

Herr Privatdozent Dr. R. Schenck-Marburg i. H.:
 ÜBER DIE NATUR DER KRISTALLINISCHEN FLÜSSIGKEITEN
 UND DER FLÜSSIGEN KRISTALLE.

Meine Herren! Herr Geheimrat Lehmann hat sich liebenswürdigerweise bereit finden lassen, die Gesellschaft heute Nachmittag mit seinen Untersuchungen über die flüssigen Kristalle bekannt zu machen, uns die so merkwürdigen, von ihm in ihrer Bedeutung erkannten, Phänomene durch Projektion vorzuführen.

Als Einleitung zu diesen Demonstrationen möchte ich Ihnen eine ganz kurzgedrängte Uebersicht über das Verhalten jener Flüssigkeiten, welche wir als kristallinische bezeichnen, geben, ich möchte Sie mit den Gründen bekannt machen, welche uns das Recht verleihen, sie mit einem derartig paradoxen Namen zu belegen, und des weiteren die Beziehungen zu den festen kristallisierten Stoffen erörtern.

Wir wollen direkt an unseren Gegenstand herantreten und uns mit den Erscheinungen beschäftigen, welche Reinitzer im Jahre 1888 am Cholesterylbenzoat beobachtete. Diese Substanz (bei gewöhnlicher Temperatur wunderschöne, glänzende, farblose, kristallographisch wohldefinierte Blättchen) schmilzt bei $145,5^{\circ}$ zu einem trüben Schmelzfluss von der Konsistenz des Olivenöles. Es besitzt die merkwürdige Eigenschaft, sich bei $178,5^{\circ}$ zu klären.

Unter dem Polarisationsmikroskop zeigt die trübe Masse trotz ihres flüssigen Zustandes Doppelbrechung, zwischen gekreuzten Nicols bleibt das Gesichtsfeld aufgehellt. Es wird aber dunkel, sowie die Temperatur von $178,5^{\circ}$ überschritten wird, die Masse verhält sich alsdann wie eine gewöhnliche Flüssigkeit. Die optischen Verhältnisse sind von Herrn Lehmann eingehend untersucht worden.

Im Laufe der Zeit haben sich noch mehr Stoffe gefunden, welche ein ganz ähnliches Verhalten zeigen wie die Derivate des Cholesterins, aber in mancher Beziehung als Beobachtungsmaterial besser geeignet sind. Hier ist vor allen Dingen der p -Azoxybenzoesäureäthylester zu nennen, an dem Vorländer das Auftreten der Erscheinungen konstatierte. Wenn man zu dem isotropen Schmelzfluss dieser Substanz kleine Mengen fremder Stoffe mischt und das Präparat unter dem Mikroskop vorsichtig abkühlt, so beobachtet man die Ausscheidung langer, dünner Kristallnadeln, welche optisch einachsige sind, im polarisierten Lichte Dichroismus zeigen, und bestimmte Auslöschungsrichtungen besitzen.

Jeder Druck mit der Präpariernadel deformiert diese Gebilde, welche übrigens nie scharf ausgeprägte Ecken und Kanten besitzen. Die Ab-rundung wird verursacht durch die Wirkung der Oberflächenspannung. Ihr Einfluss zeigt sich vor allen Dingen darin, dass Nadelchen, welche

sich berühren, zu grösseren zusammenfliessen. Stossen sie unter einem Winkel aufeinander, so erfolgt zunächst Parallelrichtung und dann Vereinigung der parallelen Stücke. Die kleineren lagern sich als Wülste an die grösseren an. Noch eigentümlicher ist das Verhalten der Nadelchen, wenn sie mit einer Luftblase in Berührung kommen. Erfolgt das Aufstossen mit der Spitze, so verbreitert sich die Nadel an der Berührungsstelle unter dem Einfluss der hier kräftig wirkenden Oberflächenspannung, so dass schliesslich eine der Luftblase mit breiter Basis aufgesetzte Pyramide mit gekrümmten Seitenflächen entsteht. Die Streifung und die Auslöschungsrichtung stehen stets normal auf der Luftblase. Merkwürdigerweise erfolgt gar keine Beeinflussung, wenn die Nadel mit ihrer Breitseite mit der Luftblase in Berührung kommt. Man muss daraus den Schluss ziehen, dass die Oberflächenspannung an der spitzen Seite viel höhere Werte besitzt als an der breiten.

Wegen ihrer unzweifelhaften Kristallnatur und ihrer Fähigkeit, unter dem Einfluss der Oberflächenspannung zu fliessen, hat Herr Lehmann diese nadelförmigen Gebilde als „fliessende Kristalle“ bezeichnet.

Bald nach der Publikation der Lehmannschen Beobachtungen fand Herr Gattermann bei einigen Abkömmlingen des p -Azoxyphenols, z. B. beim p -Azoxyanisol und p -Azoxyphenetol trübe doppeltbrechende Schmelzflüsse, welche genau wie das Cholesterylbenzoat bei einer bestimmten Temperatur klar werden.

Beobachtet man sie aber unter den gleichen Bedingungen wie die fliessenden Kristalle, so ergeben sich erhebliche Unterschiede. Aus der isotropen, mit fremden Stoffen versetzten Schmelze kommen nicht nadelförmige Gebilde heraus, sondern Tropfen von Kugelform. Diese Tropfen verdanken ihre Gestalt lediglich der Oberflächenspannung.

Sie sind im Gegensatz zu grösseren, aus ihnen zusammengesetzten Massen völlig klar und zeigen bei 300- bis 700 facher Vergrösserung eine ganz besondere Struktur, wie sie bei Tropfen gewöhnlicher Flüssigkeiten gar nicht vorkommt. Die scheinbare Struktur ist eine Folge davon, dass die Lichtbrechung in den verschiedenen Richtungen eine verschiedene ist. Hauptsächlich treten zwei Erscheinungen auf, welche verschiedenen Lagen der Tropfen entsprechen. Die eine, die sogen. erste Hauptlage, zeigt einen centralen dunklen Punkt, welcher von einem grauen Hof umgeben ist. In dünnen Präparaten orientieren sich die Tropfen meist in der zweiten Hauptlage, sie gleichen durch-

ON CRYSTALLINE LIQUIDS
AND LIQUID CRYSTALS

R. Schenck

(Lecturer at the University of Marburg)

Good afternoon, Gentlemen. Professor Lehmann has studied the strange phenomena of liquid crystals and recognised their importance. This afternoon he has kindly consented to give a demonstration of these phenomena, making use of projection.

As an introduction to these demonstrations, I should like to give a brief overview of the behaviour of these liquids, whose properties are such that we describe them as crystalline. In this talk, I should like to explain to you why we have taken the step of labelling them so paradoxically, and then go on to discuss their relationship to solid crystalline material.

We launch into our topic immediately. We are studying the phenomena first observed by Reinitzer in cholesteryl benzoate in 1888. At room temperature this material is a shiny colourless solid with well-defined crystallographic planes. At 145.5 °C it melts, now forming a cloudy liquid with the consistency of olive oil. This liquid possesses a strange property: at 178.5 °C, the turbid liquid becomes clear.

Under the polarising microscope, notwithstanding its liquid state, this turbid material can be seen to be birefringent. When placed between crossed nicols, light transmission is not extinguished. Once above 178.5 °C, however, the sample does extinguish light, and the material behaves like a normal fluid. The optical behaviour has been studied in detail by Professor Lehmann.

Since then more materials exhibiting behaviour extremely similar to that of the cholesterol derivative have been discovered. In many respects these are more suitable as experimental materials. I mention the most significant of these substances. This is ethyl *p*-azoxybenzoate, and we owe the introduction of this material in this context to Vorländer. What happens is that a small concentration of impurity is mixed with the isotropic phase of this substance, and the sample is then cooled carefully under the microscope. One then observes the expulsion of long, thin crystallites, which are optically uniaxial, which exhibit dichroism in polarised light, and which possess definite extinction directions.

-Marburg i. H.:
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These structures are deformed whenever they come into contact with the preparation needle. They never possess sharply defined corners or edges. The rounding is caused by surface tension. The surface tension manifests itself above all when small needles in contact amalgamate into a larger ones. If the contact occurs at an angle, the needles first line up in parallel to each other, and then the parallel pieces merge. The smaller ones adhere to the larger one as a bulge. Even more characteristic is the behaviour of the small needles when they touch an air bubble. When the needle touches the air bubble at its tip, it spreads around the contact point under the influence of surface tension, which acts strongly in this situation. Eventually it takes the shape of a pyramid with a broad base and curved sides. The striations and the extinction directions are normal to the air bubble. By contrast there is no effect when a broad side of the needles comes into contact with an air bubble. From this phenomenon one concludes that the tip surface tension is much greater than that along the sides.

The needle-forming objects are evidently crystalline. They flow under the influence of surface tension, and are thus viscous. As a result of the coexistence of these two properties, Professor Lehmann has given these objects the name 'flowing crystals'.

Soon after the publication of Lehmann's observations, Dr Gattermann studied some derivatives of the *p*-azoxyphenols, in particular *p*-azoxyanisole and *p*-azoxyphenetole. In these materials he found turbid birefringent melts, which lose their turbidity at a definite temperature, just like cholesteryl benzoate.

However, when these materials are observed in the same set-up as the flowing crystals, considerable differences arise. When the isotropic melt is doped with an impurity, needle-forming objects no longer appear. Rather, spherical droplets appear, whose shape follows merely from surface tension effects.

These are perfectly clear, whereas by contrast aggregates of such droplets are not. Magnified 300 to 700 times they show a unique structure, unlike anything occurring in drops in normal liquids. The apparent structure is a result of the fact that the refraction of light is different in different directions. In the main two kinds of effect occur, each of which corresponds to a different drop position. The so-called 'first principal position' shows a central dark point surrounded by a grey region. However in thin samples the drops mainly orient themselves in the so-called 'second principal position'. They now resemble transparent spheres. In the centre of each transparent sphere there appears to be a lens with a different refractive index.

In contrast to drops in normal liquids, these droplets are birefringent. They exhibit dichroism in polarised light. Depending on the drop position, a cross or other figures appear when the sample is observed between crossed Nicols.

We must forego the details. I mention only that the optical phenomena can be altered by external forces in very many different ways. When the drops are rotated, the crosses turn into spiral crosses. In a magnetic field the drops take on a very definite form. They all now adopt the first principal position, if the lines of force lie vertically on the microscope stage.

If the drops are prevented from orienting themselves as a whole, effects on the molecules are felt. The magnetic effects compete with those forces which the

initial crystal drop structure seeks to preserve. These forces are the so-called 'molecular directional forces'. The final result is a compromise between the magnetic and crystallographic directional forces. This compromise of course leaves an optical signature.

When several crystal drops touch each other, they flow together into a larger drop. The observations on drop amalgamation now enable the structure of larger volumes of mixing fluids to be understood. We can think of these larger volumes as large aggregates which have been deformed by pressure, thermal currents and mechanical obstacles. The images under the microscope show that the optical orientation is different in different places.

We shall define the large aggregations of liquid crystals and flowing crystals, which have been stuck together and unified, as 'crystalline liquids'.

The turbid crystalline liquids transform, at an absolutely precise temperature, into normal clear liquids which refract in the conventional way. The liquid and flowing crystals might be said to melt. The clearing point corresponds completely to a melting point. The transformation is accompanied by a volume increase. Adding impurities significantly reduces the temperature of the clearing point. From this result one can deduce that the transformation possesses a small latent heat. This conclusion is confirmed by the change of the transition point under pressure. The latent heats obtained from cryoscopic data agree with those calculated from the Thomson-Clausius equation and those given by direct calorimetric measurement.

So far, 21 substances have been found which exhibit liquid crystallinity. However, there is little doubt that this number will increase significantly in the future. Their appearance is not restricted to particular classes of chemical compounds. Liquid crystals occur in many groups of organic materials. There is even an inorganic material, so-called regular silver iodide, which one can find a justification for including amongst liquid-crystal-forming substances.

Thus the synthesis of these compounds presents little difficulty. Some may be obtained very easily indeed, such as, for example, *p*-azoxyanisole. These materials only need to be melted for the phenomenon of crystalline viscosity to be studied. One can then also see that they can be poured and are fluid in the way that normal fluids are. Of course the viscosity varies from substance to substance. The table below shows viscosities relative to water at 0 °C (which takes the value 100).

<i>Material</i>	<i>Viscosity</i> (<i>water at 0 °C = 100</i>)
cholesteryl benzoate	893-621
ethyl <i>p</i> -azoxy benzoate	856-472
<i>p</i> -diacetoxychlorostilbene	327-309
<i>p</i> -azoxyanisole phenetole	171-111
<i>p</i> -azoxyanisole	141-128
<i>p</i> -methoxycinnamic acid	106-91
<i>p</i> -azoxyphenetole	79-66

We have a complete range. The initial cases possess a viscosity of the order of olive oil. These are flowing crystals. Later cases are much less viscous than water. They rapidly follow external forces. Drops of these substances thus take on a spherical shape. Between the two there are all possible intermediate forms.

The picture adopted by Professor Lehmann and myself is that the cloudy anisotropic liquids are aggregates of birefringent flowing or liquid crystals. This point of view has not remained unchallenged. Professors Quincke and Tammann prefer to interpret these observations in terms of chemical inhomogeneity. Quincke regards crystalline liquids as mixtures in which solid crystallites are suspended. Tammann considers them to be emulsions. Both are agreed that crystalline fluids are a two-phase phenomenon.

I want now very briefly to summarise the main reasons why we are sticking to our original point of view.

Professor Tammann bases his opposition on the fact that crystalline fluids are cloudy. He believes that the experiments of Rotarski are evidence for an emulsion picture. Rotarski observed that when *p*-azoxyanisole is distilled, the clearing point of the distillate decreases more quickly than that of the distillation residue. But it is generally known that azoxy compounds decompose on heating. If the decomposition products are more volatile than the original material, this behaviour would immediately follow.

Professor Tammann has further observed that his samples precipitate just like emulsions. De Kock, Lehmann and I have had the opportunity of working with Tammann's original materials. We have been able to show conclusively that his samples contained a high impurity concentration, in particular of *p*-azoxyanisole originating during synthesis. Pure samples do not show a precipitate, and it also does not appear if the crystalline fluids are placed in a centrifuge or subjected to electrophoresis. This last experiment has been carried out by Bredig and Schukowsky, and also by Coehn. In very many cases these methods enable emulsions to be separated. In the case of crystalline liquids, however, nothing indicates the existence of emulsions.

By contrast there are a large number of facts which sharply contradict the emulsion point of view. In particular, the transition from a cloudy liquid state to an isotropic liquid is associated with a sudden change in many physical properties. I mention here the density (Fig. 330) and the viscosity (Fig. 331).

The crystalline liquid phase occurs at temperatures lower than the isotropic liquid phase. It is a strange fact that despite this, in all materials which form crystalline liquids, the viscosity is lower in the crystalline liquid than in the isotropic liquid. Equally mysteriously, at the transition to the isotropic liquid, the viscosity jumps suddenly and substantially. Emulsions also exhibit a clearing point, and the viscosity above and below the clearing point can be measured. We have made these measurements for water-phenol and alcohol-carbon disulphide mixtures. In Fig. 332, I show the relationship between flow time and temperature in these experiments. There is no sign of a discontinuity in these experiments. Furthermore, there is absolutely no theoretical reason to expect one in the case of emulsions such as these.

The fact that in turbid melts the light absorption is independent of temperature indicates that they are homogeneous. In an emulsion, however, the number of

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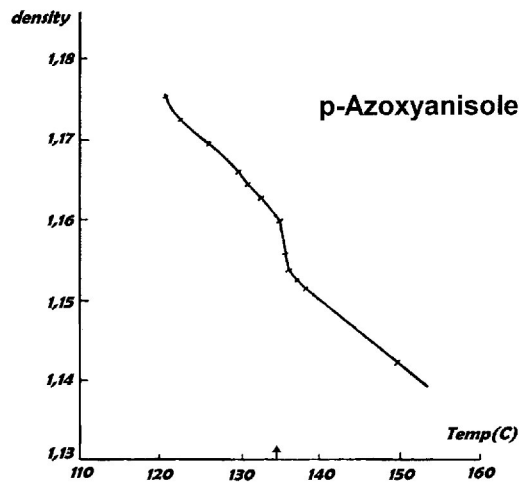


Fig. 330

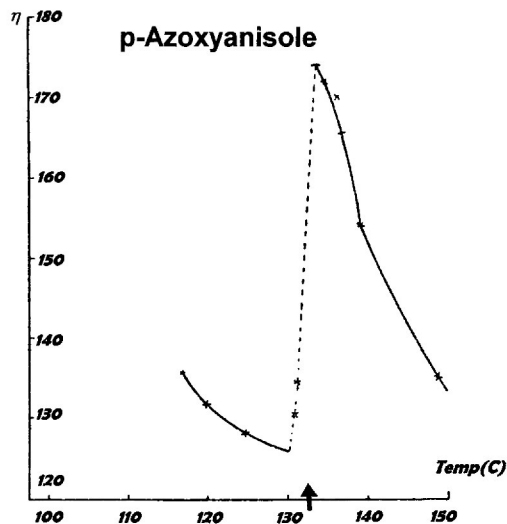


Fig. 331

droplets would have increased with decreasing temperature, causing increased absorption. The phase diagram close to the melting point was studied by de Kock. His experiments can also only be interpreted by supposing that the cloudy melts are chemically uniform.

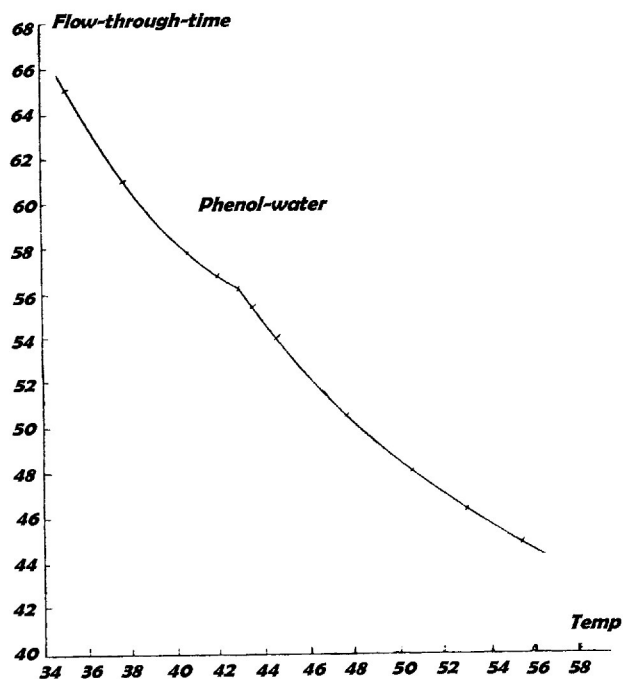


Fig. 332

One might also conceive of cases in which a reversible chemical process takes place. In this scenario a melted crystal might consist of two components which are only weakly miscible. The two components would only mix completely at a higher temperature. The clearing point would then correspond to the consolute point of the mixture. However, the experiments which I have just described really exclude this possibility.

The isotropic phase immediately above the clearing point would have to be a mixture of two components whose relative concentration changes with increasing temperature. Now we do have a quantity which will signal a uniform fluid mixture with a temperature-dependent concentration. This is the temperature coefficient of the molecular surface energy. Dr Ellenberger and I have studied this quantity. The normal value of this quantity is 2.12, but in reversible reactions deviations from this value appear¹.

¹ Schenck is referring to Eötvös's law: $\sigma v^{2/3} = k(T_c - T)$, where T is the temperature, T_c is the critical temperature, σ is the surface energy, v is the molecular volume, and k is the Eötvös constant which takes the value of 2.12 for a range of normal fluids. This is a primitive version of the law of corresponding states and can of course be easily derived from density functional theory, although Schenck didn't know that. Relevant references are: R.V. Eötvös, *Wied. Ann.*, **27**, 456 (1886); W. Ramsay and J. Shields, *Phil. Trans. A* **184**, 647 (1893) (*ed.*).

In *p*-azoxyanisole and in several other materials, our experiments always find the normal value of k just above the clearing point. We conclude with a high probability that the chemical composition is uniform and temperature-independent.

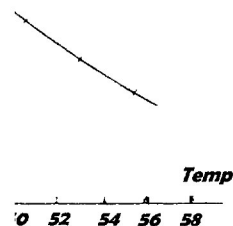
There are more reasons to believe that the cloudy liquids are homogeneous, but time forbids me to pursue this problem further. Tammann's opinion is that the crystalline liquids appear cloudy, and that therefore they must be two-phase systems. This conclusion is unjustified. An emulsion might sustain transmission through a sample between crossed Nicols and the depolarisation of polarised light. However, the strong birefringence which actually occurs would never be seen. Under the microscope one sees that in large systems, the optic axis varies from place to place. Even if the sample is transparent on the smallest scales, such media must, as Professor Lehmann has stressed, necessarily appear cloudy.

I now summarise. Objections have been raised to the hypothesis that crystalline liquids are homogeneous. These objections have been dealt with. The subject area has been exhaustively evaluated from different points of view. A broad experimental basis for Lehmann's viewpoint now exists.

I only need now to answer questions about the relationship between liquid crystals and solids. We cannot consider the liquid crystalline state in isolation. A range of experiments on different materials have shown that liquid and flowing crystals are part of a continuum of increasingly viscous materials. The flowing crystals already possess hints of a crystalline form, but in particular circumstances exhibit surface tension effects. From flowing crystals to soft crystals such as white phosphorus or camphor is but a short step. Soft crystals can be distinguished from true solids only by the degree to which they can be deformed by external forces.

We should consider liquid crystal drops as very soft crystals. Their softness makes them susceptible to surface tension effects. The special optical properties should then be explained by a surface tension deformation effect. The drop structure is a combined effect of the surface tension and the directional forces which occur in all crystals. If one could turn off the surface tension, then these bizarre materials would exhibit what might be called proper crystal structures as well as normal optical behaviour. We have no reason to consider flowing or liquid crystals as particularly special. We should be able to classify them in the normal crystallographic system. Indeed Professor Lehmann has in the past not hesitated to do this.

I have given you a rather brief overview of the field. There are other interesting questions which I have not discussed, but I must refrain from doing so because time is pressing. The demonstrations should speak more convincingly than I. I would like to hope that when you have seen the phenomena for yourselves, you will be persuaded to adopt the point of view I have advocated here.



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Discussion*Professor Tammann*

I am familiar with liquid crystals from personal experience. I want to discuss the central question: 'Are these materials anisotropic or isotropic? Equivalently, has birefringence in these cloudy liquids been conclusively established?'

First: the materials in question have been observed in parallel films between crossed Nicols. Professor Lehmann has described a situation in which the image is divided into segments. When the sample is rotated, their brightness changes. This seems to demonstrate birefringence, and I would not object to calling these liquids crystals. But then one observes that the segmentation and the change in brightness are not properties of the liquid itself. Rather there seems to be an anisotropic dust adsorbed onto the glass plates surrounding the sample. If the liquid is shaken violently the picture does not change. The phenomenon is thus not a property of the liquid. It can be disrupted by interfering with the adsorbed dust. Then no segmentation can be observed. I have made such observations on many occasions, and Professor Lehmann has essentially described the same thing. I conclude from this that the liquid is not itself birefringent.

A second observation is as follows. Professor Lehmann has observed droplets of liquid crystals in Canada balsam. He has seen black crosses and suchlike on their images. I have to confess that these phenomena have given me the most trouble. They do indeed seem to imply anisotropy. But very similar crosses can be seen in the images of air bubbles in Canada balsam, and air bubbles are unambiguously isotropic. Consequently I cannot concede that the so-called liquid crystals exhibit birefringence. In other respects we are certainly in agreement. The anisotropy relates only to optical properties. In all other contexts there is complete isotropy, and this even applies to growth phenomena. All liquid crystals are optically turbid media. They are thus emulsions, and contain at least two components. However, a complete analysis of this phenomenon has not yet been successfully carried out. In my own view, distillation of the liquid crystals offers the best prospect for the resolution of the problem, but this is an extremely difficult task.

We must also take into account that Dr Schenck has found discontinuous changes in certain properties as a function of temperature. However, a discontinuous change in any given property is difficult to establish beyond doubt. Finally I would like to come to the so-called flowing crystals. There are certainly such things as soft crystals. I am happy to concede flowing crystals, but *not* liquid crystals. The existence of liquid crystals is a key question when considering the lattice theory of solids. I would thus assign enormous theoretical importance to the question of the existence of liquid crystals!

The discussion ran out of time and was closed by the chairman. As a result, a reply to Professor Tammann's points was impossible. However, the discussion reconvened in a small group for the liquid crystal demonstration. This had been arranged in the Institute of Physics as part of the afternoon

Session

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programme. Taking part in this were Messrs Lehmann, Tammann, van't Hoff, Schenck, Muller, Elbs and Bredig. Geheimrat Lehmann's main points are contained in the paper presented immediately below. At this meeting Herr Professor van't Hoff proposed the formation of a commission of experts which could examine liquid crystal problems further. This commission should include, *inter alia*, Messrs Tammann and Lehmann.

(end of the official report)

Rudolf Schenck The University of Halle plays an important role in the history of liquid crystals and it is appropriate that Rudolf Schenck was born in that city in 1870. In 1889 he entered the University in Halle to study chemistry. His Ph.D in organic chemistry under the supervision of the well-known chemist Jacob Volhard was awarded in 1894.

Remaining in Halle, his interests then turned to problems in physical chemistry, attempting to determine a relation between the heat of sublimation and the saturation vapour pressure of solids. This work was relatively unsuccessful and in any case came to an abrupt end when his apparatus was smashed by a cleaning lady in the department. Following this incident he retired to the library in a bad mood, and by lucky chance



came across Gattermann's recent publication [A3] on *p*-azoxyanisole and its two liquid states. This stimulated him to study liquid crystals, and led directly to the publication translated in this volume, which supported the Lehmann view of liquid crystals against that of Tammann. This work continued at the University of Marburg, where he obtained his Habilitation degree in 1897 and was then appointed to a lectureship.

In 1906 he was appointed to a full professorship in physical chemistry at the University of Aachen, after which his interests turned to other areas of physical chemistry. In 1910 he moved to the recently founded Technical University of Breslau, where he was the first Rector. In 1916 he moved to the University of Münster in Westphalia, where he was full professor of physical chemistry and worked mainly on problems of metallurgy. He retired in 1935, and even in his seventies and eighties continued to work in the field of metallochemistry at the University of Marburg.

In later years he achieved eminence in German physical chemistry. He was President of the *Deutsche Bunsen-Gesellschaft für Physikalische Chemie* 1933–4 and 1936–41. In particular, although never a member of the National Socialist Party, he was a vociferous Nazi sympathiser and was extremely but controversially active in scientific politics.

Although his research interests had moved, he maintained a parental affection for the study of liquid crystals/crystalline fluids (unlike others he did not allow himself to be drawn into controversy over nomenclature!). As we shall see in the next section, as late as 1930–1 he contributed extensively to the general discussion

on liquid crystals edited by P.P. Ewald in the review volume in *Zeitschrift für Kristallographie* [B4].

Schenck died in 1965 in Aachen. He lived to the ripe old age of 95, the only early liquid crystal pioneer to see the emergence of the beginnings of the liquid crystal display industry and the scientific maturation of the field which he influenced so profoundly.



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