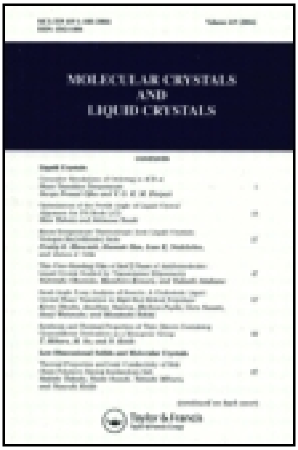

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Survey of the Early History of Liquid Crystals

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Survey of the Early History of Liquid Crystals†

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CONTENTS

1. INTRODUCTION

How did liquid crystals come to the knowledge of the scientific world? It is generally supposed and accepted that a letter from Friedrich Reinitzer (March 14, 1888) (Figure 1) to Otto Lehmann, (Figure 2), is the most significant landmark in the development of liquid crystal research.

The question is, why the addressee of this letter was just the young physicist Lehmann who worked at this time at the technical high school at Aachen as an assistant of Wüllner. In 1885 Lehmann was nominated associate professor, being the author of about 35 papers.[1] A long monograph, "Molecular Physics," was published in 1888/89 in two volumes.[23,24]

Lehmann's main interest was the phenomenon of phase transitions and the question what kind of "molecules" might be involved. Lehmann had already become a well known specialist in this field, who had introduced the heating-stage microscope, the "Kristallisations-

†Dedicated to Professor W. Fresenius, Wiesbaden.

FIGURE 1 Friedr. Reinitzer (1857–1927).

FIGURE 2 Otto Lehmann (1855–1922).

Mikroskop," into experimental physics. He had already been in contact with the famous crystallographer v. Zepharovich at the University of Prague.

Reinitzer, a botanist at this time, studied the function of cholesterol in plants, and synthesized esters of this compound, starting always with native cholesterol, being well purified but by no means structurally known. So he discovered the unusual phenomenon of the "two melting points." Between these temperatures the melt showed birefringence and iridescent colours. v. Zepharovich, being perplexed too, adviced Reinitzer to address himself to Lehmann. So, a correspondence began which was to lead to the discovery of a completely new phenomenon, to "liquid crystals."[2] In order to understand the whole story which followed, the dramatic development of further research, it might be helpful to have a first glance at the previous history, and then to describe the situation around 1888. After that, the development during the next 20 years shall be reported. At that time, the existence of liquid crystals was proved, and the methods of investigation well established, at least in principle.

2. THE PREHISTORY, COVERING THE TIME UNTIL 1888

As Lehmann received the cholesterol esters from Reinitzer[3]: nobody had the slightest idea of its molecular constitution. Even the principal structure of a crystal was not established, and it was the object of visionary, hypothetical ideas. The best theory existing was that of Hauy, others followed (Weisz, Neumann, Bernhardi). To imagine this situation, one should consider that the existence of a crystal lattice was proved as late as 1912 by the x-ray experiments of v. Laue and Knipping. The only base for speculations concerning the structure of the three states of aggregation was the fact that molecules, whatever this might be, and atoms, were accepted as elementary units—but even this was denied by some authorities.[4] Ions were practically unknown, so the different types of lattices could not be differentiated.

The development of physical and chemical sciences during the 19th century need not be repeated here in detail, but it should be kept in mind that the greatest discoveries were still as fresh as the revolution of physics is for our generation. In Chemistry, Berzelius, Wöhler, Liebig, Bunsen and Kirchhoff had opened the view into a correct interpretation of a rather chaotic matter of experience. Most of the chemical elements had just been or were about to be discovered. The rules of thermodynamics became established (Carnot, Joule, Clausius, and later Helmholtz), the existence of free molecules just anticipated by Avogadro. Magnetism and electrodynamics became elucidated and theoretically understood: Faraday, Maxwell, H. Hertz, the predecessor of Otto Lehmann in the chair of experimental physics at Karlsruhe, had discovered the electromagnetic waves. Less well and generally known than these great authorities are several physicists who have held the chairs of four universities in Germany (Göttingen, Heidelberg, Halle, later Marburg). We shall come back to them, to Riecke, Quincke, Dorn, and Voigt. They are well worth being recognized as the predecessors and pathfinders in the field of liquid crystal research. Others served by opposition . . .

As it often happened in science, important events started in the "border regions." So, a very important investigation on organic material took place as early as in the 1850's, when Rudolf Virchow (Figure 3) described a soft, floating substance from nerve core, that he named Myelin.[5] Later, the ophthalmologist Mettenheimer (see Figure 4), in 1857 discovered that Myelin showed birefringence.[6] The "liquid crystals" were discovered.

It should be mentioned that the polarizing microscope had been used quite early by physicians and biologists, long before it became the important instrument in mineralogy and chemistry. From 1857 on, systems which we call lyotropic ones became a permanent object of studies until today. For a more extended historical explanation see Reference 8.

Preparing this paper, it seemed desirable to find some details about

Rudolf Virchow (1821–1902).
FIGURE 3

C. Chr. Fr. von Mettenheimer (1824–1898).
FIGURE 4

Mettenheimer.† Following the information given in a monograph "700 Jahre Heilkunde in Frankfurt am Main" by W. Kallmorgen,[7] Mettenheimer was born on December 19, 1824 at Frankfurt. He studied at Göttingen and Berlin, and he became installed as a medical doctor at Frankfurt in 1847. He died on September 18, 1898 at Schwerin, highly honoured. Mettenheimer was the physician of Arthur Schopenhauer. He gave numerous lectures in the Society of Microscopy, and in the "Naturforschenden Gesellschaft Senckenberg" at Frankfurt. In 1861 he was called to Mecklenburg-Schwerin as physician extraordinarie to the Grand Duke. He was knighted, thanks to his work on anatomy, physiology, pathology, and clinical medicine, and for his numerous merits in public welfare. Mettenheimer was extremely busy literarily.

The fact, that as many as 40 years had passed before Lehmann claimed the myelin forms for his system of "flowing" crystals, is the reason for the curious situation, that the year 1888, not 1855/57, is considered the birth-year of liquid crystals! So, if one prefers to accept 1888 as the main discovery, one should be correct and designate this year as the beginning of thermotropic liquid crystal research. For more details see our report from 1986.[8] Even this attribute is doubtful in a certain way, because substances with "two melting points" had been already observed around the year 1850. It is well known that

†Thanks to M. Simon, Hoechst A. G., valuable information became available.

Reinitzer himself has discussed by correspondence with Lehmann (letter from March 6, 1908) some results of W. Heintz, a leading authority in fat chemistry. Heintz had already observed the phenomenon of a "second melting point."[14] Heintz wrote[9]: "Stearin becomes cloudy at 51–52°C, at higher temperatures it opalizes, and at 58°C it is completely opaque. Above 62.5°C it is molten and quite clear." It was Duffy, who a short time thereafter showed that the stearin is first molten at 52°C, and that it really has a second "melting point" at 62.5°C. This has been confirmed by Heintz, see also H. Kreis and A. Hafner.[10] Lehmann himself cited these results, which had come to his knowledge by the letter from Reinitzer, cited above. In this context it should be mentioned that the early remarks about the "cholesteric" colour phenomena being reported by Planer,[11] Löbisch,[12] and Raymann,[13] already being cited by Reinitzer. This shows clearly, how carefully Reinitzer had prepared his studies of the cholesteric substances. Lehmann, regrettably, used this information as arguments against Reinitzer's claims for an at least partial priority.[14,16] Lehmann was not the man to accept the general rule that scientific results generally have multiple and different roots.

In the early history of the discoveries of Lehmann and Reinitzer one finds indications for a strong interaction between well-known scientists and Lehmann, who had tried to absorb the whole field of physical knowledge in his head and in his voluminous publications. Later, he entitled one of his more or less popular books "The New World of Liquid Crystals" (Die Neue Welt der Flüssigen Kristalle).[17] Something of Lehmann's "New World" had been well prepared during the decennials from 1830 to 1888. So, for example, the name of G. Quincke must be laudably mentioned, even if Lehmann had listed him later as part of the "trefoil" Tammann-Nernst-Quincke, his competitors, as he stated erroneously and full of preoccupation. Quincke, born 1834, was an intimate friend of the young E. Haeckel and his family. Quincke advised Haeckel, who was born in the same year, with respect to his academic career.

From 1875–1907 Georg Quincke was Professor of Physics at Heidelberg, following Kirchhoff on his chair, when Kirchhoff was called to Berlin. Some of the preferred objects of Quincke were all kinds of soft materials, intermolecular forces, movements, periodically extending substances, protoplasma motions, foams, and last but not least: Myeline forms!

One of his papers, which is most typical for his style of work appeared in 1894[18]; some others followed.[19,20] Two comprehensive obituary notices[21,22] convey a picture of the overwhelming work of this man. Figure 5 shows his portrait. He lived to be 90 years old!

FIGURE 5 G. Quincke (November 19, 1834–January 13, 1924). Professor of Physics at Heidelberg, 1875–1907.

The relations between Quincke and Lehmann seemed to be quite clear: Lehmann mentioned Quincke's work on the Myeline forms as early as 1888 in his Molekularphysik, vol. I.[23,24] Lehmann again picked up the Myelin object in his "New World," and in 1895 in a special article.[25] It is quite typical for this object, that it was revitalised again and again, mostly in connection with "Contact Movements" and growing phenomena resembling living systems. Later, the ill-reputed monograph of Ernst Haeckel, the "Kristallseelen" shows, as an example of "living, crystalline material," the same nice wood-carved printing block Lehmann had designed already in 1888. See Figure 6.

As already mentioned, the polarizing microscope was used nearly exclusively by physicians and biologists. So we should not be surprised, that we find Virchow and Mettenheimer using this instrument. The educated citizen, too, when interested in natural sciences, used his microscope as Lehmann's father did, introducing his son to natural sciences. There exists a nice monograph on the early practical mi-

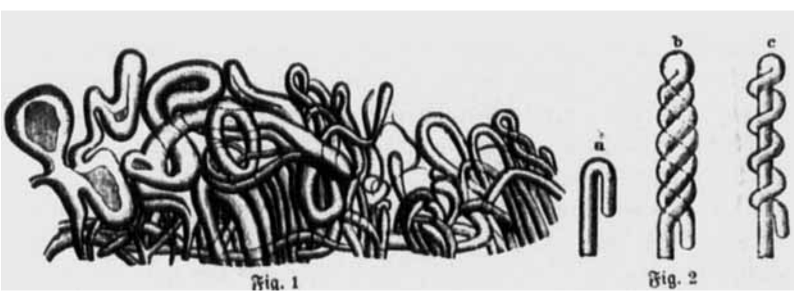


FIGURE 6 Myelinformen, original printing block, from 1888 (Design by Lehmann).

croscopy, showing the general tendency: "Die Untersuchung der Pflanzen und Tiergewebe im polarisierten Licht,"[27] by G. Valentin, Leipzig 1861. The main objects were crystalline inclusions of living material, as, for example, blood, eye lenses, mother-of-pearl, the inclusions of certain plants as the raphides, *i.e.* oxalate needles. Even in spermatozoids and frog eggs, birefringence was found. Very much later, F. Rinne, the originator of the term "Parakristall," had taken up the studies of such "living" crystalline substances from new.[28]

Brewster, Cordier, Nicol and many others promoted the use of the polarisation microscope, establishing new techniques and introducing it into crystallography, mineralogy and even into chemistry. Valentin already summarized the complete technique, and Mettenheimer is also explicitly mentioned by him.[29] At the end of the 19th century the technique had arrived at its absolute perfection, as can be seen from the work of W. Voigt,[30] F. Pockels and E. Weinschenk,[31,32] to cite only the best known standard textbooks.

The preferred objective of Lehmann was the study of crystal growing and phase transitions. He developed during a period of 20 years a heating-stage microscope that he called "Kristallisationsmikroskop." We shall come back to this later.[33,34]

Finally, we mention some members of the "young" generation who were to play the central role in the further development of liquid crystal research. R. Schenck, who would later contribute the most convincing experiments and arguments for the somewhat nebulous "theories" of Lehmann. He was born in 1870 and entered the university of Marburg, after having studied at Halle, where he had already worked with E. Dorn, J. Volhard, and D. Vorländer. Schenck reported about his life and scientific career in a paper entitled "Aus der Entwicklungszeit der Chemie des festen Zustands," when he received the Bunsen Commemorative medal.[35] Schenck and Vorländer (Figures 7 and 8) were to become the pioneers of the further development of liquid crystal research; Volhard and Dorn represented the elder generation. Volhard, a pupil of Liebig, supervised the work of Schenck as well as of Vorländer, who was promoted in 1890, still being far away from liquid crystal synthesis. Schenck's interest was directed against the molecular states during phase transitions.

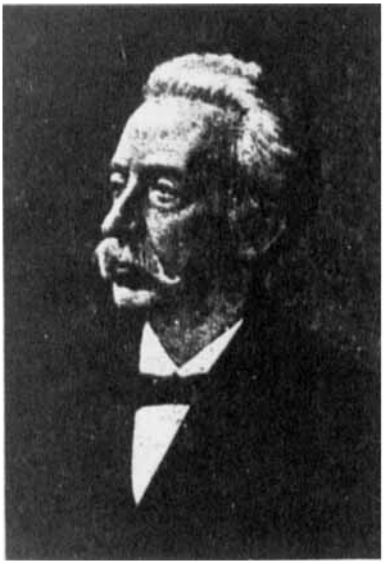
Daniel Vorländer had begun his studies of chemistry at Kiel University, continued at München and served his military year 1887/88 at Berlin. Vorländer had later become (1902) the successor of Volhard; one of his famous pupils is H. Staudinger, the Nobel-prize winner.[37] Remember, that the theory of "chemical polymerism," developed by O. Lehmann, had its origin in the 1880s. Vorländer, being

Rudolf Schenck (1870–1965).
FIGURE 7

Daniel Vorländer (1867–1941).
FIGURE 8

a typical organic synthesist, was soon to be confronted with liquid crystals, which in the 1890s became his preferred object of studies.[36] He died in 1941 in his 72nd year as the director of a tool plant of military importance.

E. Dorn (Figure 9) should be presented with emphasis; he came to Halle in 1886 and worked in a narrow and fair cooperation with his colleagues of the chemistry department. Very important results were to come from this rather unusual teamwork. Finally, the University of Göttingen must be introduced. Here, in a small town near Hannover, historical movements—not only in Physics and in Chemistry—originated. It is the place, where Georg Christoph Lichtenberg (1742–1799), the well known Professor for experimental physics and author of beautiful papers lived. One of his late successors in the chair of Physics is E. Riecke, who came in 1881 to Göttingen, and in 1883 associated with W. Voigt. From here, the principal part of modern solid state physics and of so-called "Physical Chemistry" developed. The merits of Riecke (Figure 10) and Voigt (Figure 11) can hardly be overestimated. Scientists from each part of the world were called to Göttingen during the years to follow, and skepticism as well as consent to liquid crystal research arose from this place.



Ernst Dorn (1848–1914).
FIGURE 9

Eduard Riecke (1845–1915).
FIGURE 10

Woldemar Voigt (1850–1919).

FIGURE 11

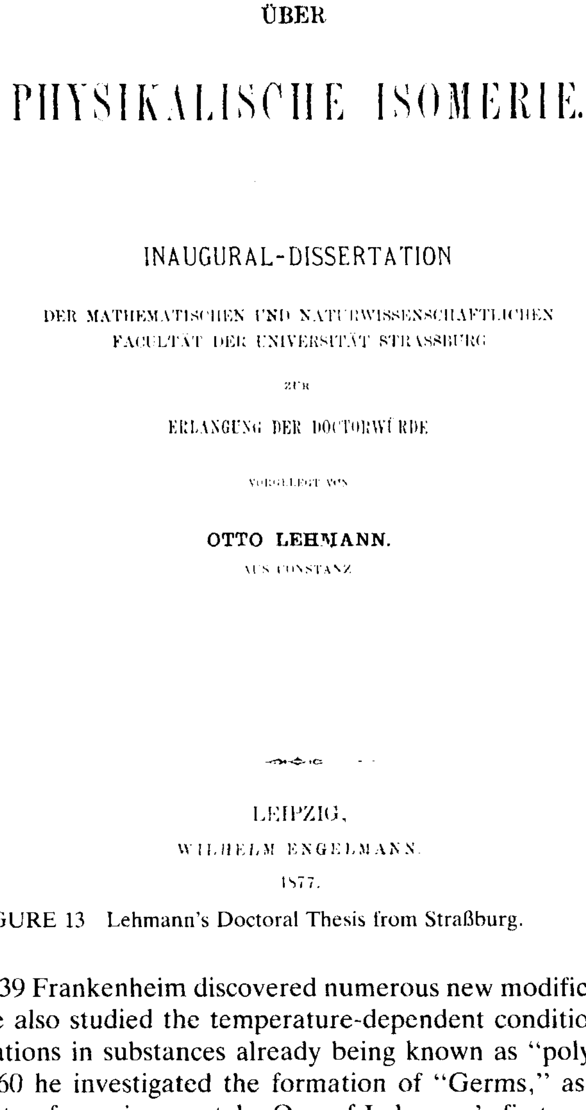
3 OTTO LEHMANN, AND HIS PART IN THE PREHISTORY OF THE DISCOVERY OF LIQUID CRYSTALS

The Universities of Halle, Göttingen, and Heidelberg have been presented as the preparatory sources of a knowledge that was necessary to develop the science of liquid crystals. Before we enter into the dramatic events up from 1888, a name, already mentioned several times, must now be placed into focus: Otto Lehmann. Born in 1855 as a son of a teacher of mathematics and natural sciences at Constanz, Baden, he early became motivated for microscopic studies. As a pupil he already studied reports on the publications of Ernst Haeckel (Figure 12), who had just finished his great work "Generelle Morphologie" (1866). Consequently, Lehmann studied Physics at the Straßburg University from 1872 to 1876. For a general review see Refs. 38 and 39. One of his earliest literary impressions was the famous old book by Ledermüller, "Microscopische Augen- und Gemüts-Ergötzungen" (Nürnberg, 1763). Lehmann's teachers were: the petrographer Rosenbusch, in chemistry Adolf Baeyer, the famous organic Chemist who later changed for a chair at München, and—very important—A. Kundt and P. Groth. Kundt, professor of experimental physics, well known as the inventor of the "dust pictures" (Staubfiguren) to measure the velocity of light in solids and gases. Kundt also discovered a phenomenon that was to be found later in quite a different system, in Cholesterics: the rotation of the polarisation vector of light in ferromagnetical layers (Fe, Ni), reaching magnitudes of some 100000 degr./cm. In Kundt's laboratory, Lehmann must have also seen experiments with birefringent material, both flowing and under stress. In 1876 Lehmann got his doctor's degree, "summa cum laude," the doctor father being Groth. The theme of his thesis was "Über physikalische Isomerie" (On Physical Isometry) Figure 13 shows the title of the paper. The basic and practically only tool of Lehmann's research work was the microscope with heatable stage, an instrument he would never lose and that he developed continuously to models as being sold by Voigt U. Hochgesang, Göttingen and another type by Zeiß- Jena still in the 20th century. See Figures 14 and 15.

He called this instrument "Kristallisationsmikroskop," and he was extremely proud of this invention, see Figure 14. The first of about 20 different models he constructed is seen here. One can recognize the heating device (B) and the cooling pipe (D). This instrument was not yet equipped with polarisation devices, they were added in later models, some of these being shown in Figure 15.[33] The curve added in Figure 14 shows some transition points as turning points in the heating curve (temperature vs. time).

FIGURE 12 Ernst Haeckel and his latest work (1834–1919).

An important source of ideas converging into the discoveries of 1888 is the work of Moritz Ludwig Frankenheim, Professor of Physics at the University of Breslau. Frankenheim was a contemporary of Joh. Wolfgang v. Goethe, born 1801 at Braunschweig. For more detailed information see Ref. 41. One of his numerous publications is entitled "On the Cohesion of Liquid Bodies," another "On the Arrangement of Molecules in Crystals." No wonder that the young Lehmann got strongly motivated by these publications; some of his ideas are directly related to Frankenheim. During the years 1836–



ÜBER

PHYSIKALISCHE ISOMERIE.

INAUGURAL-DISSERTATION

DER MATHEMATISCHEN UND NATURWISSENSCHAFTLICHEN
FACULTÄT DER UNIVERSITÄT STRASSBURG

ZUR

ERLANGUNG DER DOCTORWÜRDE

VORGELEGT VON

OTTO LEHMANN.

AUS CONSTANZ

LEIPZIG,
WILHELM ENGELMANN.
1877.

FIGURE 13 Lehmann's Doctoral Thesis from Straßburg.

1839 Frankenheim discovered numerous new modifications of solids. He also studied the temperature-dependent conditions for transformations in substances already being known as "polymorphous." In 1860 he investigated the formation of "Germs," as the embryonal state of growing crystals. One of Lehmann's first successes, the discovery of enantiotropic (reversible) and monotropic (irreversible) phase transitions, relates directly to Frankenheim's observations, which were more precisely specified by Lehmann. Frankenheim called the transition points "Grenztemperaturen," Limiting Temperatures, as already Mitscherlich had done. Later, he found some transitions to be reversible, e.g. with saltpetre. So, Frankenheim could already speak of "Umwandlungstemperatur." Here is an original text from

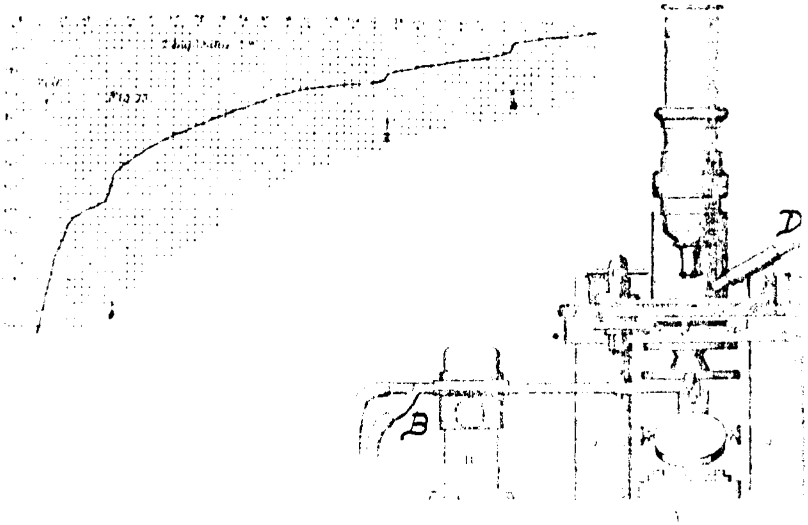
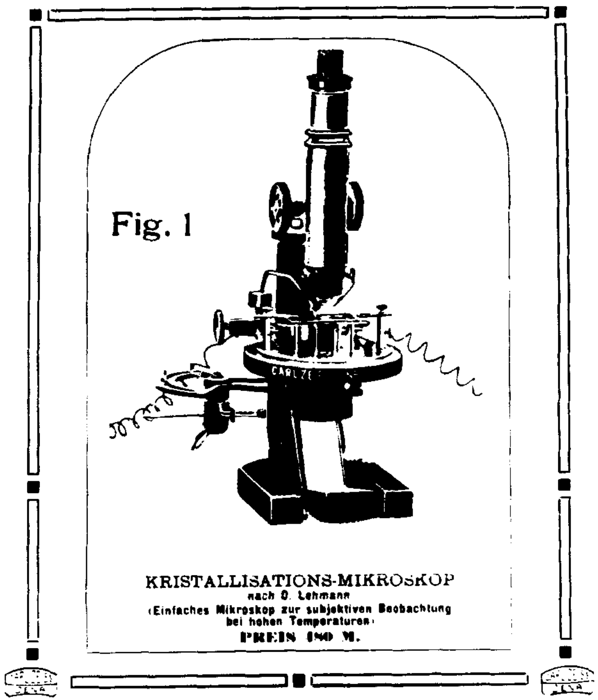


FIGURE 14 The first type of a Crystallisation Microscope.

Lehmann, in order to demonstrate how closely he was indebted to Frankenheim, and to show how difficult it was for him to demonstrate the merits of having forged ahead.

Citation (56, p. 188): "Der Wahrheit näher kommen die Untersuchungen Frankenheim's bei Salpeter; er gebraucht auch in den späteren Arbeiten bereits den Ausdruck Umwandlungstemperatur, verfällt aber in den Fehler, das, was er bei Salpeter beobachtet hatte, sofort nicht nur für alle polymorphen Stoffe, sondern, da er diese zu den chemisch isomeren rechnete, auch für die ungeheure Zahl der letzteren als gültig anzunehmen, und auch jeder polymorphen Modifikation drei Aggregatzustände zuzuschreiben. In dieser Hinsicht sind die Ergebnisse Frankenheims als unrichtig zu bezeichnen, und dies mag auch der Grund gewesen sein, daß selbst das, was an ihnen richtig war, keine Beachtung fand, daß kein Lehrbuch sie berücksichtigte. Frankenheim konnte noch nicht zu einer klaren Einsicht gelangen, weil die Zahl seiner Versuche viel zu klein war, und vor allem, weil ihm das Kristallisationsmikroskop fehlte, was jeder, der zuerst mit einem gewöhnlichen Mikroskop zu arbeiten versucht hat, ohne weiteres einsehen wird." Etc. Here is the schoolmaster speaking! . . . This utterance is typical for Lehmann's style and regrettable, because such sentences overshadow the high merits as much as the numerous self-citations do. Indeed, Lehmann became a teacher at the gymnasium of Freiburg (1876), and one year later he changed to



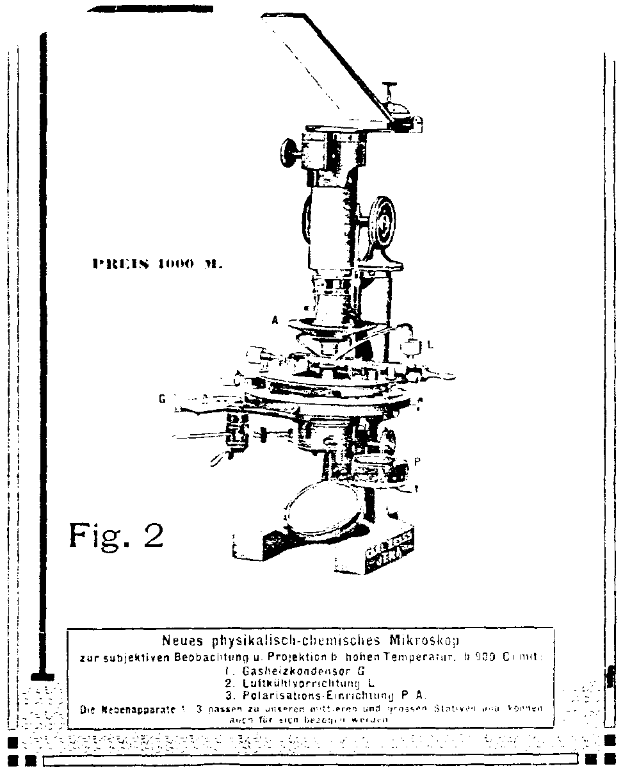


FIGURE 15 Later types of heating-Microscopes, as manufactured by Zeiss-Jena. The polarizing unit was either a reflecting glass plate, or a Nicol-prism.

Mühlhausen/Elsaß. Remember that the departments Elsaß and Lothringen were reintegrated after the German/French war of 70/71 into the German Empire. This was also the reason for re-founding the German University of Straßburg, and calling the most distinguished scientists to this place, as for example A. Baeyer.

Lehmann remained for 7 years at Mühlhausen and he served there also as a food controller, as he remarks elsewhere. In 1883 he received a call to the technical school in Aachen (Polytechnikum). He became a lecturer and assistant of Wüllner; In 1885 he was appointed as an assistant professor. Among several other projects, he again studied phase transitions and problems of crystal growing, themes being actual at that time, as it has been described before. He extensively used his crystallisation microscope, and he was very busy in composing voluminous books of review character; so the "Molekularphysik" appeared in 1888 with a second part in 1889. Altogether 1550 pages and 755 figures, with 2000 citations, including at this time already 450 from his own papers.[23,24] A really tremendous work, where nearly all the facts known at that time were reported. Wilhelm Ostwald wrote a recension about this book, Reference 56, p. 249. It is really appropriate and characteristic:

> "The author has collected material widely distributed and dispersed. It is reported in a fullness which is nearly confusing. It is a peculiar, rich and comprehensive work from which we can get instruction at infinity, but which gives no perception about the field."

There is no better description of Lehmann's style of working.

The central problem in crystallography as transitions were concerned, has always been polymorphism. It was accepted, as still today, as the most general expression of the fact that a certain element, compound or even a mixture can exist and be transformed in different modifications that are characterized by a different crystal geometry and crystal symmetry, and whatever other properties. The term "Allotropy" was originally used by Berzelius to describe different modifications of a chemical element, e.g. sulfur, contrary to the term "isomerism," being reserved for chemical compounds which were regarded as clusters of electrically charged atoms. As soon as the theory of different binding types between charged and uncharged atoms, respectively, had been abandoned, the general term isomery was used exclusively, but also in the same sense as the term allotropy to describe the general phenomenon. Frankenheim used these words to describe the temperature dependent transition processes. Lehmann reflected about further possibilities of isomerism, and he came to the result that two forms of isomerism should exist. He distinguished between chemical and physical isomerism. Note, that isomerism is the generic term, but it is not so easy to define what real differences are constituent to separate "chemical" from "physical" isomerism. Let us first reproduce the pictures as given by Lehmann. Chemical isomerism was thought to exist in two principal forms, called "polymerism," and "metamerism," respectively (Polymerie and Metamerie in the German text). These two different cases of chemical isomerism are illustrated as shown in Figure 16.

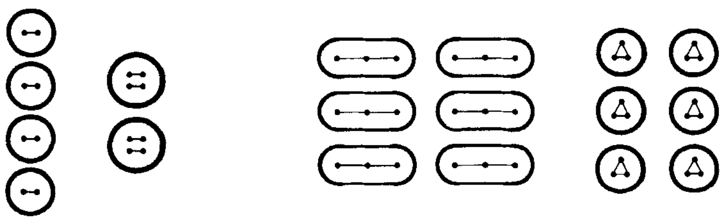
It is interesting that the term "polymerism," originally coined for a different association of atoms (see Figure 16a) has been preserved in an only slightly varied way up to present. Lehmann has not yet included the macromolecules as higher polymer units. The metamerism is easily understood: the term corresponds to our modern definition: same number of elementary units, e.g. atoms, within a molecule, but arranged differently (*n*-propane/cyclopropane). Remember that Lehmann has coined the terms Enantiotropism, and Monotropism in order to describe a reversible or an irreversible transition. Lehmann's correlation of these types of transition with case *a* or case *b*, respectively, is rather obscure. The terms themselves have been accepted by van t'Hoff, who corresponded with Lehmann.

If the primary units—e.g. atomic aggregations—remain invariable during transition, different associations can occur, as shown in Figure 17. Now the transitions were called "Physical Isomerism."

In this case chemical molecules or whatever units with saturated valencies are regarded as primary units, being associated with one another to an unit that we would name a "physical molecule." The primary units are always the same. If the association number has

Chemical Isomerism

a) Polymerism b) Metamerism



kind of transition,

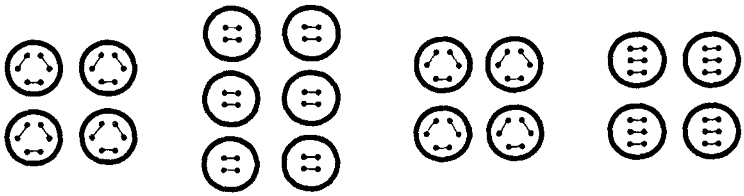
before after before after

transition transition

FIGURE 16

Physical Isomerism

a) Polymerism b) Metamerism



kind of transition

before after

transition

degree of association being changed.

before after

transition

degree of association being unchanged, structure of association changed.

FIGURE 17

changed, Lehmann called the transition type "Physikalische Polymerie," if only symmetry and/or structure have changed, "Physikalische Metamerie." His definitions became criticized by K. Fuchs.[100] All these nice pictures do not lack certain consequences, beginning with bound atoms to form real molecules, being charged or not, following stoichiometric laws, and being able to form associates by a weaker binding process, as we may name it "van der Waals forces." The most unacceptable statement of Lehmann is his hypothesis that there exists a correlation: Polymerism/Enantiotropy and Metamerism/Monotropy.[42] The largest obstacle in molecular crystal theory was the difficulty to imagine a lattice as the basic construction principle. Sure, there existed plausible models, so that of Hauy and Bravais which seemed to be acceptable to explain the structure of crystals. The principal difficulty must have been the imagination, how to identify a Hauy elemental block with a group of atoms or molecules which have their special degrees of freedom and different shapes. It must have been difficult to believe that one and the same molecule can be arranged in different lattices, but this has been a special problem only for Lehmann, others already had better models at hand. It can be stated, somewhat in contrast to Lehmann's molecular models, that as early as in 1888 the majority of scientists had already accepted the hypothesis, that different modifications are only different with respect to their spatial order, their lattices, but not by different elementary units, by different "molecules" as defined by Lehmann's models.

An important consequence of the lattice hypothesis was of course the interpretation of Mitscherlich's "Isomorphieregeln" (rules of isomorphism).[43] Identity—or at least strong resemblance of the crystal parameters (forms, angles) are explained by congruent elementary groups of the lattices. The classical example is the isomorphism of the phosphates and arsenates as being studied by Mitscherlich during the years 1819–1829. Numerous examples have become known from the mineral kingdom, e.g. the apatite group (apatite, pyromorphite, mimetesite, vanadinite).

To understand the historical situation, it should be pointed out that as early as 1879 Sohnke had laid the base of understanding crystal structure[44] Entwickelung einer Theorie der Krystallstruktur." Some years later, in the memorable year 1888, he had completed his work.[45] The position of Lehmann as opponent of lattice theories had become more and more difficult, his comments rather schizophrenic, the more quickly the crystallographic sciences developed. Lehmann defended enthusiastically his model of physically isomeric molecules, being defined as different units in coexisting phases, even in different states of aggregation of one and the same substance. On the other hand, he claimed to be a representative of the lattice theory. Here is a typical citation:
Lehmann wrote *1907*[46]

K. Fuchs wirft mir vor, ich wolle die ganze Raumgittertheorie umstürzen. Derjenige, der meine Arbeiten genau kennt, weiß, daß ich niemals versucht habe, die Raumgittertheorie zu bestreiten. Nicht einmal den flüssigen Kristallen wird regelmäßige Molekularstruktur von mir aberkannt. This was the reply to K. Fuchs in *der Phys. Zeitschr.*,[47]

where Fuchs had criticized Lehmann's inconsequence. In further reply to Lehmann, Fuchs cites Lehmann's statement from 1906:

Absolut unverträglich mit dieser Kontinuumshypothesis† oder Raumgittertheorie ist die Existenz wahrhaft plastischer Kristalle, d.h. solcher, deren Raumgitter bei plastischer Deformation gestört wird—ohne Änderung der Kristalleigenschaften—und ganz besonders die Existenz flüssiger Kristalle,

There are many more contradictions in Lehmann's papers, which indicate the rapid progress in the field. The nicest one I found in his dissertation:

"Eine Flüssigkeit ist ein Körper, . . . dessen Kohäsion zu gering ist, um die Moleküle entgegen der Wärmeabstossung in bestimmter gegenseitiger Stellung zu halten, welcher also niemals mit krystallinischer Struktur auftreten kann"

(A Liquid is a substance . . . which never can exist with crystalline structure) (note on page 25:40). See also page 23. Contradictions

†The continuum—or identity—hypothesis was based on the fact, that the molecules are always the same, if any phase transition takes place. Only the arrangement changes.

distributed on different places, or diffuse statements are valuable for later citations, to show that the author was always right.

Here a question arises which is from a certain historical interest: to what extent are the works before 1888 connected to the later papers devoted to liquid crystals? This question seems to be rather important, because Lehmann was to cite later his early work on Silver Iodide, this substance being a precurser or even the "first liquid crystal." We shall come back to this question in part 4; the following remarks shall be devoted strictly to early papers of Lehmann, especially those dealing with AgJ. Because the table of self-citations in the "Molekularphysik" is certainly the most complete one (about 500) we can hope to find those being related to silver iodide "liquid crystals," as referred to after 1889 so extensively.

The first study of AgJ is that from 1877: Enantiotropy and electrolysis of AgJ[62] published in *Zs. Krist.*, vol. 1. A larger publication is devoted to the electrolysis of AgJ,[107] to mixed melts of AgCl/AgJ and of AgBr/AgJ.[108]

Lehmann referred to Rodwell[56] who has found the transitions of AgJ (116°C/ "X" /450°C isotrope-liquid), and he claimed to have seen first, that the modification "X" be crystalline. So 1908[14]

Let us inspect the original texts. The surprise is complete: The "first study" in Zs. Krist. of AgJ has a forerunner, namely the Dissertation of Lehmann itself, which has served as the context of this publication. Here, we find the first citation of Rodwell (*Chem. News* **30**, 288; **31**, 4. *Chem. Jahresber.* **1874**, "72) and—on page 24 the title of chapter 6:

"Umwandlung flüssiger Modifikationen in flüssige und gasförmiger in gasförmige."

Lehmann has obviously reproduced the experiment of Rodwell and found the transition point of 450° "zähflüssig/hellgelbrot" . . . "leichtflüssig dunkelbraunrot" well proved. Then he wrote:

"Die rasche Umwandlung bei einem bestimmten Punkte erinnert sehr daran, dass hier ein Fall vorliegt, welcher einen gewissen Übergang bildet zur Umwandlung fester Körper in flüssige und umgekehrt, da ja auch die zähflüssige Modifikation nicht eigentlich mehr Flüssigkeit gennant werden kann, sondern bereits einen merklichen Grad von Cohäsion besitzt."

The viscous ("zähflüssig") modification crystallizes in the regular system, as Lehmann has found, and he has really observed a transition between two liquid modifications, as the title says. Well, the regular modification shows no birefringence, today we would call it "plastic." The curiosity is, that Lehmann had really seen a "liquid crystal," but he had denied its existence "because there cannot be that may not be." He declared the liquid to be solid, following a dubious dogma (see note on page 25, Reference 40). To my knowledge, he never cited these sentences later.

The early papers of Lehmann show a special interest in electrical discharges, the first still being published at Mühlhausen, later ones in Aachen. We can omit them here because they do not contain any relations to our theme. But another, broadly laid out field of interest are experiments on crystallisation processes, which always are sustained by improvements of the heating stage microscope. To observe the mixing behavior of two pure components at one glance, he invented the contact preparation. This technique remained up to date one of the most simple ways to get informations about phase behavior, eutectical temperatures and formation of mixed crystals. One example among numerous ones is given in Figure 18.[34] In special cases he observed such a preparation in an additional electric field (d.c.), so for example his favoured silver iodide.[107,108] Lehmann's style of working is unique: any teamwork is impossible. He never had pupils, assistants, maybe Mie for a short time. He liked the tools as much as the results. The latter being always given in pictures. Formulas and laws do not exist in his reports, nearly no quantitative measurements exist, but his knowledge in crystallography must have been

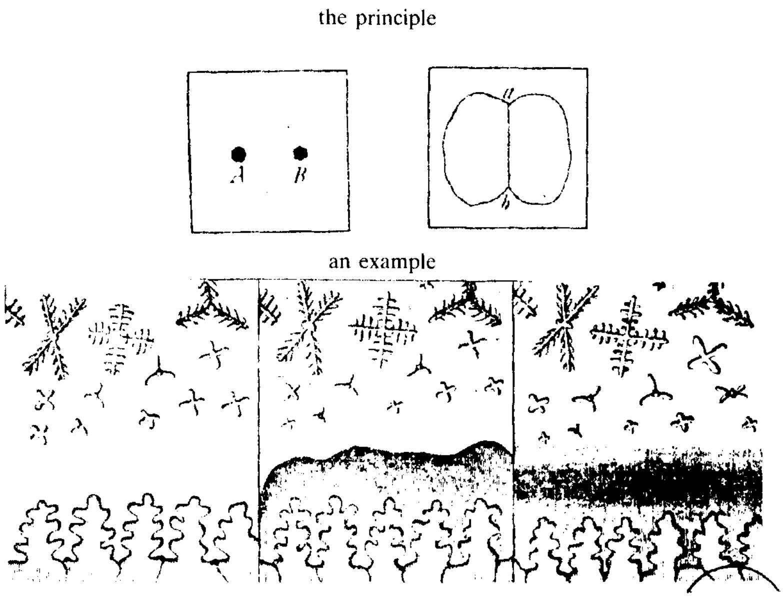


FIGURE 18 A contact preparation, from Reference 34.

excellent. Reading his papers about crystal growing, one has the impression as if he talks as Leuwenhoek or Ledermüller. Streamlines throw themselves like Infusoria to and fro, particles of silver creep like Amoeba from negative to positive Electrode, and the whole is equal to an ant-hill.

4 THE PRIORITY QUESTION: O. LEHMANN OR F. REINITZER?

October 1888, Lehmann followed a call for the Dresden Polytechnikum, and early in the year, when he was still in Aachen, he had received a letter from Reinitzer (Prag), and a correspondence was opened which represents the development of liquid crystal research in a strict sense. Lehmann answered promptly and did not hesitate to add the strange observations on cholesterol esters that Reinitzer had reported to his second volume of the "Molekularphysik" from 1889.[24]

The letter from Reinitzer, dated March 14, 188, 16 pages written by hand, represents a masterpiece of a scientific report, being absolutely clear and ready for the press. The following translation is taken from our paper Ref. 2, page 7, the original is written in German, it will be published elsewhere.[39]

> 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.

Reinitzer prepared his cholesterol esters from native cholesterol. These substances were optically active by its natural constituents. It must be remarked that the base was a natural product, and so it was possible that the strange properties could be related to a biological phenomenon.

Lehmann confirmed Reinitzer's observations, but there was a complete perplexity and helplessness on both sides. Wüllner, too, did not know any answer. At Dresden, Lehmann did not find time for further studies, and in 1889 he left Dresden to accept a call for Karlsruhe, as the successor of Heinr. Hertz, the discoverer of the electromagnetic waves. At Karlsruhe, the work on the "Cholesterics" was taken up again. The birefringent parts of the melt had to be regarded as crystals, another explanation did not seem to be possible. The liquid was traversed by floating "oily streaks" (ölige Streifen). Figure 19 shows the first drawing of Reinitzer's substance from August 30, 1889. Lehmann, supplied with a disposition for strange effects in phase transitions must have been convinced that somewhat exceptional happened. Reinitzer had published all about his findings in 1888,[3,57,58,59] and Lehmann took up the matter instantly into the second part of his Molekularphysik: p. 221, Reference 24. Here he describes even the light scattering behavior under the influence of an electric field. He gives also an account of the anisotropic behaviour of the melt: "A beautiful liquid with net-like white stripes resembling uniaxial crystal needles which become dark where they run parallel to the principal directions of the Nicols. The reason for this curious polarizing effect could not be elucidated, but obviously, the white ribbons represented streamlines. If the liquid is in movement, between stripes new stripes add themselves to the already existing, and a broad ribbon emerges." See Figure 21. Similar structures emerge around the top of electrodes, forming concentric circles around them, Figure 20. The electric field forces the substance to violent movement which originates from a single point of the electrode. We see that Lehmann

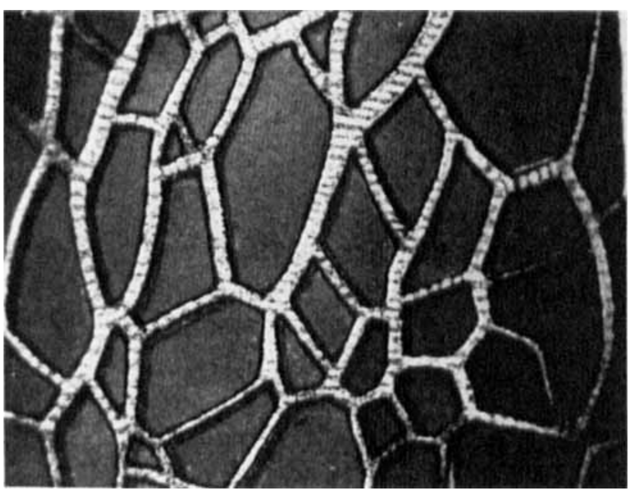


FIGURE 19 The first drawing of Reinitzer's substance,[61] by O. Lehmann.

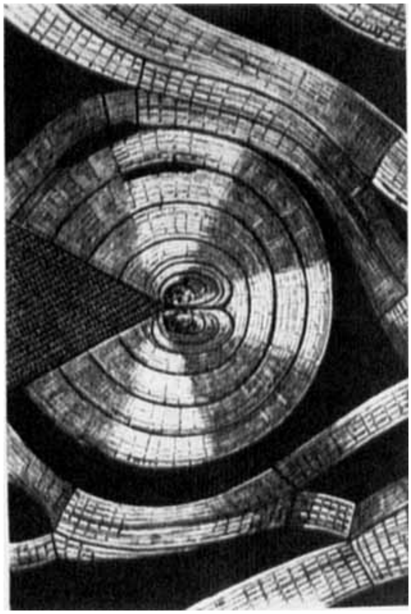


FIGURE 20 A cholesteric phase in an electric field.

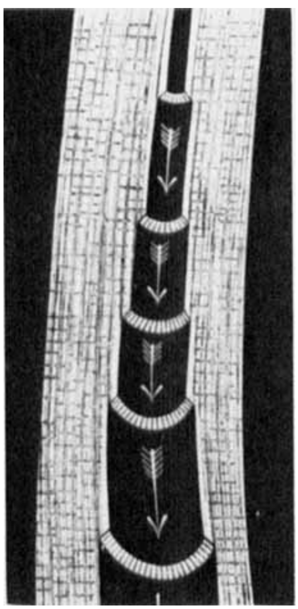


FIGURE 21 A cholesteric structure.

experimented as early as 1888—the exact date is not available—with "dynamic scattering." This report is incorporated in the main part of the "Molekularphysik," vol. II, whereas the description of the cholesteric colours as a function of the temperature, etc., is given in the supplement on page 586 ff. On page 589 there is an interesting statement[24]:

"Die Farbenerscheinungen, welchelzwischen den hellen Kanälen befindliche Masse zeigt, . . . nur erklärt werden können durch eine Anhäufung von Kristall-Lamellen in einer Flüssigkeit."

And on p. 591:

"Es kann somit nur Drehung (der Polarisationsebene) in Folge von Superposition zahlreicher dünner Krystallamellen in Frage kommen, wofür der Umstand spricht, daß die Farben im durchgehenden Licht blasser sind als die im auffallenden und zu diesem complementär. Möglicherweise kommen dabei auch die von Christiansen (*Wied. Ann.*, **23**, 298, 1884) beobachteten Phänomene in Betracht."

The optically active colour phenomenon has been compared later with the set of mica leaflets as described by Reusch.[60] Another substance with equal effects had been discovered by Reinitzer the "Hydrocarotin" benzoate and -acetate. Hydrocarotin was regarded as a member of the cholesterol group.†

The correspondence between Lehmann and Reinitzer had been interrupted from April 1888 until August 20, 1889. In his last letter from Aachen (April 20, 1888) Lehmann confessed once more that "It seems as if the polarisation of the ribbons be of the same nature as that of the lamellae, and it seems so, as if all changes (Übergänge/transitions) from the crystalline lamellae and the liquid stripes were possible, i.e. "The impossible becomes possible." Remember Lehmann's studies with silver iodide, where he excluded consequently the existence of a floating crystalline modification. It is absolutely erroneous to believe that Lehmann had already seen any correlation between the observation of the cholesteric materials and the "plastic" AgI, as it has been asserted twenty years later by him. In the summer of 1889, Lehmann wrote a letter to Reinitzer which confirms, that Lehmann had come to new insights. In this letter from August 20, 1889 he stated: "and so my new results confirm your already in good time declared view, that the "Grieß" (i.e. the substance which causes the turbidness) *consists of very soft crystals*, that are to be considered as a physically isomeric modification of the substance. It is absolutely homogeneous, and another liquid—as you assumed formerly—is not present." The letter ends:

†Lehmann writes: Hydroceratin.

"It is of a high interest for the physicist, that crystals exist which are of such a considerable softness that one could almost call them liquid."

It can be regarded as sure that 16 months had passed until the important result had been reached: April 20, 1888 until August 20, 1889. Ten days later, on August 30, 1889, he formulated a statement with the title

"Über fließende Krystalle" [61]

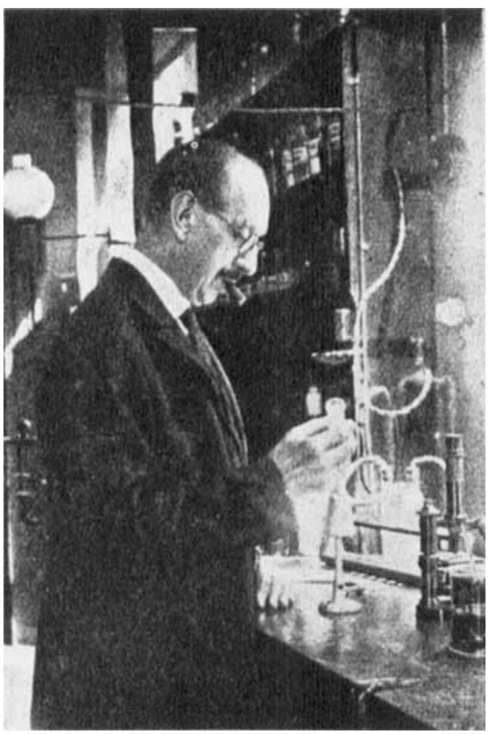
to be published in the Zeitschrift für Physikalische Chemie. The article ends with the sentence:

"Gibt man diese Deutung der Beobachtungen als richtig zu, so läge hier ein bis jetzt *einzig* dastehender Fall vor, daβ eine kristallisierte stark doppelbrechende Substanz so geringe Festigkeit hat, daß sie nicht imstande ist, auch nur der Einwirkung des eigenen Gewichtes Widerstand zu leisten."

In this context we find no remarks on silver iodide. Lehmann says explicitly "Durch eine Entdeckung des H. Reinitzer in Prag scheint indessen in neuester Zeit eine so leicht flüssige krystallinische Substanz wirklich aufgefunden zu sein" . . . "die rätselhaften Krystalle fließen mit der Flüssigkeit, als ob sie nur mit Polarisations-fähigkeit ausgestattete Teile dieser selbst wären."

It is absolutely clear that "Floating Crystals" have been first recognized by O. Lehmann, but exceptionally with Reinitzer's substances. This fact cannot be turned around or modified by later casuistry, as blown up by the late Lehmann. An absolutely correct report on the history of the discovery is that from Reinitzer.[62] Reminiscences of Lehmann in his later years are most interesting from a psychological point of view: they demonstrate the fanaticism of the elder man to show his merits. This is a pity, regarding the fact that his part on the discovery was so large. So he ruined much of his reputation in the scientific world by an imprudent dogmatism and by permanent priggishness. A friend characterized him as a "typical schoolmaster." The year 1889 had gone, and Lehmann eagerly improved the Crystallization Microscope.[33] In 1890 he published the next article "The Structure of Crystalline Liquids."[63] Note the changing names of the object. One year before, it was called "Floating (Fließende) Crystals." The reason for changing the title was weighty, indeed. Meanwhile something happened that was to be of utmost importance for the events to follow, at least as dramatic as the discoveries of Reinitzer.

It was Gattermann at Heidelberg who had synthesized—together with A. Ritschke—the Azoxy-ethers p,p′ Azoxyanisole, -Phenetole, and -Anisole-Phenetole. Gattermann knew the publication about the "Floating Crystals." He had observed an analogous behaviour with his Azoxy compounds, the two transitions, and the typical, even more easily floating turbid melts. So he asked Lehmann for a nearer inspection of his substances. Substances having been synthesized without any natural product. Lehmann must have been extremely happy about this finding; he confirmed the results of Gattermann and coined the new term "Crystalline Fluids" (Krystalline Flüssigkeiten) because the viscosity of the substances was indeed much lower than this of the cholesterics. Lehmann published the new findings quite instantly,[63] March 24, 1890. The paper of Gattermann and Ritschke which reports briefly the results of Lehmann in an annexe, is dated June 11, 1890. Both papers are highly interesting! That of Gattermann, the 30 year old assistant professor, represents an impressive example of advanced organic chemistry, including separation techniques. The microscope already had its place on the bench. Later, Gattermann became full professor of chemistry at the University of Freiburg (1900). See Figure 22. Every student knows him, even today, as the author of the text book of preparative organic chemistry:



Ludwig Gattermann, Heidelberg, later Freiburg (1860–1920).
FIGURE 22

"Die Praxis des Organischen Chemikers."

Lehmann's publication can only be designated as ingenious. It contains descriptions of the structure of nematic droplets, of discontinuity walls, of the Schlieren texture, of homeotropic and homogeneous textures. This paper[63] must be regarded as the base of all structural investigations which followed!

Lehmann's experiments were always based on a condition which is difficult to understand today. Even when he spoke of anisotropy of crystalline liquids, he anticipated individual crystal beings. By this reason, he always tried to get single crystals grown from a liquid phase, a solvent. Unfortunately, the physicist did not realize that his "solvents" changed the substances dramatically. Using Colophony (abietic acid) as his favorized solvent, the solutes became infected by the optically active solvent. But in spite of these confusing boundary conditions the study of his single crystals, more or less being droplets, are extremely interesting. The principal operations to elucidate symmetry principles were dividing and unifying droplets.

So he arrived at singularities which correspond amazingly well to the Oseen-Frank topology. For a better understanding what Lehmann is talking about in numerous varieties of definitions one should translate:

plastic crystals	weiche Kristalle
nematic phase	tropfbar flüssige Kristalle
smectic phase	fließende; schleimig—flüssige Kristalle

The confusion in terminology lasted for more than 50 years, even still after 1922, when G. Friedel had cleared up the situation in a really classical way, being accepted up to now.[65] The term "tropfbar flüssige Kristalle" was introduced[66] to underline that the limit of elasticity (translation) is Zero. The curvature elasticity has been introduced much later, by Oseen. The paper cited last appeared at the same time as paper 63, March 24 and[66] March 18, both 1890. In the paper from March 18, we find interesting deviations from the "droplet-monocrystal" concept Figure 114[66] shows a typical "schlieren-Texture" of an infinitely bounded phase. From this time on, Lehmann distinguished 2-wing and 4-wing Schlieren; the latter being called "Konvergenzpunkt" the other "Kernpunkt"; see Figures 23 and 24.

The year 1890 can be regarded as the final breakthrough of Lehmann's conception. Research in this field began at different places. The following table gives a picture of the events between 1890 and 1900:

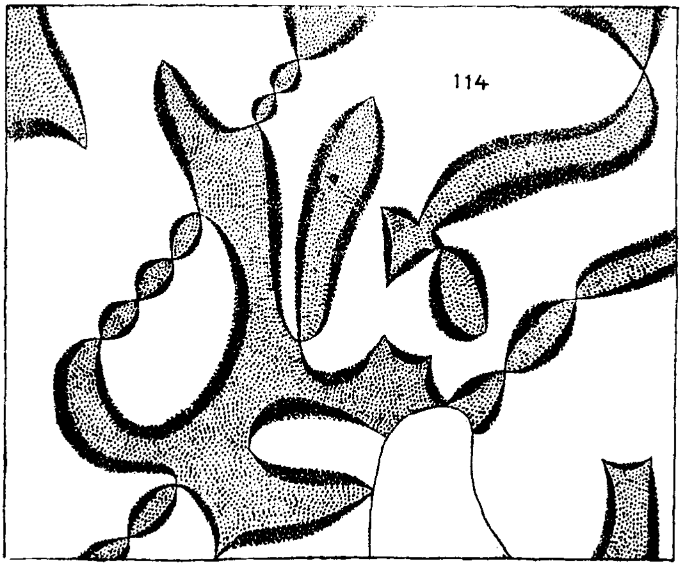


FIGURE 23 The first picture of a Schlieren Texture.

1894: On the formation of hollow bubbles, lather, and Myeline forms by Quincke[18]

1895: On flowing together and healing of floating soft crystals by Lehmann[68]

1895: Contact movement and Myeline Forms, by Lehmann[69]

1897: Investigation on the crystalline liquids, the habilitation paper by Rudolf Schenck, Marburg, see Ref. 70

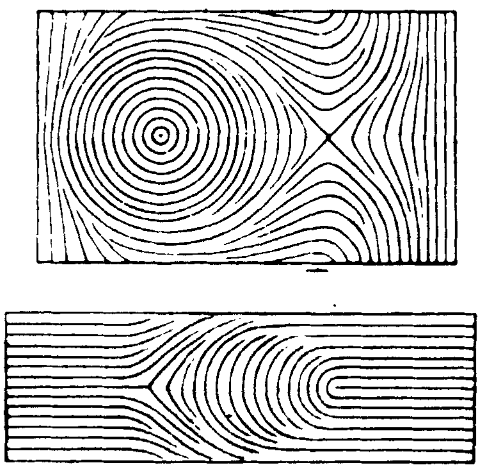


FIGURE 24 Disinclination points as seen by O. Lehmann.

1898: Investigations on crystalline liquids, 3 publications by Schenck[70,71,72]
1899: Investigations on L. C. part IV, by Schenck and Schneider, Marburg[73]
1899: Contributions to the knowledge on crystalline liquids: Thesis F. Schneider, Marburg 1899
1899: The continuous transition solid/liquid, by Hulett[74]
1899: Dielectric Behavior of a crystalline liquid, R. Abbeg and W. Seitz[75]
1900/ On the crystalline constituent of the etheric oil of Kaempferia
1901: Galanga (*p*-methoxy cinnamic acid) by Van Romburgh
1900: A Reply of R. Schenck to Bakhuis-Roozeboom
1901: On the so called liquid crystals[77] (Über die sogenannten flüssigen Kristalle) by G. Tammann, Dorpat
1901: Reply to Tammann[77] by O. Lehmann[78]

An objective report on the early history may not omit the facts around the central figure O. Lehmann, his predecessors and contemporaries, being so much involved in the development. Outstanding scientists, who played a central role—also apart from mineralogy and crystallography. They will later often be named by Lehmann, mostly as contrahents or incompletely informed colleagues. The most important personalities who shall cross his way are the already mentioned Georg Quincke, (Figure 5), Eduard Riecke (Figure 10) Walther Nernst (Figure 25), Gustav Tammann (Figure 26), Woldemar Voigt (Figure 11), Emil Bose (Figure 27), Rudolf Schenck (Figure 7), Eduard Riecke (Figure 10) and the late Ernst Haeckel (Figure 12). E. Riecke (1815–1915) was the director of the Physical Institute of the Göttingen University since 1881. It is his merit to have assembled the most outstanding physicists at this place. In 1899 he founded the "Physikalische Zeitschrift," where some of the most important papers on liquid crystals were published henceforth. The young E. Bose served as the editor's assistant; later he presented a first, amazingly competent theory of the liquid crystalline state which laid the fundaments of the "swarm theory,"[49] W. Voigt himself, the "grand old man" in crystal physics, holding no less than five honorary doctor's degrees, later offered an advanced seminary on liquid crystals.[50]

W. Nernst was born in 1864, he lived for some years at Graudenz, he studied physics in Berlin with Helmholtz, at Graz with Boltzmann and at Würzburg with Kohlrausch, where he graduated. 1887 was a very important year for physico-chemical development in Europe.

Walther Kernst (1864–1941).
FIGURE 25

Gustav Tammann (1861–1938).
FIGURE 26

Van t'Hoff's theory of diluted solutions, Arrhenius' theory of electrolytic dissociation coined the scientific landscape. Another Journal was founded by Wilhelm Ostwald and van t'Hoff: The Zeitschrift für Physikalische Chemie. W. Ostwald changed from Riga to Leipzig, and Nernst became his assistant. 1890, Riecke called him, and he

Prof. Dr. Emil Bose (1874–1911).
FIGURE 27

followed to Göttingen, where he remained until 1905 when he changed to Berlin. Nernst's merits in liquid crystal research are easily overlooked if one follows the development only by accepting the permanent complaints and criticisms of Lehmann, being mostly directed collectively against "Nernst-Tammann-Quincke." The open discussion on liquid crystals began in 1905, and Nernst was strongly interested in a fair solution of all the open questions.[51,52] Riecke promoted important papers in his new journal "Physikalische Zeitschrift" from authors such as E. Bose, W. Voigt, O. Lehmann, and others.

Gustav Tammann (1861–1938) was generally regarded as the absolute authority in solid state chemistry, melting and related processes, especially concerning phase transitions. His later monograph "Aggregatzustände" even refused to accept liquid crystals as late as 1922. Citation:

"Zusammenfassend kann man sagen, daß flüssige Kristalle oder anisotrope Flüssigkeiten chemisch homogener Stoffe bisher nicht nachgewiesen sind. Die trüben anisotropen Flüssigkeiten der Azoxykörper sind chemisch nicht homogen,"[53] page 290.

Tammann came to Göttingen just in the moment, when the public discussion had begun, when the first physico-chemical publications became known to a broader community. He came from Dorpat, and he presented himself as a disagreeable, aggressive, and arrogant dogmatist even at a time, when the existence of liquid crystals had already proved by his notable colleagues, when Woldemar Voigt at Göttingen explained the matter to his students.[50] Fr. Pockels, assistant professor at the Heidelberg University, published 1906 his famous textbook "Lehrbuch der Kristalloptik."[31] This book follows W. Voigt's "Kompendium der Theoretischen Physik" (Vol. II, 1896) and is closely related to Liebische's "Physikalischer Kristallographie" (Leipzig, 1890), as well to his "Grundriß der physikalischen Kristallographie." Groth's new edition of the "Physikalischen Kristallographie," IV, completes the series of highly sophisticated publications in the field Pockels used the "unattainable illustrations" of H. Hauswald, Halle: "Interferenzerscheinungen im polarisierten Licht," a wonderful collection[54] of photographs with convergent light, axis pictures, which have been completed by corresponding pictures of liquid crystals later by Vorländer and Hauswaldt (Figure 28).

The last decennium of the 19th century is characterized by a renewed interest in Myeline forms. We remember this already classical theme being touched by Lehmann in the "Molekularphysik I,[79] where he refers to works of Brücke and Famintzin.[80,81] The two pictures

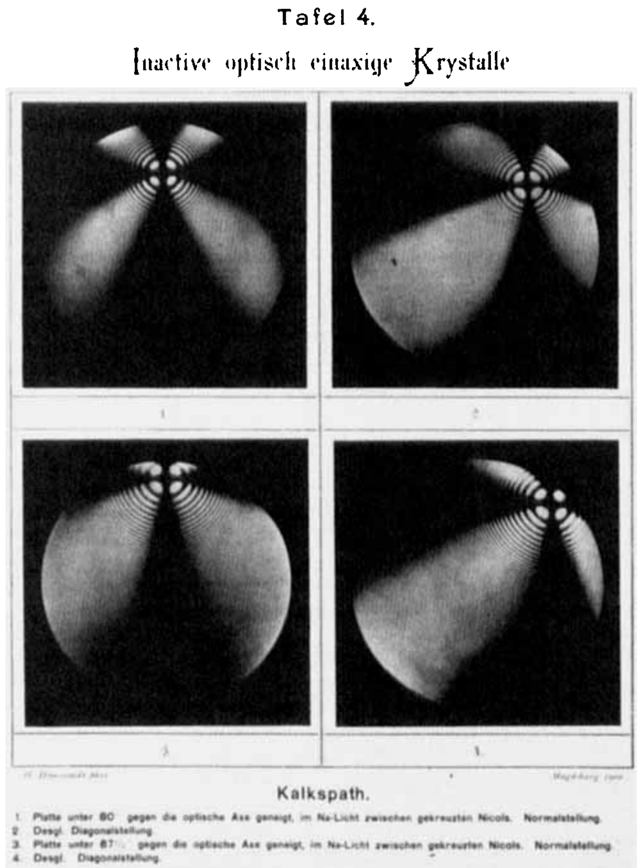


FIGURE 28 Pictures from the Hauswaldt Atlas.

which we know from later Lehmann publications are given here for the first time (Figures 279 and 280), long before Myeline was regarded as a special class of liquid crystals. A very important contribution and the cornerstone of systematical physico-chemical studies have been given by the young Rudolf Schenck, just coming from Halle, now working at Marburg. Schenck reported how he found the entrance to liquid crystal research.[35] At Halle, he worked as the assistant of Jacob Volhard, a pupil of Liebig and Wöhler. Ernst Dorn, who years later was to present important, basic treatises to the optical behavior of liquid crystals, inspired Schenck with respect to the thermodynamics of W. Gibbs and H. v. Helmholtz such as the theories of solutions, dissociation, and ions. Even the advice of Volhard: "Herr Schenck, leave this stupid stuff" did not hinder him to work further in this sense. A central question was still the molecular state of substances which could not be vaporized or brought into solution. As the liquid state is concerned, W. Ramsay had elaborated a criterium to check the molecular weight in the liquid and in the gaseous state by comparison of the EÖTVÖS constants, the temperature coefficient of the molar surface energy. "Measurements at high pressures were very difficult at this time, and the broomstick of the scrubwoman finished the vitreous work of art." (Original text of Schenck). Schenck was so enraged that he threw some volumes of the "Chemische Berichte," just lying round back to the table. "It was a coincidence of fate, that just at that time the paper of Gattermann had been presented, which reports about the two-phase behavior of azoxyanisole. From the works of Lehmann I became acquainted to the few other substances with equal properties." Schenck measured the EÖTVÖS constants of the azoxyethers, and he proved that the molecular weight was nearly the same in both liquid phases. These investigations opened to him the way to the academic career. The results, completed by some investigations of his coworkers at Marburg, are summarized in the monograph

"Kristalline Flüssigkeiten und Flüssige Kristalle"[82]

In the meantime, van Romburgh had discovered a new family of liquid-crystalline compounds, the bimolecularly associated free acids, represented by the *p*-methoxy cinnamic acid.[76]

The whole period is characterized by successful observations and was at its end clamorously accompanied by harsh criticism which came from Gustav Tammann, being still at Dorpat. The struggle was opened by the paper[77] from the year 1901:

"On the so-called Liquid Crystals"
(Über die sogenannten Flüssigen Kristalle)

His arguments against Lehmann and Schenck:

1) Double refraction of the turbid liquids is not proved.
2) It is even improbable that the turbid liquids are emulsions
3) If the so-called fl. Kristalle really are mixtures of two liquids, they must be separable
4) Cholesterol derivatives are poorly appropriate as examples because they are substances of doubtful provenience.

Tammann did some experiments to support his statements, but he did not succeed, not even by distillation: the "mixtures" could not be separated. His coworker, Th. Rotarski, seemed to have proved his master's hypothesis, but he was blamed for having worked under erratic conditions and with impure substances.[84,85] Lehmann answered in a short notice,[78] clearly and objectively, but Tammann would not give up; a second part of his paper, still coming from Dorpat,[83] in February 1902, followed. He referred to the results of Rotarski. Tammann's final theory soon obtained the fame of a classical example for a typical error, born by preoccupation. Tammann's utterances, and the so-called emulsion theory, as originally proposed by Walter Nernst, govern the discussions to come.

5 THE STRUGGLE FOR TRUTH, AND THE FINAL BREAKTHROUGH

This period is introduced by the confusing hypothesis of Tammann. One should not overlook that Tammann was already an authority, being well prepared for his change from Dorpat to Göttingen, which took place 1903. In this year, his famous monograph "Kristallisieren und Schmelzen" appeared, a really outstanding textbook[86]; Tammann, being an extremely clear-thinking and ingenious experimenter felt himself as representative of modern physical chemistry, and regarding liquid crystals he must have felt that there was something beyond his horizon.

The next provoking event was the publication of Lehmann's great work, entitled

FLÜSSIGE KRISTALLE
sowie
Plastizität von Kristallen im allgemeinen,
Molekulare Umlagerungen
und Aggregatzustandsänderungen

(Leipzig, Engelmann, 1904)[56]

Lehmann had been able to collect important new material, which he combined with his beloved Oldies. The work of Schenck was now one of the most convincing base of the new findings and their theoretical foundations. Riecke himself has quite positively reported about this book.[102] Another sensational discovery from F. Meyer and K. Dahlem, Halle, was the synthesis of *p,p'*-Azoxy benzoic acid ethyl ester, the first fully synthetic "floating" liquid crystal, later being named "smectic." This work had been induced by Daniel Vorländer, being already mentioned on page 7. The goal of these synthetical work was to clear some questions concerning the existence of certain azo- and azoxy compounds.[87]

This substance exhibited basically new textures, but the principal differences to the azoxy-ethers had never been worked out as Friedel did twenty years later.[65] The publication of Meyer and Dahlem had come just early enough to be incorporated by some photographs of the beautiful "Bâtonets," as they were named later by Friedel. Lehmann classified them as "Fließende Kristalle. See Table III in the monograph.[56]

The general discussion on Liquid Crystals came to a climax at the XIIth general meeting of the Deutschen Bunsengesellschaft in Karlsruhe, June 1–4, 1905. The congress was opened by Dr. Böttinger. The society consisted of 660 members, about 180 being present at Karlsruhe. It had been founded at Freiburg 1894 under its first president J. J. van t'Hoff. The Karlsruhe meeting was held under the patronage of the Grandduke of Baden, Friedrich I., represented by his son Friedrich II, because the Grand-Duke was at Berlin, to celebrate the marriage of the German Prince Royal. Present were, among other authorities, Wilhelm Ostwald, W. Nernst, van t'Hoff, G. Tammann, Bredig, Dolezalek, Förster, O. Lehmann, and the young R. Schenck.[88]

In the afternoon of June 3, Schenck presented his paper

"Über die Natur der kristallinischen Flüssigkeiten und der flüssigen Kristalle,"[88]

a splendid apology for Otto Lehmann, who had just passed the 50th anniversary, who had married in 1899, and who had been nominated "Geheimer Hofrat" in 1902. Schenck gave a convincing demonstration, a great success for himself, and a beginning of a extraordinary academic career. His arguments were those being fixed in his monograph from 1905. The Schenck paper was thought as an introduction to an experimental demonstration from Lehmann, which was to follow. Some refutations of Tammann's points of view were included, but in a most objective and modest manner. Some details about melting point behavior established by de Kock[89] were mentioned especially, and convincing proofs of a real discontinuity at the clearing points were given, concerning density and viscosity. The emulsion theory had been reduced to absurdity. Only Tammann responded:

"Soft crystals do exist, without doubt; for my sake floating ones may exist, but liquid ones? No!"

"Whether they exist or not is a vital question of the lattice theory and therefore I would assign an important theoretical significance to the problem of liquid crystals." Regarding this aspect of the problem, we can easily follow Tammann's argumentation, and we remember that Lehmann himself did not succeed in giving clear statements as such as lattice theories were concerned. The discussion was closed by the chairman van t'Hoff, so no reply was possible. It was continued, as foreseen, in Lehmann's institute by Lehmann himself.

The participants were: Tammann, van t'Hoff, Schenck, Müller, Bredig, Elbs, and Lehmann. The statements of Lehmann were published as a record, following the Schenck paper in the publication.[88] Van t'Hoff proposed to establish a commission to examinate the problem. Tammann and Lehmann were nominated as the first members, P. v. Groth was called in as the representative on crystallography. Unfortunately, this commission never came into action. There exists an unpublished letter from Lehmann which indicates that Lehmann himself blew it up. Why? Teamwork, communication, and respecting contrary points of view did not belong to his tools.

The next year, 1906, two main events were—at least partially—dedicated to Liquid Crystals, the International Congress of Applied Chemistry at Rome, April 26–May 3. Her W. Nernst gave his—and it seems to me to be the first—comment on the theme liquid crystals. He supposed that the turbid liquid is an emulsion of two partially mixable tautomeric forms of the substance concerned.[105] Dölter and Bruni defended the point of view of Schenck and Lehmann, but by lack of the protagonists of both parties, an agreement could not be reached.[90] A later reply of Lehmann demonstrates the most interesting and comprehensive picture of teh general situation.[90] Later, after having performed own experiments, Nernst kept his distance from his remarks at Rome.

1906, a splendid article appeared: "The color phenomena of Liquid Crystals," one of the best papers of O. Lehmann.[103]

We have already seen the young physicist Emil Bose, who served at Göttingen as an assistant of Riecke, editing the "Physikalische Zeitschrift. Now he was a full Professor at Danzig, later he went to La Plata, where he died soon after, in 1911.

Bose is the first who offered a complete theory of liquid crystals, founded on Schenck's work and dealing also with the Emulsion theory of Tammann/Nernst.[49] The central part of his theory is based on viscosity measurements and on the picture of molecular form anisotropy as given by Vorländer. The latter is an important base of his reflections; Lehmann has never had a clear model of his primary units, even the optical character, the sign of his homeotropic uniformly oriented layers has never been determined, "because he never used a conoscopic picture to determine it," as Vorländer stated elsewhere, p. 71 of Reference 94.

Bose's experiments and theoretical arguments result in the picture of the "swarm theory," this concept being used in connection with an early paper of Bose (1907), and also by Ambronn[101] in a study of pleochroic metal mirrors. Bose's extremely advanced and convincing studies already contain a consistent explanation of the clear and continuously ordered phases and droplets (Vorländer, Lehmann) which can be formed from the turbid bulk phase (see *Physikal. Zs.* **9**, 709). Bose's papers signify the absolute end of the emulsion theory; they have been used as the base of Nernst experimental work which presents a model for the explanation of the transition anisotropic/isotropic.[51]

Before we come to the end, let us remember the memorable Bunsen-Tagung, June 1905:

Schenck had been cordially invited by Lehmann and his family. A picture may serve to illustrate the situation, Figure 29. On June 17, 1905, he wrote a letter to Lehmann, thanking him for his hospitality, but coming back to scientific problems, he wrote:

"Ihr Brief, den ich heute empfing, hat mich sehr interessiert und die Winkelzüge des Herrn T., von denen Sie erzählen, übertreffen noch meine Erwartungen. Daß er Versuche unternehmen wird, die ganze Commissionsangelegenheit im Sande verlaufen zu lassen, war vorauszusehen, denn die Commission ist ihm äußerst unangenehm. Aber gerade deshalb dürfen Sie ihm keinerlei Concessionen machen. Diesem "Ehrenmann," der jede Thatsache leugnet bezw. verdreht, wenn sie ihm nicht in den Kram paßt, darf kein Pardon gegeben werden etc. etc. . . Der weiteren Entwicklung der Commissionsangelegenheit sehe ich mit Spannung entgegen.

Mit herzlichen Grüßen etc.

Ihr sehr ergebener R. Sch.

A great event was the 78th Assembly Deutscher Naturforscher und Ärzte at Stuttgart, September 16–22, 1906. On September 21, Lehmann presented a paper:

Flüssige Kristalle und die
Theorien des Lebens[91,104]
(Liquid Crystals and the Theories of Life)

This is probably not the original title. H. Grossmann reports[91]: "In der zweiten allgemeinen Sitzung sprach Prof. Bälz, Stuttgart über die

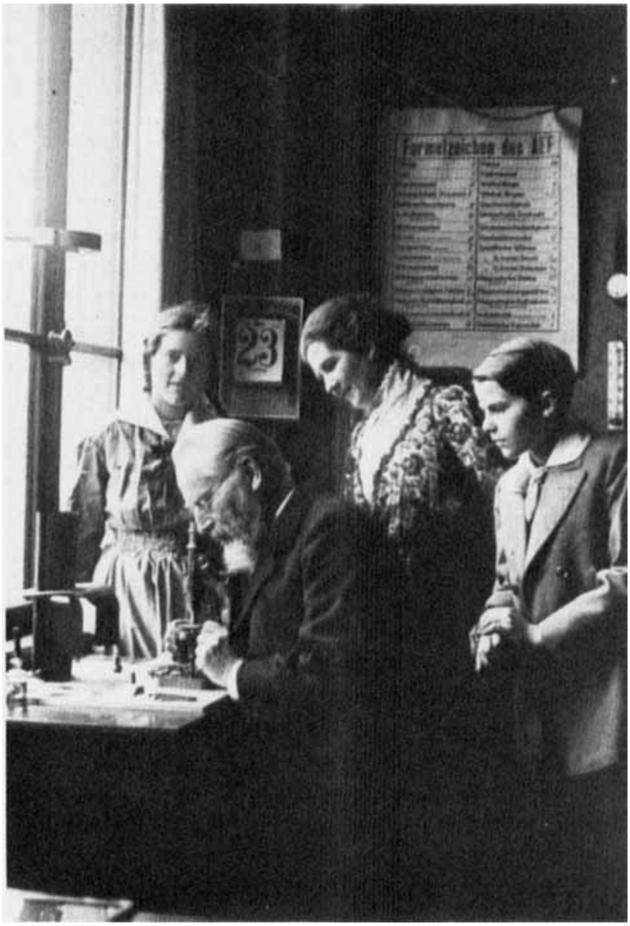


FIGURE 29 A visit at the work bench: the Lehmann family.

Besessenheit und verwandte Zustände. Den zweiten Vortrag hielt Professor Lehmann über flüssige und scheinbar lebende Kristalle."

This presentation marks a turning point in Lehmann's scientific life. He starts with his silver iodide stories, he presented beautiful pictures, among others the floating crystals of Vorländer, photographs of Siedentopf, showing analogues between crystals and living substances.

From this time on, all the papers of Lehmann are variations of one and the same theme, "Liquid Crystals and Life." More than twenty papers, the last one being published in Abderhalden's "Handbuch der Biologischen Arbeitsmathoden," 1922,[92] see also Ref. 8. The story ends with the old-age publication "Kristallseelen" by Ernst Häckel,[93] see Figure 12.

Intensive work on Liquid Crystals, beginning 1905/10 has been taken over by the next generation. Among others, it was W. Nernst, who worked earnestly on the solution of questions as being posed by E. Bose.[51] We did not find any animosities against Lehmann. We find it unjustified to designate Tammann, Nernst, and Quinckert as the "enemies" of liquid crystal research. Only Tammann was inflexible.[53]

The next period is governed by Vorländer, the organic chemist. He liked to polemize against Lehmann and Nernst.[94] He synthesized "as many liquid crystalline substances as one wants," because he detected the building principles.[94] A detailed report on the Vorländer circle at Halle has been given elsewhere.[97] More citations about the history can be found in our "Handbook;" [98] the whole complex of "liquid crystals and living beings" is well covered by a special monograph which contains 172 abstracts, edited by R. Brauns[99] and extracted from "Neues Jahrbuch und Centralblatt für Mineralogie, Geologie, and Paläontologie." A somewhat shorter review of the field has been collected for a plenary lecture at the Munich "Analytica," in 1984.[8]

From these years on, many names should be cited, I confine myself to the best known ones:

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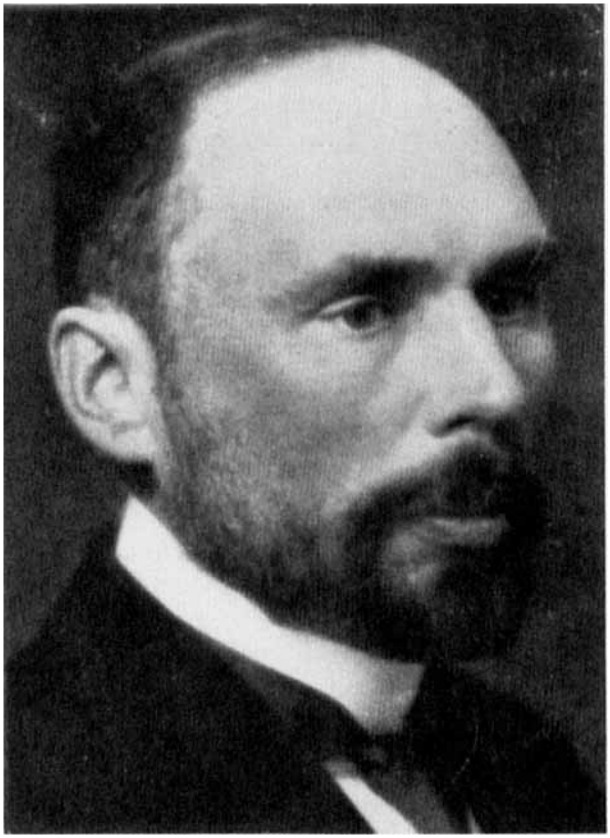

C. W. Oseen (1879–1942).

FIGURE 30

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