Peter M. Knoll
Hans Kelker

Otto Lehmann

Researcher of the Liquid Crystals

A Biography with Letters to
Otto Lehmann

3 The Discovery of Liquid Crystals

3.1 The Pre-History until 1888/89

In the previous chapter, the development of Lehmann's most important instrument was described, namely the crystallization microscope. His discoveries, beginning with his dissertation (1876), are almost solely due to his enormous clever dealing with this instrument. His theory of the "physical isomerism" is contradictory to Mitscherlich's term of isomorphism and to the idea of similar molecule individuals ("identity-theory") in coexisting phases. Apart from discovering the phenomena of enantiotropy and monotropy for reversible and respectively irreversible phase change, and shaping these terms, Lehmann was an opponent of the identity-theory. He rather assumed that at the phase transition one atom- or molecular compound changes which he calls "physical molecule". In the early days, he never alluded to the lattice changes, but it might be, with some knowledge at that time of highly developed mineralogy and crystallography, it was a well-known fact to him. Therefore, you have to assume that he accepted implicitly lattice (symmetry) transformations as a consequence of a modified form of the "physical molecules". Later, he admits that in the end the changed lattice properties are after all, the basics of both modification changes.

With today's knowledge of crystal structures, which are definable by x-ray crystallography, Lehmann's suggestions of the "physical molecules" are considered as outdated but basically remain understandable, if you identify the "physical molecules" approximately with unit cells. Apart from that, the problems with proving the existence of "free" molecules in condensed phases – unlike gas and solute in an ideal dilution – are all well-known from the latest literature. Studies on polymorphism were most important in his research. He discovered the quintuple polymorphism of ammonium nitrate. He also concentrated on kinetics and morphology of epitaxy and examined the plastic modification of iodine silver, particularly with its electrical conduction and the behavior during electrolysis. A paper on nucleation, boiling point suppression and inhibition of crystallization (1887) shows how universal his domain was.

Anyhow, until the momentous year of 1888, in which Reinitzer's letter arrived, he published about 20 original papers on the subject of "micro- crystallographic researches" and "physical isomerism" and he wrote – to a certain extent for completing this period – the significant work on "molecular physics". Unsurprisingly, he was considered as the connoisseur on the subject of micro crystallography and phase transformations. He corresponded with van t'Hoff, B. Roozeboom and other authorities of his days, and, as an expert on that subject, with Reinitzer and v. Zepharovich. Later, Gattermann and Vorländer gave him extremely interesting test samples, which would become the basis of the entire liquid crystal chemistry and physics.

It is hard to believe which superficial knowledge he gained from the physical science at his days. Characteristic of his work and his style is inspired through a book review of W.Ostwald's of the "molecular physics" (Journal phys. Chem. 2, 982 (1888), 3, 368 (1889)):

The writer brought an exquisitely complex and scattered material together and told us this with abundance, which is almost bewildering. We are concerned with an exquisitely comprehensive and extensive work, from which we can gain infinite knowledge, but no clear picture of the subject in question.

Intensive studies on the plastic modification of iodine silver and on plasticity made him familiar with the state of matter a long time before the year 1888. Later, he explains over and over again, how related plastic crystals, here especially cubic, thus optical isotropic crystals are with "flowing respectively liquid crystals" and how plastic crystals gave him the right ideas about the interpretation of the substances from Reinitzer. As can be seen in the correspondence, this was anything but easy. But when we nowadays compare the thermal analysis of a plastic crystal to that of a liquid crystal, and since we can see that the field of the plastic and respectively the liquid state is limited by two clearly marked endothermic transition points, we are bound to accept Lehmann's viewpoint.

It is regrettable that the announcement of Reinitzer's discovery, and his letters, arrived to Lehmann just at the same time when he packed his bags in Aachen to go Dresden, and not before 1889 when he came to rest in Karlsruhe for intensively spending time on studying liquid crystals.

Figure 3.1 Photography of Friedrich Reinitzer.

Picture provided thanks to Mrs. Dr. Reinitzer, Graz.

3.2 The Correspondence with Reinitzer

Already having observed that a deformation of crystal lattice structures is possible without losing its crystalline properties in experimentations with silver iodide in 1881, Lehmann received a letter from the Austrian botanist Reinitzer on March 14th, 1888, who should cause a crucial turn in his researches. Reinitzer wrote:

Prague, 3-14-1888

Your Excellency

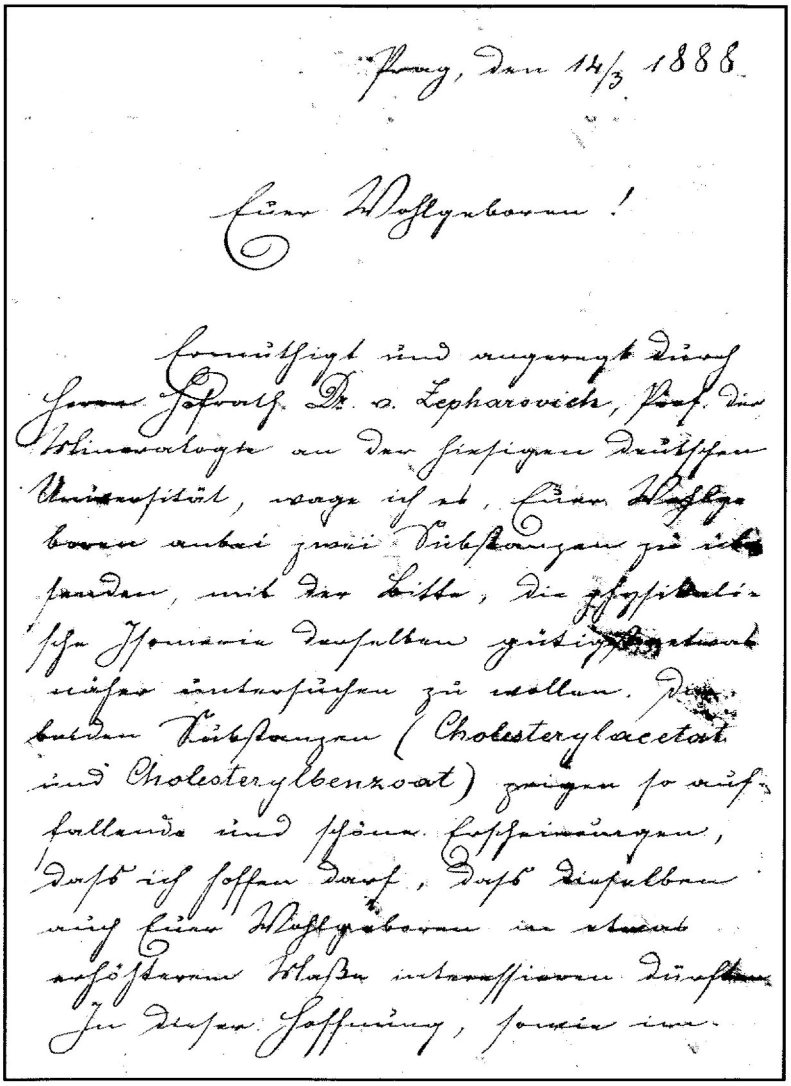
Encouraged and animated by Mr. Court counselor Dr.v.Zepharovich, professor of mineralogy at the local German university, I dare to send Your Excellency two substances, requesting you kindly to analyze their physical isomerism. Both substances (Cholesterol-acetate and Cholesterol-benzoate) show such striking and beautiful phenomena, that I may hope that Your Excellency are to a great extent interested in the same. With this hope and as well as on the behalf of this subject itself, I dare to make demands on your time with a more detailed description of these phenomena. In terms of the aforementioned matter, I basically want to have the opinion reinforced by a brilliant expert such as Your Excellency, that we are really dealing with dimorphism, as several appearances are extraordinary.

1). Cholesterol – acetate. Melting point 114 – 114,4. (Corrected: 114,3 – 144,7 °C) The substance is melting into a clear liquid. If you let it cool down in a wide capillary (as it is used for identifying the melting point) you can make out an appearance of magnificent colors before the liquid congeals. Magnificent violet, blue, yellow and orange-red colors are appearing (in reflected light), which gradually disappear soon after congealing. The heating can be done carefully above an open flame. If you are melting the substance carefully on a slide and covering it with a cover slip, you can already make out, by using a usual or even better a polarization microscope, the cause of the appearance. If you are observing the melted substance with the cross-polarized Nicol prism, suddenly, while cooling down, you can see star-shaped groups of crystals, which appear colorless and highlighted on dark ground. They look like rhombic leaflets. The rest of the substance is liquid, of what you can convince yourself by dabbing on the cover slip whereas the crystals are floating around. Soon, the substance is gradually congealing from the rim namely in its whole mass *e, 3-14-1888*

t counselor
'ocal German
bstances, re-
nerism. Both
rol-benzoate)
t I may hope
ested in the
f of this sub-
with a more
erms of the
the opinion
cellency, that
eral appear-

114,4. (Cor-
g into a clear
(as it is used
t an appear-
als. Magnifi-
re appearing
on after con-
ove an open
y on a slide
ly make out,
croscope, the
melted sub-
ldenly, while
of crystals,
ground. They
e is liquid, of
he cover slip
he substance
whole mass

and becoming huge, star-shaped aggregated needles, that show magnificent polarization colors.



Prag, den 14/3 1888.

Euer Wohlgeboren!

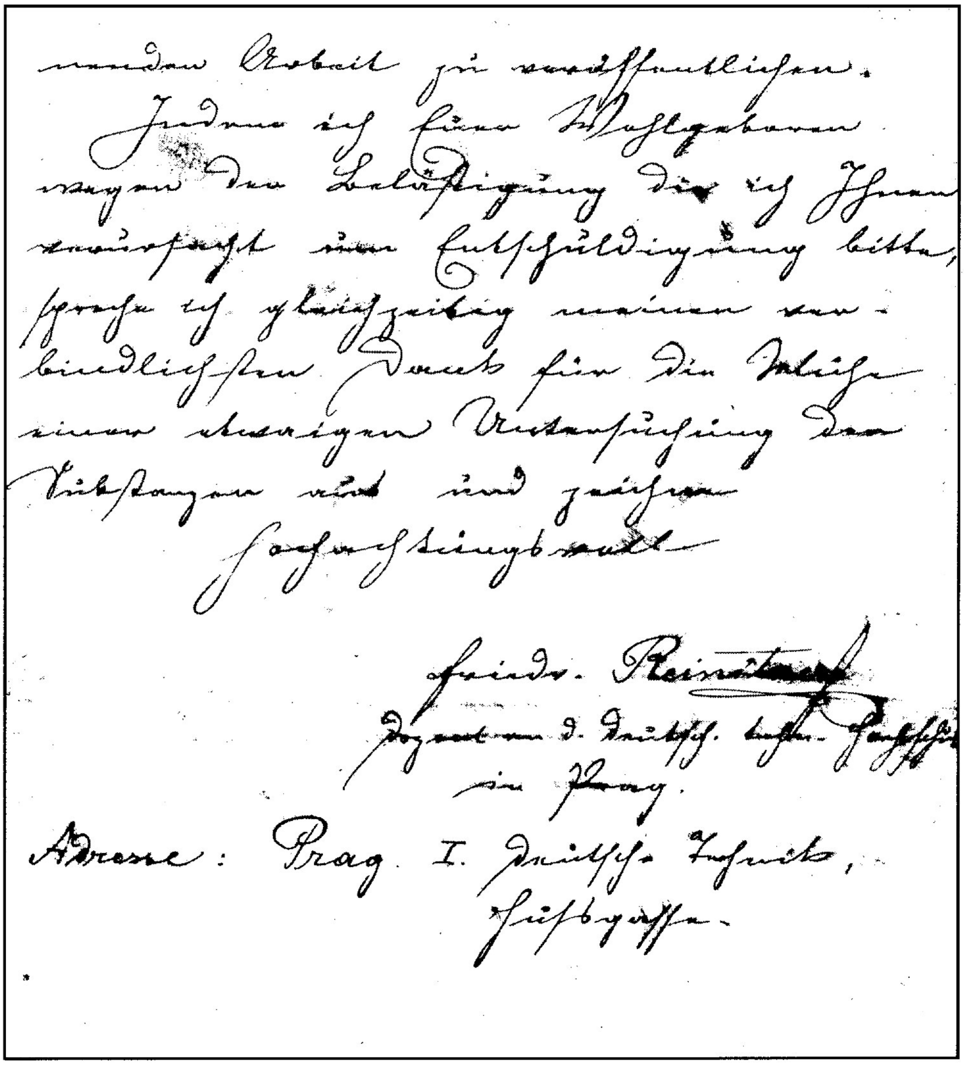
Ermuthigt und angeregt durch
Herrn Hofrath Dr. v. Zepharovich, Prof. der
Mineralogie an der hiesigen deutschen
Universität, wage ich es, Euer Wohlge-
boren anbei zwei Substanzen zu über-
senden, mit der Bitte, die physikali-
sche Isomerie derselben gütigst etwas
näher untersuchen zu wollen. Die
beiden Substanzen (Cholesterylacetat
und Cholesterylbenzoat) zeigen so auf-
fallende und schöne Erscheinungen,
daß ich hoffen darf, daß dieselben
auch Euer Wohlgeboren in einem
höheren Maße interessiren dürften.
In dieser Hoffnung, sowie im

Figure 3.2 Letter of Reinitzer to Lehmann from March 14th, 1888 (1st page)

In a similar way, Reinitzer described the observations on cholesterol- benzoate:

Cholesterol - benzoate. In all, this one is very similar to the previous substance. However, a phenomenon is added here. In particular the substance has two melting points, if I may so express myself. At 145,5 degrees, it is melting at first to a completely cloudy liquid. The same is suddenly becoming absolutely clear at 178,5 degrees. If you let it cool down, at first a violet and blue appearance of color is appearing, which quickly disappears, whereon the mass stays milky cloudy and liquid. With further cooling down once again the violet and blue color appearance is appearing and right afterwards the substance is congealing to a white crystalline mass. By the use of observation under the microscope in the abovementioned manner, the following can easily be established: while cooling down here at first star-shaped, later huge radial spicular aggregates are appearing. In the former case, the clouding is not caused because of crystals but because of certain liquidity, which forms in the melted mass oily stripes and appears bright at cross-polarized Nicols. It is obviously the melting modification of the substance at higher temperature, but in crystalline state. The change from: color appearance, to clouding, to color appearance can be explained in this way, that the crystals that are formed by cooling down, at first become big so fast, that they don't show the colors of thinner leaflets anymore, but they only cloud the liquid. During the following dissolution, they become thinner again and for that reason the color appearance reappears again. These are the observed phenomena.

To me, most conspicuously is at first the simultaneous appearance of crystals and amorphously melted mass, whose state regarding the acetate doesn't last very long in contrast to *the benzoate, but the substance in its whole mass doesn't change to star-shaped crystals. ...*



...renden Arbeit zu veröffentlichen.
Indem ich Euer Wohlgeboren wegen der Belästigung die ich Ihnen verursacht um Entschuldigung bitte, spreche ich gleichzeitig meinen verbindlichsten Dank für die Mühe einer derartigen Untersuchung der Substanzen aus und zeichne
hochachtungsvoll
Friedr. Reinitzer
Assistent d. deutsch. techn. Hochschule
in Prag.
Adresse: Prag. I. deutsche Technik,
Hussgasse.

Figure 3.2 Letter from Reinitzer to Lehmann, March 14th, 1888 (last page)

Reinitzer comments in succession on similar observations on other cholesterols, adding the crystal measurements made by Prof.v.Zepharovich and concludes by saying:

I permit myself to send enclosed: a capillary tube crystallized with cholesterol-acetate fused inside a capillary; another capillary tube of cholesterol – benzoate as well; and finally a capillary tube with pure cholesterol in case that Your Excellency want to check the same for isomerism. ...

Now I permit myself to ask you kindly to tell me the most important results of your eventual tests and to permit me to publish the same (of course with reference) in my probably soon appearing paper.

Apologizing to Your Excellency for the nuisance I caused, I owe you at the same time a debt of gratitude for all efforts of a possible test of the substances.

Yours sincerely

Friedrich Reinitzer
Lecturer at the German Technical University
in Prague

As it unfortunately can not be traced back from the available correspondence, we don't know what Lehmann's reply to Reinitzer was. It is certain that Lehmann immediately started with the examination of the substances and reported his observations to Reinitzer already on March 27, 1888. To this, Reinitzer wrote in a paper [27] about the history of the liquid crystals in the following:

On the 27th of March, he wrote to me that on the basis of a lack of time, he could not deal with the examination as he wanted to and he sent me a description of the three modifications of acetate and benzoate, which he had *found, as well as his observations of color appearances. Thereby, he mentioned that my star-shaped crystal aggregates are not crystals, but drops, which get their serrated shape from the enclosed crystal leaflets, which can only be noticed with the help of high magnification.*

The next letter from Reinitzer is dated from April 2nd, 1888. He wrote:

First of all, my sincere thanks for the kindness and effort with which you have done the examination with the substances I sent you. By confirming the receipt of your highly prestigious writing from March 27th and the postcard from March 31st, I simultaneously want to beg your pardon that I wasn't able to answer earlier. The reason of the delay was bereavement.

Coming down to business, I deeply regret that the cholesterol-acetate wasn't completely pure (what I didn't know) and I forgot to tell that the cholesterol turns the polarization to the left.

It is quite possible that the acetate and the benzoate as well turn their degree of polarization. Under these circumstances the observed turning could be very much influenced, as we can see from the fact that the pure acetate reacted differently in contrast to the one which was contaminated with cholesterol.

In terms of the "powder", the additional observation of crystal lamellae has only been so much changed, that the turn of the degree of polarization can only be explained through the presence of these crystals. However, I believe that I can assume that the presence of the droplets can be omitted completely. I am much more willing to assume that the crystals of the powder at that high temperature, which also is close their melting point, are so soft that they can be quasi kneaded and *break into fragments, which mingle with the liquid. This assumption is in my opinion not that ventured as you can macroscopically see that both cholesterol and its derivatives show right after the melting point a tough and resin like consistency. Besides, I want to say that right after receiving your first letter I immediately observed the "powder" with intense magnification, for which I admittedly have no polarization devices and I doubtlessly made out crystals.*

In terms of the chemical explanation of the development of the powder this is definitely anything but easy. The concerning matter could disintegrate in the following way: 1.) regression of acetic acid or benzoic acid on the one hand and of a hydrocarbon (cholesterol) on the other hand. Although several cholesterols are known of which the properties fit to the phenomena we find here, case 1.) is unacceptable, as here the acetic acid and benzoic acid respectively vanish and therefore you have to notice the smell as well as the phenomenon would stop after several repetitions. Case 2.) Decomposition of the cholesterol nucleus into unknown matters. As the chemical constitution of cholesterol is yet totally unknown the basic principles for a theory are missing. But since you know that cholesterol is very resistant, the assumption is quite unlikely. Case 3.) The cholesterol (in compound) converts into an isomeric, metameric or polymeric molecule (in the chemical sense). This assumption is in any case the most probable one. Here we have the same idea as with the assumption namely of physical isomerism where it is not obvious why the conversion happens only partly and not with the whole mass. Thus, the available observations regarding the decision on this are not sufficient. However I will make the attempt to keep the powder in its current state by the use of filtration of the benzoate, which is melted to a cloudy liquid, and perhaps with additive *of xylene. The kindly provided manuscript might be too detailed for a purely chemical paper, if the print was left unchanged. Thus, I just want to compile the results or if you do not prefer and want to do this on your own. In order that the same could be printed word-for-word.*

In terms of the other substances that have to be observed as well, by all means I can wait and I don't want to bother Your Excellency with these examinations as long as you are otherwise engaged. I'm simply publishing a part of my work for which present findings are sufficient. Therefore, I'm asking you to inform me as soon as you are willing to continue the examinations and informing me as well which of the mentioned substances I should send you.

As you probably intend to publish your work otherwise, you may again need the manuscript. Therefore, I permit myself to ask you when I should send the same back again.

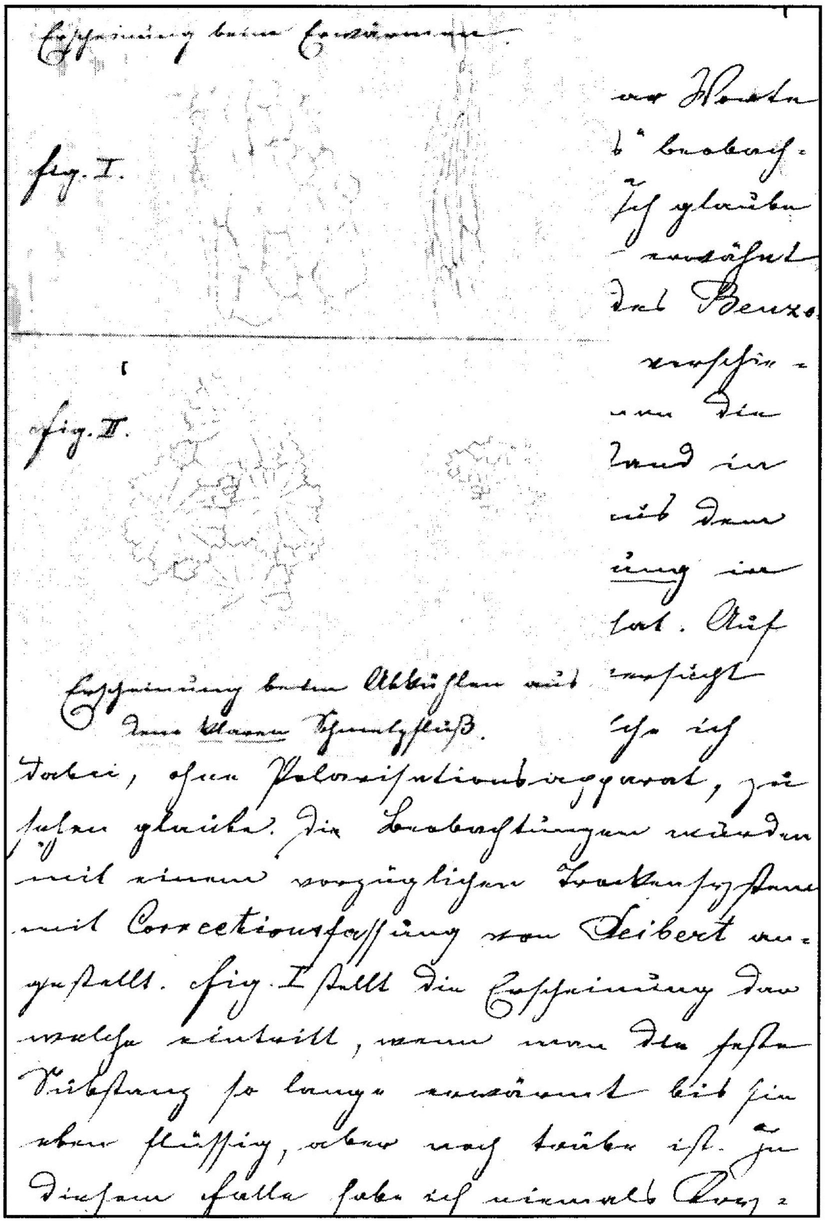
Lehmann replied immediately on March 4th. To this Reinitzer wrote [27]:

In his reply from April 4th, Lehmann at first asked me for more material as he will find time during his summer term to keep himself busy every now and then. Then, he told me that the major difference between his and my observations is the fact that I can clearly see crystals, but he however cannot and he concludes their presence from the polarization appearances. He added a drawing which clearly shows unsteady limited drops with cross polarization. You can see that we both came close to the realization of liquid crystals but without taking stock of it.

In his reply from April 10th 1888, Reinitzer wrote:

According to your request, I permit myself to send you enclosed more of the substances which are to find in the examinations. Furthermore, I also add the acetate and the benzoate *of hydro-carotene of which the matter is like the according derivatives of cholesterol. The only difference is that the temperatures, at which the different phenomena are appearing, are consistently lower. At the same time, I also permit myself to send you the bound scientific paper I published on these matters. Yet, I don't have crystallographic examinations on these matters. The substances are very precious as the results of the presentation of hydro-carotene are relatively small. In terms of hydro-carotene benzoate I sent you all I had, unfortunately not very much. I don't possess cholesterol-amine and first have to give a description of it, as my time is restricted and as the description is also complicated, I have to ask for your patience during the next months. Finally, the bromine-cholesterol-acetate, which I got in two different crystal forms, might not be appropriate for the mentioned examinations because after the melting, it stays vitreous and can't crystallize anymore, and probably might decompose. After all, I am content to send you this if desired. I still have a bit of that matter. Now, I want to say something about the "powder" situated crystals I observed. I remember mentioning already in my first letter that the cloudiness of benzoate looks different under the microscope- depending on substance, either if you are changing it from solid state to cloudy fluidity or from clear fluidity by cooling to cloudy fluidity. On the enclosed sheet of paper, I tried to demonstrate the pictures which I believed to see without polarization equipment. The observations were made with an excellent drying system with correction lens from Seibert. Figure 1 shows the phenomenon which appears when heating the solid substance until it is liquid but still cloudy. In this case, I've never seen crystals but only never uniting drops. Figure 2 shows the phenomenon which appears when heating the clear liquid substance to at least 178,5 degrees, and afterwards you let it cool down.*

ording de-
e tempera-
aring, are
myself to
these mat-
s on these
ults of the
n terms of
nately not
st have to
as the de-
r patience
holesterol-
ight not be
e after the
more, and
send you
I want to
tals I ob-
letter that
the micro-
hanging it
ty by cool-
r, I tried to
hout pola-
ith an ex-
ert. Figure
eating the
this case,
s. Figure 2
g the clear
fterwards


Erscheinung beim Erwärmen.
fig. I.
fig. II.
Erscheinung beim Abkühlen mit dem warmen Schmelzfluß.

... er Worte
... t beobach-
Ich glaube
... erwähnt
das Benzo-
verschie-
... en die
Rand im
mit dem
... ung im
... tat. Auf
... erfolgt
... ich
dabei, ohne Polarisationsapparat, zu sehen glaubte. Die Beobachtungen wurden mit einem vorzüglichen Trockensysteme mit Correctionsfassung von Seibert angestellt. Fig. I stellt die Erscheinung dar welche eintritt, wenn man die feste Substanz so lange erwärmt bis sie eben flüssig, aber noch trübe ist. In diesem Falle habe ich niemals Beug-

Figure 3.4 Excerpt of the letter from Reinitzer to Lehmann. The sketches are affixed on the margin, April 10th, 1888

*In this case, in the completely clear visual field, suddenly the crystal figures pictured in figure 2 appear, which I already defined in my first letter as star-shaped. As I don't have sufficient equipment for heating the stage, I can observe the phenomena only for awhile (few moments) and for that reason you can't make a claim on the precision of the drawing. But it might show the approximate picture. Now I assume that up to now you created the cloudiness maybe just by heating but never by cooling down in that way as it is mentioned above. I excuse myself for supposing that but for now I can't really believe that what is mapped in figure 2 shouldn't have a faint resemblance to a crystalline structure. In consequence of your converse statements I elaborated the whole phenomenon and I think I noticed some more important facts which I want to communicate to you here. But before I do so, I have to emphasize that, as I said before, I could only observe a few moments and fallacies can easily come up in order so that I am not totally sure of everything. Looking at the phenomenon in polarized light that is pictured in figure 2, you can see in every star-shaped crystal aggregate a cross, which seems to be dark blue on pale yellow ground for crossed Nicols. Upon turning the Nichol, the color changes but the cross doesn't turn around. As the object is cooling down, the cross is getting keener and clearly begins to turn around with Nicol. Finally, a liquid and isotropic liquidity *) appears between the star-shaped aggregates. So, the aggregates are melting circumferentially (during cooling down!) and swimming as solid matters in a liquid, which of course appears black along with crossed Nicols. Already at the same time, crystals – in which the substance is turning into while freezing – are coming from all sides quick like a shot. Because of these phenomena, I think I can reason that the substance, of which the state is pictured in figure 2, is congealed in its whole mass and consequently really has two freezing- and melting points respectively. This point of view raises again the question if this state in* *fig.2 doesn't correspond to a fourth "physical isomeric" modification and I want to ask Your Excellency to take the same into consideration, if my previous statements prove themselves true. ...*

At the time when the discussions on the discovery of liquid crystals already arouse, one thing is worth remarking: as one can assume from the handwriting we find here the probably later affixed, handwritten note of Lehmann marked by *) (see figure 3.5, left rim):

This liquid is not isotropic, but crystalline (pseudo-isotropic) and identically equal to the crystals which are liquid, not solid.

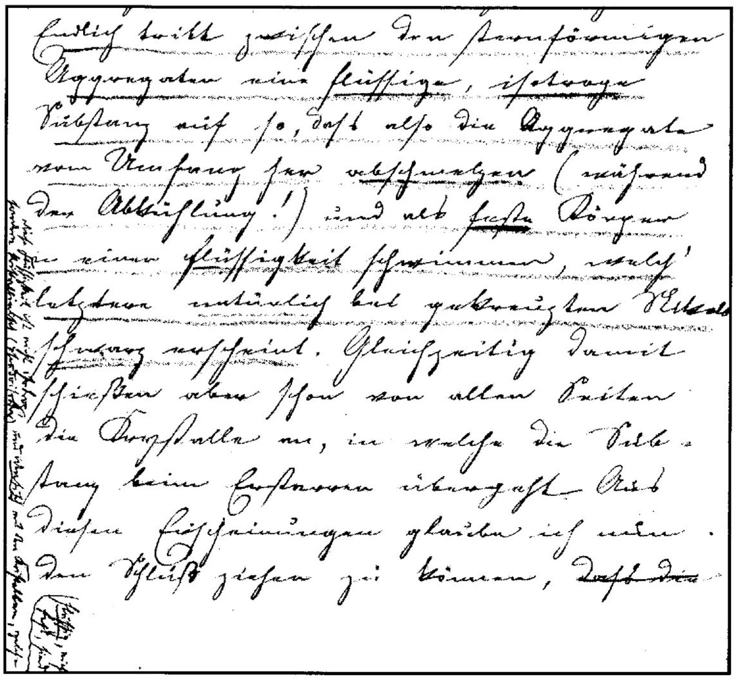

Endlich tritt zwischen den sternförmigen Aggregaten eine flüssige, isotrope Substanz auf, so, daß also die Aggregate vom Umfang her abschmelzen (während der Abkühlung!) und als feste Körper in einer Flüssigkeit schwimmen, welche letztere natürlich bei gekreuzten Nicols schwarz erscheint. Gleichzeitig damit schießen aber schon von allen Seiten die Krystalle an, in welche die Substanz beim Erstarren übergeht. Aus diesen Erscheinungen glaube ich nun den Schluß ziehen zu können, ~~daß die~~

Figure 3.5 Page of the letter from Reinitzer to Lehmann with his handwritten note, April 10th, 1888

Lehmann replied on April 13th. Reinitzer writes about the topic of the letter in [27]:

He explained that, due to my drawings, he now is able to make out the analogy between his and my observations. The sole exception is that he has never seen such beautiful orthogonal serrated shapes as my drawing illustrates. But what bothers him most is the fact that he can't deduce the crystals so that he could have clearly observed the boundaries.

Lehmann wrote:

The present preparation is the first one which seriously perplexes me so much, that, if the polarization phenomena and the sometimes firmly adhesion of the figure on the glass wouldn't indicate that these are crystals, I rather want to think of drops, though I never could have seen the characteristic spherical shape. ...

You can get very beautiful almost circular forms with a black cross around which the rest of the already liquid mass is floating and in which the forms are disappearing bit by bit. With slower crystallization, you can even get quite simple figures which don't show the black cross anymore but extinguish consistently as real crystals but always with blurred edges. The bright stripes that form the network on the cholesterol-benzoate are obviously similar. At the point of the cross, they show clear rudiments of the black cross and they extinguish, if linear, lengthwise at the same time, but they are so flexible that they at least can be considered as aggregates of extremely fine lamellae. But why do they arrange in that way so that the direction of oscillation is parallel and why do they arrange in the enclosed mass in that way that it shows circularly polarized colors? I can't understand this point if these are really *crystal lamellae and I unsuccessfully observed yesterday and today for hours the phenomena. Also privy councilor Wüllner observed with me these stripes and lamellae several times and we could not figure it out by any stretch of imagination.*

Reinitzer annotated to this in [27]:

This passage is very informatory. You can see how extraordinarily close Lehmann came to the realization of the liquid (or flowing) crystals and still, he wasn't able to specify on it and to break away from conventional views. If he then would have been familiar with the term of liquid crystals of iodine-silver, as he subsequently thinks, he had to strike on this idea immediately and it would have been impossible not to realize this through observations lasting for hours. At one point in the letter, it is conspicuous that because of my substance he had to face a completely new problem which was with the former views unexplainable and therefore forced him to find a new explanation.

In his letter from April 20th, Reinitzer replied:

At first, thanks for sending your 3 scientific papers about the construction of your microscopes. ...

As well, I'd like to thank you for clearing up the erroneous opinions of my observations and I regret having bothered you with that. With best thanks, I now return to you the notes about the acetate and benzoate of cholesterol that you sent me earlier on, as I already took the notes which are intended for the publication. Moreover, I enclose a small sample of the bromine-cholesterol-acetate in addition. It is a bit contaminated by fiber and dust particles but it is quite pure, though. I also want to annotate that it's a bit sensitive to light. After 3-4 weeks in the scattered daylight it becomes, with evolution of hydrogen bromide, yellowish and finally brown, where it loses *its ability to crystallize. It should be advised to protect it from light as much as possible. ...*

Because of personal obligations, I am forced to send my previous examinations for publishing by the end of April at the latest. From your relevant examinations, I will only tell the facts without attempting to give an explanation and briefly indicate the difficulties of the explanation, at most. At this occasion, I also want to ask you to tell me if the observed crystals in the "powder", seen with help of intense magnification, can also be found as well in benzoate and acetate or just in either one. Because of a note in one of your last letters, I had my doubts about it. Moreover, I want to mention that I will permit myself to modify the names of the three modifications. I will name the modification that you get from solvents at normal temperature, as the 1st one, the other ones will be named 2nd and 3rd, just in the order you have done it. Nor will I use the word "powder" as I consider this just as a convenient expression used in the correspondence. ...

Finally, I want to permit myself to inform you about an observation that I recently made and which is maybe quite interesting. That is to say that I melted many times a bit of cholesterol-benzoate (without adding any other matter) on a slide for observing its color appearances. Through this, it decomposed a bit, became slightly yellow and in the heat of melting, it became viscous. Besides, it showed a certain tendency to stay partly vitreous while freezing. This changed benzoate has now a feature so that can make the color appearances lasting, even at normal temperature, after the substance is completely solidified (!).What is necessary is that you have to cool down the whole mass right away (by putting it on a cold metal plate). In front of you is a completely hard, inflexible mass which shows a more or less bright blue stripe. If you gently heat the mass, *there is suddenly a change, as the blue color quickly disappears and the regarding area seems to be milky- cloudy. Under the microscope, you can see in the blue area numerous, very small leaflets laying there completely disarranged. With a crossed Nicol, they appear brighter (colorless) in a dark background and are all smaller when the concerning area macroscopically appears more in a beautiful blue. The leaflets just look like the eroded crystals in a solution. At some points, the blue starts losing its color and between those leaflets equal but bigger, and in polarized light, colored leaflets are appearing, which also appear while freezing of the not decomposed substance under normal circumstances. In this decomposed benzoate, I could see twice, along with appearing of the blue color appearances, really beautiful asteroidal aggregates, exactly like I described them in figure 2 in my last letter, but now with much more beautiful angles and edges which were so clear that I cannot doubt of their presence. Unfortunately, I wasn't able to cause these phenomena again. Now, I also notice that I did almost all my tests with the same substance. The same might be decomposed earlier and therefore showed the star outline more clearly. Despite all effort, I'm indeed not able to get the star outline by using a fresh substance. Perhaps we should look here for the cause of our different observations? Enclosed, I send you a (broken) slide with modified benzoate that shows the color appearances at normal temperature. The abovementioned leaflets can be clearly seen by name on page no.3. I'm noticing that you could also consider them as cohesive, vitreous and solidified mass. From the pages 1 and 2, fresh and not decomposed benzoate is added as you can clearly see. Maybe, this observation shed some light on this mysterious phenomenon. I'm asking you not to keep* *yourself from work just because of my substances as this concern has no hurry.*

Yours respectfully
Fr. Reinitzer

Along with this writing, Reinitzer sent Lehmann the slide with his original substance, which he analyzed constantly. However, Reinitzer wrote in [27]:

> *...for the time being he didn't take notice of it. He turned his attention rather to the "oily stripes".*

Lehmann replied to Reinitzer on April 24th [27]:

> *... what is a mystery to me are the bright "oily stripes" that allegedly should consist of such crystal lamellae, which extinguish consistently, and at the crossing points they look like the isolated lamellae, whereas the mass between the stripes shows beautiful polarization colors. The edges of the stripes are often even and the flexibility is so high that you necessarily have to consider them as liquid. Especially beautiful is the mix of cholesterol- and hydro-carotene-benzoate that the phenomenon shows. From time to time you can see isolated lamellae that stick to the slide whereas the oily stripes flow over it. Nevertheless it seems to me that the polarization of the stripes is similar to the one of the lamellae. Indeed it seems that all transitions between crystalline lamellae and liquid stripes are possible, i.e. here the impossible becomes possible. Wüllner said that the substance gives a weird impression on him. Just as with me.*

With this letter the correspondence broke off for 16 months. On August 20th 1889 Lehmann wrote to Reinitzer:

> *As a consequence of changing my workplace twice (Aachen-Dresden and Dresden-Aachen) I was not able to continue*

working on your interesting preparations. Recently, I got some inspiration and so I used it for going into detail about the conversion of cholesterol-benzoate into the slimy mass, which was earlier called "powder", whereas perception was very helpful, namely that you can get the thought-after substance through longer heating and that it is mixable with the molten mass without lowering the melting point.

Further he wrote:

In terms of the results of these newer examinations, they confirm an opinion that you expressed earlier, namely that the "powder" consists of very soft crystals which have to be considered as physical isomeric modification of the substance. The mass is completely consistent and as you assumed earlier, there is no other liquid beside these crystals.

The letter ends with this sentence:

For the physicist, however, it is particularly interesting, that crystals do exist and those are so soft that you can almost consider them as liquid.

Reinitzer replied on August 30th, 1889:

I was pleased getting to know that my suspicions about the substance called "powder" at least were partially confirmed with the help of your newer examinations. Especially important to me is the fact that the figure is a physical isomeric modification, and not a product of disintegration. Therefore the latter assumption from the chemical point of view is hard to explain. There is another point which I don't understand clearly. While heating the cholesterol-benzoate, the color phenome-

non appears at first, then displaced by an evenly gray cloudiness, reappearing during the disappearance of the latter, and only when it disappeared again the liquid is melted clearly. So now what is the cause of the color phenomenon that appears twice? I have the impression that a certain size of crystals is required for the color phenomenon, which comes about the first time when the crystals are growing and the second time when they are melting. If this supposition is correct, it still has to be proved.

At this point, Lehmann made a marginal note on Reinitzers letter:

The 2nd time round the reason is the appearance of a 2nd liquid crystalline modification.

In [27] Reinitzer commented later on these two letters:

From that, it is evident that Lehmann, only after 16 months, addressed himself to my last observation that I sent him on April 29th 1888. Only now, in a relatively short time, the circumstances became clear to him because already on August 30th 1889, 10 days after this last letter, he sent to the journal of physical chemistry his paper "About Liquid Crystals", in which he basically informed about the observations on my substances. This paper concludes by saying: "If you admit the interpretation of the observations, so there now would be existing just one single case, that a crystallized and highly birefringent substance has such little stability that it is not able to resist even the effect of its own weight. [36].

In one letter to Reinitzer from May 25th 1908, when the discussion about Lehmann's article of the discovery of liquid crystals was in full swing, Lehmann describes the reasons that led him to name the term "liquid crystals":

According to your wish I send you enclosed (asking you to send it back after use) your letters from 3-14-88 (2 sheets), 4-2-88 (2 sheets), 4-10-88 (2 sheets), 4-20-88 (2 sheets) and 8-30-89 (2 sheets) after I previously have done a copy that caused delay for what I want to express my regrets. Because of a flood in the storage room due to water-pipe rupture, they are slightly damaged.

By going through it again the circumstances then become clearly evident to me.

In Wied.Ann. 24, 23, 1885 I already talked about the waxy soft iodine-silver-crystals, but then I found on page 26 and 27, that there can be observed even more crystals which are easier deformable and that get blurred like oily liquids (molecule-physics I 826 fig. 351 and 352) by slight electrostatic forces at electrical continuity. In Aachen I also gave a speech on that and I still have the board with the demonstrations on which the flowing appearances are pictured better and more detailed as on my treatises. They are made with liquid air that only were available to me back then in Aachen.

The conversations with Forchheimer, Ambronn, Wüllner and others referred to this oily flowing of iodine-silver-crystals and I remember very well that I earlier spoke about "liquid crystals". At the time your preparations arrived I already intended to write a paper on this flowing of iodine-silver-crystals but I was dissuaded from doing this because of general protest that I had to face and probably because of my own observation, that this oily flowing of iodine-silver-crystals has only been simulated by ionic migration. This however I first saw this clearly in 1889 in Karlsruhe. My paper referring to this was published at the same time with the paper about flowing crystals (Wied.Ann. 38, 398, 1889), where it is explicitly said that I *was wrong about the slight distortion. From this it follows conversely that at that time the idea of oily, slight flowing crystals was a common term to me.*

The reason why I didn't think of those at first, while using your preparations, is due to the fact that I only (considering the small amount of substance I had) worked with the tiny portions under a cover slip, that is to say that I hadn't the opportunity to see the flowing of the mass and getting the right idea of its consistency. I completely trusted in your letters and of course I assumed that what you told about the consistency is correct. However you always spoke (by meaning the liquid crystals) of freezing of the isotropic melting into solid crystals of a physical isomeric modification, and that they have exactly the same form (rectangular leaflets, in reality pyramids) as those of the common solid modification. Furthermore, they are also having sharp edges and angles which were eroded, crumbled and exist at the same time with an isotropic liquid, which appears black between crossed Nicols.

Not before 1889 in Karlsruhe, I found out that the isotropic liquid, as you referred to it, is by no means isotropic, but birefringent and it only seems to be isotropic (pseudo-isotropic) because the principal axis automatically turns from all sides vertically to the glass slide. Your leaflets, that should cause the color appearances, are by no means leaflets and don't cause the color appearances, but that above all they are not solid, but liquid and identical with the pseudo-isotropic liquid. Today this is easier said than done, but to get this far I had to made every effort and without the preparatory work on iodine-silver, from which I already was familiar to the idea of liquid crystals, I'd never came to that conclusion, as the observation of the growth and the waxy behavior of cholesterol-benzoate is very difficult.

it follows
ıt flowing

hile using
onsidering
h the tiny
n't the op-
g the right
etters and
onsistency
the liquid
d crystals
ve exactly
amids) as
, they are
e eroded,
pic liquid,

e isotropic
, but bire-
tropic) be-
sides ver-
cause the
on't cause
not solid,
uid. Today
d to made
line-silver,
quid crys-
rvation of
enzoate is

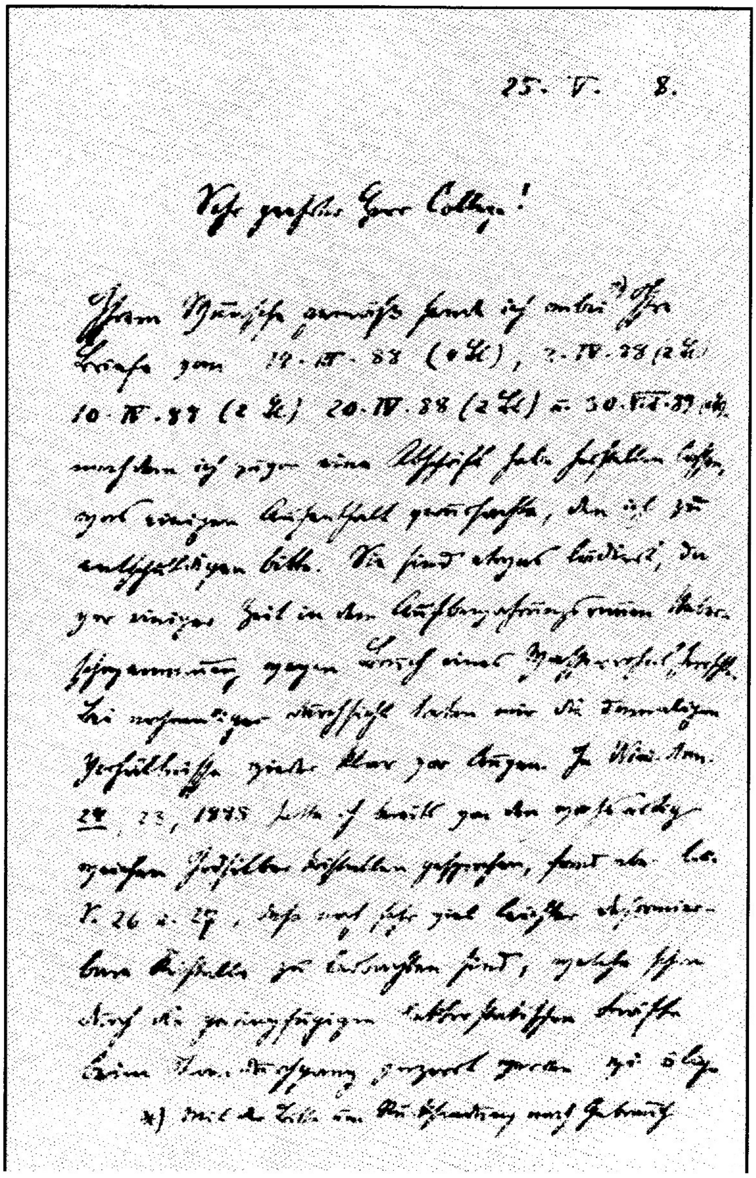


Figure 3.6 Letter from Lehmann to Reinitzer (1st page), February 25th, 1908

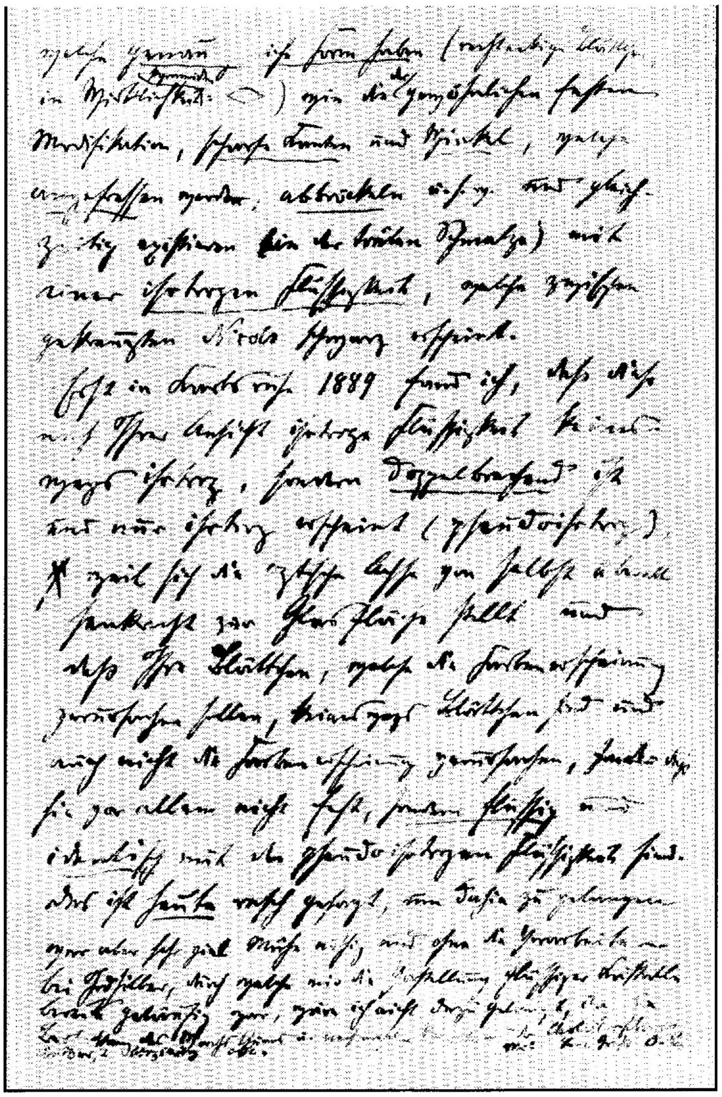


Figure 3.6 Letter from Lehmann to Reinitzer (last page), May 25th, 1908

In 1914, he commented similarly in a publication in the Physical Journal [28]:

Being occupied with examination of iodine-silver as well as with the myelin forms of ammonium oleate which I still consider as mushy masses, *Lehmann appealed to me for clearing up the cloudiness of melting of the cholesterol-benzoate he had observed and the appearing color iridescence in it as well as the aggregation polarization between the crossed Nicols. Vorländer states that I immediately noticed the obvious connections to that what I found in iodine-silver. That is not correct as I couldn't see crystals in this cloudy melting and therefore, I couldn't test if they are liquid. The mass seems to be a pulp just like ammonium-oleate-myelin. Reinitzer himself as well considered that while cooling the cloudiness is caused by the iridescent thin crystal leaflets, which are swimming in the isotropic melting. Vorländer writes (i.c.): what was missed in terms of the inorganic salt (iodine-silver) namely the birefringence in liquid state that was given by Reinitzer's new compound. Reinitzer didn't fail to notice that the birefringent liquid has a new form because he writes about "star-shaped aggregates that cause the cloudiness of the liquid". Indeed, Reinitzer meant solid crystals however he didn't write about a birefringent liquid, but only about "oily stripes" of a higher melting modification which are formed in the isotropic melting and appear birefringent because the tiny crystals in those were adjusted parallel by the flow.*

Only after many continued tests I found out that Reinitzer's isotropic liquid, in which you can find crystals and oily stripes, is different from the isotropic melting. However, according to the substance, it has to be identical with the little crystals and oily stripes because it has the same solubility, so that it seemed to be most probable that this is a random aggregate of the same molecules of which even though it consists of solid but very soft crystals and oily stripes.

After a side blow against a colleague….

R.Brauns is even today of the opinion that Reinitzer's isotropic liquid with its oily stripes is identical to the isotropic melting!

… he continues:

Only after the discovery of liquid crystals of ammonium-oleate, I came to full clarification in terms of Reinitzer's cloudy melting. With the help of the objections of H.Ambronn and G.Quincke I was led to these examinations. They defended Reinitzer's and my primary assumption, that it is a heterogeneous mushy mass, against my statement published 1 ½ years later, that it is a homogeneous flowing-crystalline modification. The argumentation was that the phenomena were exactly the same as with the myelin forms of ammonium-oleate and lecithin, with their heterogeneous and mushy constitution there is no doubt.

With the ammonium-oleate-hydrate, I succeeded now for the first time to produce the definite proof that liquid crystals really exist. The polyhedron form of the direct grown little crystals can only be explained by (more or less disordered) space lattice structure. The appearance of spontaneous homeotropic alignment, the immediate self-recovery of the structure after deformation, fragmentation or coalescence of crystal individuals eliminates the existence of an elastic limit. So what we have here are undoubtedly crystals, namely liquid crystals. So, the problem was now solved and I could start to think about publishing the paper about liquid crystals, which was published right after that.

After that, Lehmann found and discovered more than another 100 liquid crystalline substances. He differentiated between two types of anisotropic liquids:

1.) The so-called "dropping liquid crystals" (e.g. p- Azoxyphenetol or p-Azoxy-anisole) equal to a one-dimensional order of molecules, filament form = nematic phase according to Friedel. After Lehmann's observations these dropping liquid crystal substances show in levitating drops a spherical form and they are anisotropic. However, they often have an isotropic spindle inside which twists to a helix by slightly adding a solvent. Figure 3.7 pictures a hand-made sketch from Lehmann. With a temperature drop between topside and underside of the drop, the helix can rotate.

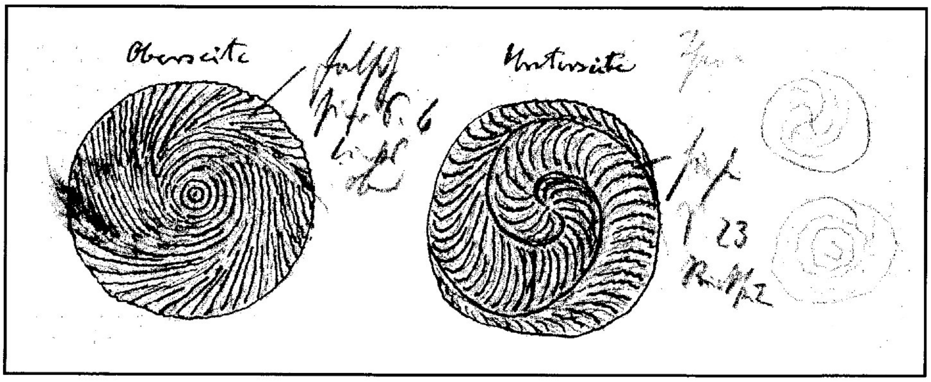


Figure 3.7 Hand-made sketch by Otto Lehmann

2.) The so-called "mucous liquid crystals" (e.g. ammonium-oleate) equal to a two-dimensional structure of molecule compound = smectic phase according to Friedel. On those, Lehmann observes typical formed areas like little rods or double cones which heal up on their own after a division or coalescence of similarly orientated areas ("creative power contingent on molecules"). Because of coalescence, sometimes twin structures in form of "conic disorders" arise. Lehmann also observed "mixed crystals" of liquid crystalline substances.

The crystal drops show (like solid crystals) during the growth "self purification ability". Some of the substances that Lehmann found show distinctive formation of trichina, i.e. growth of long stretched birefringent filaments which originate from the abovementioned spherical areas.

3.3 The Struggle for Scientific Validation

Lehmann's works and publications about liquid crystalline substances aroused many and lively discussions. Despite his extraordinary mathematical talent, his working method on the crystallographic field was only observant and descriptive [17]. His tests were partly very complicated and subtle and hardly reproducible for others without special microscopy equipment. To this, Lehmann says in a letter to Tammann:

> *... these difficult and precise works, on which I worked for years, cannot be demonstrated just within some hours. I even made my examinations mostly after midnight because the vibrations of the frequent traffic near the institute disturbed my observations.*

This made the discussions of his results difficult because they didn't fit in the then rationalistic-scientific world view of the 19th century. This favored the skeptical attitude of many of his colleagues from the sphere of physical chemistry, who partly, sharply criticized his publications, which mostly were publications and lectures, and doubted on the existence of liquid crystals.

Most of all, Lehmann was sharply criticized and combated by the physicist and chemist Tammann from the University of Göttingen. Lehmann was very enraged and indignant at a comment in a discussion that Tammann said at the meeting of the German Bunsen Association on the 3rd of June, 1905 in Karlsruhe. The meeting consisted of 660 members of whom 180 were present in Karlsruhe. The meeting was under the patronage of the Grand Duke of Baden, Friedrich I., who was represented by his son because the Grand Duke was at the wedding ceremony of the German crown prince.

Among other well-known scientists, Wilhelm Ostwald, Walter Nernst, van t'Hoff, Tammann, Bredig, Dolezalek, Förster; Lehmann and the young Schenk were present. Tammann, who was a clear thinker and outstanding experimenter, saw himself as the representative of modern physical chemistry and in terms of the topic "liquid crystals" he represented the motto "what must not be, cannot be".

In the afternoon of the 3rd June, Schenk pronounced a speech on the topic:

About the nature of crystalline liquids and liquid crystals.

It was a brilliant defense of the observations of Lehmann, who just celebrated his 50th birthday, and it was a convincing demonstration that liquid crystals do really exist. Sure enough, Schenk didn't omit replying – however objectively and moderately- to Tammann's attitude, by which the emulsion theory was reduced to absurdity. Tammann, however, replied lapidary:

> *Soft crystals exist unquestionably, there also should be flowing crystals for all I care, but liquid crystals? Never!*

Because of lack of time, the anchorman didn't give Lehmann the possibility to reply. This occurrence motivated Lehmann to start a real campaign, which should rehabilitate him and demonstrate the quality of his research works. A brisk correspondence came up, from which some passages are quoted in the following:

Lehmann described the course of events in the letter from June 20, 1905 to professor Abegg in Breslau (Wroclaw):

Dear colleague!

It is much to my regret, that after the lecture of Dr. Schenk at the meeting of the German Bunsen Association on the 3rd of this month, an unedifying discussion with Mr. Tammann followed, which wasn't my intention. ...

.... Although, after the lecture of Dr. Schenk, the chairman Mr. van t'Hoff immediately got back to agenda and allowed no argument, Mr. Tammann rose to speak for explaining that considering the incisive meaning, namely proving the existence of liquid crystals, if this evidence really would be provided, the declared cannot be passed unchallenged. On the base of his observations, he has to explain the following:

1.) The so-called crystal drops are constantly cloudy namely in their whole mass as a consequence of the presence of solid or liquid dust. This causes especially the gray (cloudy) points, referred to as crucial point or striae of lines, which are supposed to be the consequence of the peculiar refraction due to anisotropic structure and which should already appear under natural light.

2.) The so-called crystal drops show no birefringence. All appearances, which are allegedly based upon this, as well as the dichroism arise from the reflection and refraction of light of the dust particles and can be observed in the same way as bubbles.

3.) An intergradation from the so-called liquid crystalline state into an isotropic liquid state cannot be stated, the transition is always, as with emulsions, constant.

After all these comments - which briefly were: liquid crystals don't exist and everything that was published on that is based on delusion - Mr. Schenk immediately wanted to speak. Except him, there were also others who wanted to comment on this, so I, but the chairman ignored this and got back to agenda, because of alleged lack of time, but he never really expressed this.

If the lecture was only given by experts, I could calm myself. But yet the adviser of our department – who supported my paper on liquid crystals – was present as well as representatives of the local press, members of the scientific society, of the electrical society, students, even women who all had the impression that I was brilliantly proved wrong by Mr. Tammann, namely that liquid crystals are nothing but a phantasm. ...

In the afternoon on the same day, a special meeting was summoned specially for this purpose. Lehmann had now the opportunity to respond and to prove with the help of experiments the correctness of his previous works. He continues:

... The chairman was in agreement with me that the respond to the issue isn't sufficiently clarified and therefore, he proposed to appoint a committee which has to prove both assumptions...

At the first meeting of the German Bunsen Association in 1906, the committee was brought into being with the task to resolve the issue of the existence of liquid crystals and to give a report until 1908.

The chairmanship was taken by professor van t'Hoff from Amsterdam. Tammann and Schenk were nominated as additional members. The manager of the German Bunsen Association, Dr. Julius Wagner, informed Lehmann about this in a letter from January 22nd, 1906, and asked him at the same time to become a member of the committee, too. In trying to provide to the committee as much authentic material as possible from many scientists, Lehmann wrote a letter, requesting for help, to approximately 100 of his home and foreign colleagues. Just with a few but brilliantly formulated sentences, he argued the all-embracing wealth of branches of science that were at this time tangent to liquid crystals.

Karlsruhe, 31st January 1906

Dear colleague!

As you can see on the enclosed "paper on the demonstration of "liquid crystals" " – which is a separate print from the Zeitschrift für Elektrochemie (journal for electrochemistry) 1905, no.50, page 955 – sometimes a by a lack of time affected discussion about the abovementioned topic took place at the meeting of the German Bunsen Association for applied physical chemistry on June the 3rd last year. After the resolution of the standing committee, the *discussion should be pursued with the help of an appointed commission presided and made by Mr. Privy councilor van t'Hoff in Berlin. In consideration of the complicatedness of the issue, to the commission the availability of preferably authentic material, which is gained by independent examinations from different sides, is highly required. If you, dear colleague, engaged yourself in observations on the mentioned topic, if you plan to deal with it or if you want to give your students appropriate ideas, I kindly and sincerely want to ask you to send me the related publications as an allowance for the consultation of the commission. In terms of artificial chemical preparations, which appear in solid crystals and of which the crystal individuals are so small that you can hardly see them, the same applies to flowing or liquid crystalline modifications. If you want to examine liquid crystals (not liquid crystalline phases, i.e. aggregates of liquid crystals), the main difficulty that you have to overcome is the need of using the (crystallization-) microscope, of which the handling requires a lot of practice. To avoid fallacies caused by peculiar refraction, a certain degree of experience on the field of crystal optics (and the theoretical optics in general) is required. The analysis of the state of aggregation has to base on precise statements of terms that are part of mechanics and molecular physics. The decision of the question, if due to vectorial properties the division into the existing crystal systems is possible, belongs to the field of crystallography. The studies of magnetic property belong to that of the electrician. The main question, namely if the preparations – in a chemical sense – can be considered as even, can only be answered by the chemist. The studies of the scalar properties and thermodynamic relations however are the business of the physicist and chemists. The physiologist and the biologist have to decide, if the peculiar procedures, which are observed at apparently living crystals, are not only externally similar to the relating pro-*

cedures of the smallest living organism but are based on real relation of the physical powers that are acting here.

The attention of the physicist is attracted by the fact that a derivative of these procedures, considering already known facts, seems to be impossible.

With united forces it might be possible to eliminate all lacks of clarity that are coming from all sides.

Yours respectfully

O. Lehmann
Professor of physics
Karlsruhe, Kaiserstr. 63