmann, O., *Ann. Phys.* 4. Folge, **5,** 236 (1901).
30. Lehmann, O., *Verhandl. d. Deutschen Phys. Ges.*, Sitzung v. 16.3.1900, p. 1.
31. Voigt, W., *Lehrbuch der Kristallphysik*, Leipzig, 1910 (cit. p. 17, 18, 19); reprinted by Johnson Reprint Corp. New York, B. G. Teubner Verlagsges. Stuttgart (1966).
32. Ambronn, H., cf. H. Gause, H. Ambronn u. seine Bedeutung für die Polarisationsmikroskopie, *Jenaer Jahrbuch 1965*, pp. 7–14.
33. Lehmann, O., *Flüssige Kristalle und die Theorien des Lebens*, 2. Aufl., p. 60, J. A. Barth, Leipzig, 1908.
34. Wallerant, F., *Rivista di Scienza* (1907), p. 224.
35. Meyer, F. and Dahlem, K., *Ann.* **326,** 331 (1903).
36. Christiansen, C., *Wiedermanns Ann.* **23,** 298 (1884).
37. Jäger, F. M., *Rec. Trav. chim. Pays-Bas.* **25,** 334 (1906).
38. Lehmann, O., *Ann. d. Physik* (4) **21,** 381 (1906) (note on p. 389).
39. Prins, A., *Zs. phys. Chem.* **67,** 689 (1909).
40. Romburgh, P. V., Über *p*-Methoxyzimtsäure, *Proc. Kon. Nederl. Akad. Wetenschapen* **9,** 9 (1901).
41. de Kock, A. C., *Zs. phys. Chem.* **48,** 129 (1904).

42. Dave, J. S. and Dewar, M. J. S., *J. Chem. Soc.* (London) **1954,** 4617; **1955,** 4305.
43. Sackmann, H. and Demus, D., Fortschritt der chemischen Forschung, *Angew. Chemie* **12,** 349 (1969).
44. Wiener, O., Zur Theorie der Stäbchendoppelbrechung, Leipzig, Ges. d. Wiss. S. Ber. **61,** 113 (1909).
45. Lehmann, O., Les cristaux liquides, *J. de Phys.* **7,** 713, Conf. faite le 16 Avril 1909—Extr. de *Bull. des séances de la Soc. Franc. de Physique,* Fasc. 2, 1909.
46. Lehmann, O., Cristaux liquides et modèles moléculaires, *Archives des sciences physiques et naturelles,* tôme XXVIII, Genève 1909, p. 205–226.
47. Mauguin, Ch., *Phys. Zs.* **12,** 1011 (1911).
48. Dorn, E., *Ann. Phys.* **29,** 533 (1909); *Phys. Zs.* **11,** 777 (1910).
49. Wallerant, F., *Compt. rend.* **143,** 605 (1906); **148,** 1291 (1909).
50. Mauguin, Ch., *Phys. Zs.* **12,** 1011 (1911); *Compt. rend.* **151,** 886 (1910); **151,** 1141 (1910); **154,** 1359 (1912); **156,** 1246 (1913); *Bull. soc. Min.* **34,** 71–117 (1911).
51. Lehmann, O., *Verh. d. Naturwiss. Vereins in Karlsruhe* 19. Bd. 107 (1906) (Sonderdruck 27 S.).
52. Vorländer, D. and Hauswaldt, H., *Abh. d. Kaiserl. Leop. Carol. Dtsch. Akad. der Naturf.* **90,** 107 (1909).
53. Lehmann, O., Die Struktur in homogener tropfbar-flüssigerkristallinischer Schichten (Spurlinien, Fäden und Höfe), *Ann. d. Phys.* (4. Folge) **52,** 445 (1917).
54. Lehmann, O., *Ann. d. Phys.* (4. Folge) **2,** 649 (1900).
55. Nehring, J. and Saupe, A., *J. Chem. Soc., Faraday Trans.* (2), **68,** (pt. 1), 1 (1972).
56. Svedberg, Th., *Ann. d. Phys.* **44,** 1121 (1914); **49,** 437 (1916). Cf. also *Jahrb. d. Radioakt. u. Elektronik* **12,** 129 (1915).
57. Ornstein, L. S., *Ann. d. Phys.* (4. Folge) **74,** 445 (1924).
58. Kast, W., Diss. Halle 1922; Anisotropie der flüssigen Kristalle bezüglich ihrer Dielektrizitätskonstanten und ihrer elektrischen Leitfähigkeit, *Ann. d. Phys.* (4. Folge) **73,** 145 (1923).
59. Ornstein, L. S., *Zs. f. Kristallographie* **79,** 90 (1931).
60. Riwlin, R., Diss. Utrecht 1923; Das Wesen der Lichtzerstreuung in flüssigen Kristallen.
61. van Wijk, A., Diss. Utrecht 1929; Invloed van Magneetveld, Zwermen en Wa op de kristaloptische Eigenschappen van vloeibaar kristallijn *p*-Azoxyanisol. *Ann. d. Phys.* (5. Folge) **3,** 879 (1929).
62. Fréedericksz, V. and Zolina, V., *Trans. Faraday Soc.* **29,** 919 (1933).
63. Björnstahl, Y., Untersuchungen über anisotrope Flüssigkeiten, *Ann. d. Phys.* **56,** 161 (1918).
64. Maier, W., Habilitationsschrift Halle 1944; Zur Frage der molekularen Struktur kristalliner Flüssigkeiten: Änderung der Dielektrizitätskonstante der pl-Phase des *p,p′*-Azoxyanisols durch magnetische Felder, *Phys. Zs.* **45,** 285 (1944); *Zs. Naturforsch.* **2a,** 458 (1947).
65. Biltz, W., Fischer, W. and Wünnenberg, E., *Zs. phys. Chem.* Abt. A, **151,** 13 (1930).
66. Lawrence, A. S. C., *Trans. Faraday Soc.* **29,** 1008 (1933); **34,** 660 (1938).

67. McBain, J. W. and Stewart, A., *J. chem. Soc.* (London) **1933**, 924.
67a McBain, J. W., Vold, R. D. and Frick, M. J., *J. Phys. Chem.* **44**, 1013 (1940).
68. Vold, R. D. and Vold, M. J., *J. Amer. Chem. Soc.* **61**, 808 (1939); **61**, 37 (1939).
69. Fréedericksz, V. and Zwetkoff, V., *Acta physicochim. URSS* **III**, 895 (1935); **III**, 879 (1935); *Phys. Zs. d. Sowj.-Union* **6**, 490 (1934).
70. Fréedericksz, V., *Acta physicochim. URSS* **III**, 741 (1935). Fréedericksz, V., Michailow, A. and Beneschewitsch, D., *Comp. rend. de l'Academie des Sciences de l'USSR*, No. **3–4**, 208 (1935).
71. Zwetkoff, W. and Marinin, W., *Acta physicochem. URSS* **XIII**, 219 (1940). Zwetkoff, W., *Acta physicochem. URSS* **XVI**, 132 (1942).
72. Björnståhl, Y., *Zs. phys. Chem.* (A) **175**, 17 (1935).
73. Chatelain, P., *Compt. rend.* **200**, 412 (1935); **203**, 1169 (1936); **213**, 875 (1941); **214**, 32 (1942); **218**, 652 (1944).
74. Naggiar, V., *Compt. rend.* **200**, 903 (1935).
75. Zwetkoff, V., *Trans. Amer. El. Soc.*, **55**, 85 (1929).
76. Configurations and interactions of macromolecules and liquid crystals. (A general discussion), *Disc. Faraday Soc.*, No 25 (1958).
77. Brown, G. H. and Shaw, W. G., *Chemical Reviews* **57**, (6), pp. 1049–1157. (1957).
78. Kast, W., *Landolt-Börnstein*, Vol. II, part 2a, K. Schäfer u. E. Lax, eds., Springer, Berlin, 1960, pp. 266 ff.
79. Usol'tseva, V. A. and Chistiakoff, I. G., *Uspekhi Khim* **32**, 1124 (1963).
80. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London and New York, 1962.