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### N. V. Tsvetkov

# VSEVOLOD KONSTANTINOVICH FREEDERICKSZ – THE FOUNDER OF THE RUSSIAN SCHOOL OF PHYSICS OF LIQUID CRYSTALS

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*V.K.* Freedericksz was born on April 29, 1885 in the family of a major Russian official. After graduation from the high school, Freedericksz continued his education at the University of Geneva. He wrote his PhD thesis under the C. Guye's supervision in 1909. Afterwards Freedericksz worked at the University of Göttingen, at first with V. Voigt, and since 1914 together with D. Hilbert he was developing the General Theory of Relativity. In 1918 Freedericksz returned to Russia and started his work at the Leningrad State University (LSU) and at the Institute of Technical Physics (ITP). Freedericksz began to study LC in 1923. The first article written together with A. Repieva was published in 1927. It was proved that the nematic LC in a magnetic field is oriented due it's diamagnetic anisotropy  $\Delta \chi$ , and the effect has a threshold. In 1929 together with V. Zolina Freedericksz derived and experimentally proved the «Freedericksz's equation»:

$$H_c z = \pi \left(\frac{K}{\Delta \chi}\right)^{\frac{1}{2}}.$$

In 1935 V. Freedericksz and V. Tsvetkov published four articles in which the behavior of nematic LC in the electric field was studied. The observed effects and their interpretation are the basis of all modern LC display devices. After Freedericksz was arrested in 1936, the LC studies were continued at LSU (SPbU) until the present. **Key words:** liquid crystals, effect of the Freedericksz transition.

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### Н. В. Цветков

# ВСЕВОЛОД КОНСТАНТИНОВИЧ ФРЕДЕРИКС – ОСНОВАТЕЛЬ РУССКОЙ ШКОЛЫ ФИЗИКИ ЖИДКИХ КРИСТАЛЛОВ

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В. К. Фредерикс родился 29 апреля 1885 в семье крупного российского чиновника. После окончания гимназии Фредерикс продолжил свое образование в Женевском университете, где под руководством Ш. Гюи защитил диплом доктора физики в 1909. Затем Фредерикс работал в Геттингенском университете у В. Фойгта, а с 1914 – у Д. Гильберта, с которым начал заниматься вопросами общей теории относительности. В 1918 Фредерикс вернулся в Россию и начал работать в Ленинградском государственном Университете (ЛГУ) и в Физико-техническом институте (ФТИ). Исследования ЖК Фредерикс начал в 1923. Первые статьи с А. Н. Репьёвой выходят в 1927. В них доказано, что нематик в магнитном поле ориентируется за счет его диамагнитной анизотропии  $\Delta \chi$  и эффект носит пороговый

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характер. В 1929 с В. В. Золиной В. К. Фредерикс вывел и экспериментально доказал известное уравнение Фредерикса:

$$H_c z = \pi \left(\frac{K}{\Delta \chi}\right)^{\frac{1}{2}}.$$

В 1935 В.К. Фредерикс с В.Н. Цветковым опубликовали 4 статьи, в которых изучено поведение нематиков в электрическом поле. Обнаруженные эффекты и их физическая интерпретация лежат в основе всех современных ЖК-устройств отображения информации. После ареста В.К. Фредерикса в 1936 работы по ЖК были продолжены в ЛГУ (СПбГУ) и продолжаются по настоящее время. Ключевые слова: жидкие кристаллы, эффект «переход Фредерикса».

*Some aspects of V.K. Freedericksz' biography.* Vsevolod Konstantinovich Freedericksz descended from an old noble family. During the Great Northern War between Russia and Sweden, one captured soldier or officer of the Swedish army was exiled to the Russian North. He remained in Arkhangelsk and started a family. His son, Hans Jorgensen (Ivan Yurievich, in Russian) (Fig. 1) went to St. Petersburg and made a successful career for himself. He became a court banker during the reign of Catherine the Great, was ennobled and given the title of baron (Fig. 2). Ivan Yurievich had many descendants.



*Fig. 1.* Hans Jorgensen (Ivan Yurievich) Freedericksz

ТЕРБЪ РОДА БАРОНОВЪ ФРИДРИКСОВЪ.

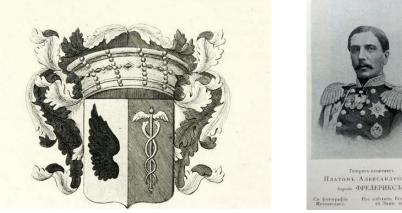


Fig. 2. The coat of arms of the Freedericksz barons

*Fig. 3.* Platon Aleksandrovich Freedericksz

Grandfather of V.K. Freedericksz (Platon Aleksandrovich, 1828–1888) (Fig. 3) served in the army, got the rank of Lieutenant General and became Governor of East Siberia. One of his sons, Konstantin Platonovich (1857–1918) (Fig. 4), father of V.K. Freedericksz, served as a Vice Governor of Tobolsk. Also he was an official in Nizhny Novgorod and held the post of Governor of Nizhny Novgorod for a short time. He held a rank of actual state councilor. In 1907 he was dismissed from office and moved to his estate near Tula.

Konstantin Platonovich Freedericksz married Olga Vladimirovna Mengden. She was a descendant of even older baron family which traces its roots to the Rurik dynasty. Olga Vladimirovna wrote stories for children under the name of Vsevolodova and read them to her son Vsevolod.

V.K. Freedericksz was born on the 29 of April 1885 in Warsaw, where his father was a special government official at the time. The eldest brother of Vsevolod Konstantinovich (Vladimir Konstantinovich) became a biologist, and his sister Natalia Konstantinovna was a mathematician (Fig. 5). It is of interests that before all Freederickszs in the male line were either soldiers or civil servants.



Fig. 4. Konstantin Platonovich Freedericksz

Soon the family returned to Russia. First they lived in Tobolsk, and later in Nizhny Novgorod. V.K. Freedericksz studied in the First Male Gymnasium (or the Alexander II Nizhny Novgorod Institute for Nobles) which was very prestigious. V.K. Freedericksz did well in studies, but was not an excellent pupil, probably due to his temper. He was calm and deliberate by nature throughout all his life. V.K. Freedericksz wanted to become a scientist, and he was interested only in natural sciences.

After graduation from the high school, he went to Western Europe to continue studies of physics. At the time, the main science centers were situated in Germany and France. But the Freedericksz family was not well-off, and thus they decided to send him to the University of Geneva which was rather new. In the University the humanities were mainly taught. The



Fig. 5. Natalia, Vsevolod and Vladimir Freedericksz

outstanding specialist in experimental physics in the University was Charles Guye (1866–1942). His most famous work was devoted to the proof of increase in electron mass with increasing of its speed. This is among the most important proofs of the Einstein special theory of relativity.

V.K. Freedericksz studied elastic properties of noble metals in a wide temperature range. This topic was selected for a reason. The most important parts of Swiss watch mechanisms (balance wheels) were made of noble metals. There are some works by Guye and Freedericksz on this subject [1]. Freedericksz performed the experiments very carefully, developed necessary setups. Freedericksz defended his thesis [2] under supervision of Guye and obtained doctoral degree of the University of Geneva in 1909 (Fig. 6).



*Fig. 6.* Diploma of the University of Geneva



Fig. 7. V.K. Freedericksz, 1910



Fig. 8. Woldemar Voigt



Fig. 9. David Hilbert

After taking degree, Freedericksz (Fig. 7) first went to Paris, but soon moved to Göttingen which was a major physical and mathematical center. On the first of September 1911 Freedericksz was taken on as a junior assistant in the Department of Theoretical Physics of the Institute of Physics. He started to work under supervision of Woldemar Voigt (Fig. 8). Voigt was not only a brilliant physicist, but also a welleducated person and a Bach expert.

At that time, Voigt studied the influence of magnetic and electric fields on crystal structure. Besides, Voigt held the office of the rector of University of Göttingen for two terms. Before the First World War, Freedericksz accompanied Voigt in his lecture tour to USA. As an assistant of Voigt, Freedericksz worked as an experimental physicist. He studied optical properties of some metals (dependence of refractive indices and absorption coefficients versus light wavelength) and published several papers. All these experiments required extreme care and development of experimental setups [3-4]. At the time, the article on piezoelectric properties of quartz under torsion and bending was published. Theoretical part was written by Voigt, and the experiments were performed by Freedericksz. This paper is considered as a classical work on piezoelectricity and has been widely cited [5].

But the First World War started. In 1914 Freedericksz became a civil prisoner and was interned. He was discharged from the University, denied the right to work and earn a salary in academic institutions. Voigt recommended Freedericksz for a work with David Hilbert (Fig. 9). Hilbert was the outstanding mathematician; he also was greatly interested in physics and was always surrounded by young physicists. These young people were jokingly called «Hilbert's physics teachers». Before the war, Hilbert became interested in the problems of gravitation and general theory of relativity. When his assistants were drafted into the army, Freedericksz replaced them. Hilbert made Freedericksz his private assistant and himself paid for his work. From this point on, Freedericksz took a great interest in general theory of relativity. This area of physics was among his main scientific interests throughout the life.

After the Treaty of Brest-Litovsk was signed in the summer of 1918, Freedericksz returned to Russia. He already was an experienced experimenter and had capability for theoretical thinking. First he came to Moscow. The situation in Petrograd was very hard. The population decreased by more than half. Spanish influenza and hunger raged in the city. In Moscow, Freedericksz became a laboratory assistant at the Radiological Department of the Moscow People's Health Care Institute. However, he worked in Moscow only for a short time. The main research studies in physics were conducted in Petrograd. Besides, two new scientific institutions were created in Petrograd in 1918. They are:

1) The State Roentgenological and Radiological Institute. Until 1921, it included three departments: Biomedical (under the leadership of M.I. Nemenov), Physico-Technical (A.F. Ioffe), Radiological (V.I. Vernadsky). Later these departments were reorganized into independent institutes. At the same time, new Physico-Mechanical Department was created in Polytechnical Institute.

2) The State Optical Institute was founded by Professor of Petrograd University D.S. Rozhdestvensky, who became its first Director. The research studies in the Institute were closely related to the work at Physico-Mathematical Department and Institute of Physics of Petrograd University (now Saint-Petersburg State University). Their buildings were situated nearby. The main areas of research at the Institute were spectroscopy and the development of optical glass.

Freedericksz came to Petrograd in 1919 and obtained a position of assistant professor at Physico-Mathematical Department of the University. At the same time, he was employed as a senior research worker at the State Optical Institute and professor at Herzen Pedagogical Institute. At the end of 1923, Freedericksz left the State Optical Institute and started working at the Physico-Technical Institute where he held a position of a senior physicist. He carried out studies of piezoelectricity and later became interested in liquid crystals.

In the autumn of 1927 Freedericksz married Maria Dmitrievna Shostakovich (Fig. 10–12). In 1928 they had a son Dmitry (Fig. 11). Maria Dmitrievna was the elder sister of Dmitri Dmitriyevich Shostakovich. The famous Russian artist B.M. Kustodiev has painted her portraits (Fig. 10).

Freedericksz was deeply involved in electrical exploration of minerals. Practical use of this method requires theoretical calculation of characteristics of electric current passing through crust in the presence and in the absence of an ore. Freedericksz also participated in the development of set apps for electrical exploration. Freedericksz took part in many geological expeditions (to Ural mountains, Nizhny Tagil region and Khodzhent (Tajikistan)) (Fig. 13). He is the author of several works on electrical prospecting of minerals. The most widely known monograph is titled «Electrical exploration of minerals using the method of alternating electrical fields» [6] and was published in 1929.

At the beginning of the 1920s, Freedericksz and Alexander Aleksandrovich Friedmann (Fig. 14) were the only experts in general theory of relativity in Russia. Friedmann was a prominent physicist and the author of the theory of an expanding universe. In these years, there were no translated works on general theory of relativity in USSR. Freedericksz possessed physical intuition and deep understanding of principal problems of general theory of relativity. The first review by Freedericksz devoted to this topic was titled «Einstein's general principle of relativity» and published in 1921 in the journal «Advances in physical sciences» [7]. In was the first paper on general theory of relativity in Russian. Freedericksz presented the main statements of Einstein's theory very clearly and in detail and provided his own comments. In this work, he used simple and understandable special cases to demonstrate validity of Einsten's equations.

In 1924 Freedericksz and Friedmann published the book entitled «The basics of relativity theory. Part I» [8]. It was devoted to tensor calculus. They intended to write five books, but only the first one was written. Friedmann died suddenly from typhoid fever in 1925.



*Fig. 10.* Portrait of Maria Dmitrievna Shostakovich by Kustodiyev

Fig. 11. Vsevolod Konstantinovich and Maria Dmitrievna with their son



*Fig. 12.* Photograph after the premiere of the ballet «Bolt» 1931. Freedericksz sits next to Dmitry Shostakovich



*Fig. 13.* V.K. Freedericksz in geological expedition



*Fig. 14.* A.A. Friedmann, 1916 (in the uniform of a military pilot)

Freedericksz was interested in a connection between general theory of relativity and quantum mechanics and published a number of works on this subject. In the 1920s and 1930s Freedericksz actively promulgated general theory of relativity. He was a coauthor of an article on this theory in Technical Encyclopedia (1931) [9]. In 1935 (on the occasion of the thirtieth anniversary of relativity theory), Freedericksz published a long article in the journal «Socialistic reconstruction in science». The paper was titled «The modern state of the problem of relativity theory» [10]. He also edited the books on this topic which were translated into Russian. Freedericksz published 14 works in all devoted to general theory of relativity.

Freedericksz was also a lecturer in the University and Polytechnical Institute. He taught courses in optics, theory of electricity, theory of relativity. The textbook «Electrodynamics and introduction into theory of light» [11] was based on a course of lectures given at the Physico-Mathematical Department of Leningrad State University. Together with Afanasiev, Freedericksz was the editor of the textbook «Course of general physics» [12]. Freedericksz was very interested in the history of physics and possessed extensive knowledge in this area. His most important works in this field are:

1) Papers in the collection devoted to Isaac Newton which was published in the journal «Advances in physical sciences» (1927) [13].

2) He edited the translation of the book by O. Fresnel «Memoir on the Diffraction of Light» (1929) [14].

3) He edited the translation of the book by C. Huygens «Treatise on Light» (1935), wrote Huygens biography and provided many comments on the text [15].

4) Together with D.D. Ivanenko, he was an editor of a collection of papers «The principle of relativity» (1935) [16].

# The studies of liquid crystals

These works were started in 1923 at the Physico-Technical Institute. The first experiments aimed at the study of orientation of liquid crystals in magnetic field were carried out by V. Kast (who was a graduate student of Prof. L. Ornstein at Utrecht University). Kast demonstrated that molecules of liquid crystals align along the magnetic field lines [17]. However, in order to describe the results quantitatively, Ornstein had to assume that the field influence on a "swarm" of molecules (the cluster containing 10<sup>4</sup> molecules) but not on the isolated molecule. At the time, Ornstein considered liquid crystals as paramagnetic materials [18]. But in the same year French researchers Foex and Royer demonstrated that *p*-azoxyanisole is a diamagnetic [19]. Freedericksz and Alexandra Nikolaevna Repieva investigated behavior of liquid crystals in magnetic field. Preliminary results were obtained in 1924, and further studies were described in Repieva's doctoral thesis. The obtained results were reported in three articles (1927-1928) [20-22]. These articles include the basic assumptions of liquid crystal state theory proposed by M. Born. According to this model, LC phase is formed due to dipole-dipole interactions. The molecules have «head-to-tail» ordering, and thus LC should demonstrate piezoelectric and pyroelectric effects. Freedericksz and Repieva tried to verify this theory using *p*-azoxyanisole. The substance was crystallized between capacitor plates in the presence of strong magnetic field. In the crystalline state, the substance demonstrated both pyroelectric current and piezoelectric effect. But in LC phase no effects were revealed due to high conductivity of *p*-azoxyanisole. Thus, the validity of the Born theory was not proved.

The main part of the work was devoted to investigation of uniformly oriented layers of nematic LC under the action of magnetic field. LC compound was placed between planar and convex (watch glass) surfaces (Fig. 15). The initial orientation of LC was either planar or homeotropic. The sample was exposed to monochromatic polarized light. Interference pattern was observed. Firstly, homeotropic layer of p-ethoxybenzalazin was studied. When longitudinal field was applied, the pattern did not change, because axes of molecules were already ordered along the field direction. When cross magnetic field was applied (the following is a quote from a paper): «under the action of magnetic field, very sharp thin circles appear at the edges of a sample; with increasing field strength, these circles are drawn towards the center, this indicating appearance of birefringence and increase of birefringence with increasing magnetic field strength».

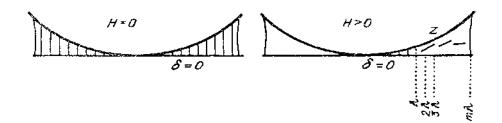


Fig. 15. Orientation of LC molecules

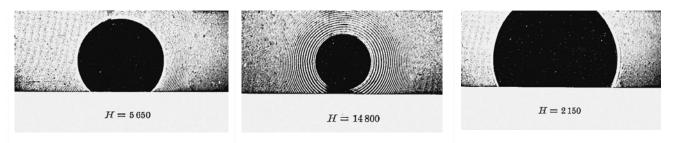


Fig. 16. Polarizing micrographs of p-ethoxybenzalazin

«In this case, as seen in the images (dark central circles), for every  $H_n$  value there is a limit layer thickness  $z_n$ ; until that thickness is achieved, the initial normal arrangement of optical axes is retained». Thus, it was established that the effect has a threshold. This can be clearly seen in the figures (Fig. 16).

Freedericksz gave the following explanation for this phenomenon. Nematic molecule is subjected to four external forces:

1) Surface force which provides adhesion to glass. This force weakens towards periphery of a sample.

2) The force generated by internal field which is created by dipoles or multipoles. Freedericksz thought that this force is constant (later it was found that it is not so).

3) Magnetic field

4) Friction force (was neglected).

Therefore, molecules of the sample become oriented only in the regions where force #3 exceeds the sum of forces #1 and #2. However, at that time Freedericksz believed that his experimental data confirm the Born theory about «dipoles which generate internal field in anisotropic fluid». This conclusion was incorrect.

It was also demonstrated for the first time that cholesteric LC are also oriented by magnetic field. The attempt to reorient smectic LC using magnetic field was not successful. The main achievement of these early works was the confirmation of the hypothesis that liquid crystals are oriented in magnetic field due to their diamagnetic anisotropy. The following works were performed in collaboration with Valentina Vasil'evna Zolina. Their first paper was published in 1929 [23]. The main result was the measurement of dependence of critical field on the layer thickness of nematic, namely  $H_c = k/z$ , where k is the constant which virtually does not depend on temperature. Further experiments were carried out at the Polytechnical Institute, because the Institute possessed a powerful magnet (25 kG). These works were aimed at verifying the above relationship ( $H_c = k/z$ ). The results were summarized in two papers [24–25].

Detailed and careful measurements involving several nematic liquid crystals were performed; it was revealed that k still somewhat decreases with increasing temperature. Freedericksz derived analytical expression for the k value. Nematic «particle» is exposed to the moment generated by other particles:

$$D = A \frac{d^2 \varphi}{dx^2}$$

where A is the constant determined by the forces acting inside nematic molecule (its physical meaning is equivalent to elastic constant),  $\varphi$  is the angle between particle axis and direction of the field, and x is the distance between a particle and the surface. Magnetic field generates the moment of force

$$D = aH^2 \cdot \cos \phi \cdot \sin \phi \, .$$

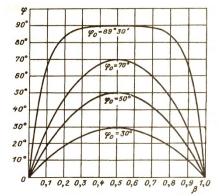
When right sides of these expressions are equated, we obtain the equation which can be solved using elliptic functions. Taking into account the boundary conditions, Freedericksz obtained the following relationship:

$$\left(\frac{a}{A}\right)^{\frac{1}{2}} \cdot \frac{H_c z}{2} = \frac{\pi}{2}.$$

This relation is called «The Freedericksz formula». Substituting *A* for *K* (elastic constant), expressing *a* as  $(\chi_{\parallel} - \chi_{\perp} = \Delta \chi)$ , and using the common notations, we obtain the following:

$$H_c z = \pi \left(\frac{K}{\Delta \chi}\right)^{\frac{1}{2}} = \text{constant (for } T = \text{constant}).$$

Freedericksz also plotted the dependence of nematic molecules angle on layer thickness for several maximum angles (Fig. 17). It was shown that maximum orientation is observed in the center of a sample, and on the surface the angle is equal to zero. These results were reported by Zolina at the First All-Union Physical Congress. The presentation attracted much interest.



*Fig. 17.* Dependence of Nematic molecules angle on layer thickness

In 1931 Freedericksz began to study the influence of electric field on LC. This problem turned out to be much more complicated than the research with the use of magnetic field, since LC demonstrates conductivity. Repieva used the same geometry as before. When using direct current voltage (2 kV/cm) with electrodes placed at the edges of a sample, no quantitative data were obtained. However, very interesting phenomenon in LC was found. It was flow of a sample accompanied by orientation.

This effect was reversible. After decreasing voltage, the initial pattern was restored (see Fig. 18: a – before applying the field; d – after switching off

the field, returning to *a*). This phenomenon is commonly termed «the Williams domain structure» [26]. In Russian literature, this phenomenon is called «the Kapustin-Williams domains» [27]. However Kapustin and Williams rediscovered this effect 30 years later than Freedericksz. Further increase in voltage led to turbulent motion of LC molecules. The sample became milky white color due to light scattering. This dynamic scattering of light in LC was also rediscovered in more than 30 years by Heilmeier [28].

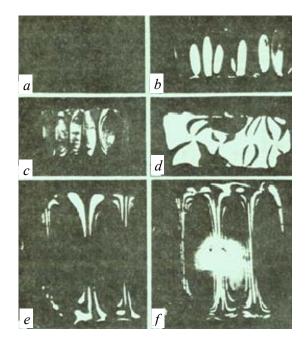


Fig. 18. Domain structure of LC

In 1931 research staff of the Leningrad State University started works devoted to liquid crystal physics. Freedericksz engaged a new graduate student (Victor Nikolaevich Tsvetkov (Fig. 19), who was a graduate of the Pedagogical Institute).



Fig. 19. Victor Nikolaevich Tsvetkov, 1930s

The first paper by Freedericksz and Tsvetkov was published in 1934 [29] and was devoted to the studies of twist deformation of nematic LC in magnetic field. A plano-concave layer of planar oriented *p*-azoxyanisole and prisms made of dense flint glass were used (Fig. 20). Refractive index of this glass is higher than those of ordinary and extraordinary indexes of the LC).

In this case, monochromatic light beam should be observed only in a limited space after the second

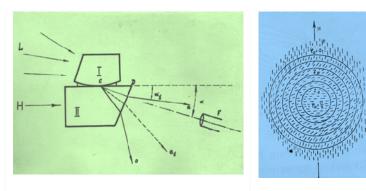
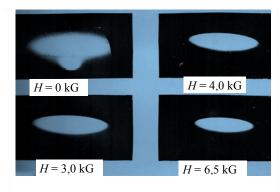


Fig. 20. Optical scheme of setup

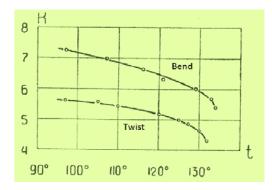
*Fig. 21.* Orientation of LC molecules

prism due to total internal reflection. The magnetic field applied normally to the director caused twist deformation (Fig. 21) and thus changed refractive index of the extraordinary beam in LC.

This phenomenon results in narrowing of the observed light area which depends on magnetic field strength H (Fig. 22). This dependence allowed the authors to determine the value proportional to the twist elastic constant of LC at various temperatures and to compare twist and bend elastic constants (Fig. 23).



*Fig. 22.* Observed light area at different *H* values



*Fig. 23.* Elastic constants of *p*-azoxyanisole versus vs. temperatire

In the following years, Freedericksz and Tsvetkov carried out a series of outstanding research works focused on the influence of electric field on orientation of nematic molecules. The results were included in four papers published in 1935 [30–33]. The importance of these works is difficult to overestimate. The established phenomena and their physical interpretation become a basis of all modern

devices which display information on LC screens (TV sets, computer monitors etc.).

The used geometry was the same (planoconcave layer of nematic). Nematic layer of *p*azoxyanisole were planar oriented. Electric field with a frequency of 1 and 300 kHz was applied parallel to the layer (edge electrodes) or normally to the layer (using 0.5 mm spaced brass mesh). The observations were made both in polarized and natural light.

When the field was applied perpendicularly to sample layer, no reorientation was observed, but motion of the liquid occurred (similarly to Zolina experiments). The preparation acquired domain structure (which was described in detail in these papers). It was pointed out that this motion cannot be «an immediate result of rotation of molecules and their complexes after switching on electric field». It was demonstrated that there is a clear boundary between stationary and moving parts of the liquid (Fig. 24, *b-c*). The position of the critical boundary obeys to the following law: zE = constant = C. The *C* value increases with temperature and the time of exposure to electric field.

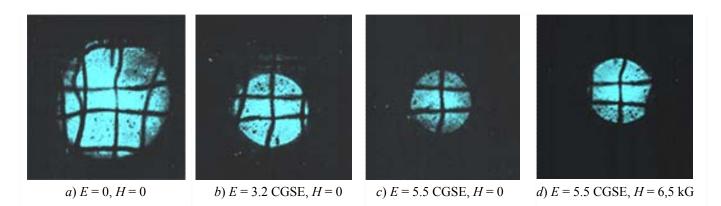


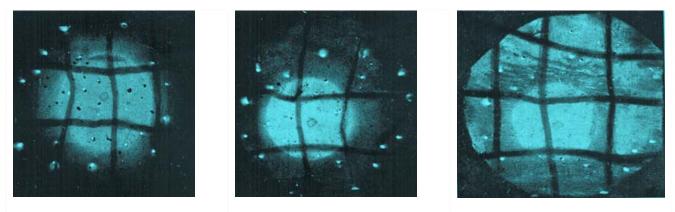
Fig. 24. P-azoxyanisole under the influence of electric and magnetic fields

When an LC sample is exposed to magnetic field (independently of mutual orientation of electric and magnetic field strength vectors), the field slows down turbulent motion of molecules, and a substance becomes more homogeneous. Unfortunately, static images cannot reflect motion in LC sample.

At the same time, it was shown that depending on mutual orientation of magnetic and electric field vectors, position of the critical boundary changes. Thus, when the E and H vectors are oriented perpendicularly to each other, magnetic field weakens the influence of electric field (Fig. 24, d). When they are oriented parallel to each other, magnetic field increases the effect of electric field. It is seen in the Fig. 25, *b*-*c*.

It was emphasized in these papers that this result indicated that during motion in electric field, nematic molecules become oriented mainly in the direction of field lines, due to viscosity and conductivity anisotropy of LC. The authors also noted that since the motion starts only in the layer with a thickness exceeding the critical value, layers with lesser thickness should be studied. However, orienting action of electric field in these conditions was insufficient.

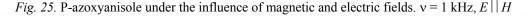
Therefore, a new original method was used. The sample was subjected simultaneously to the influence of magnetic and electric fields. Planar-oriented sample of *p*-azoxyanisole was placed between crossed polarizers. A system of interference rings was observed. Magnetic field (applied normally to the sample layer) caused reorientation of nematic molecules, and some rings disappeared. Then electric field was applied. The boundary shifted towards thicker layer of the sample, and the rings partially reappeared (Fig. 26).

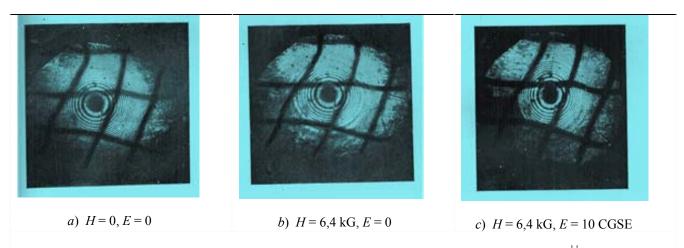


a) E = 4.5 CGSE, H = 0

b) E = 4.5 CGSE, H = 4,7 kG

c) E = 4.5 CGSE, H = 6.0 kG





*Fig. 26.* P-azoxyanisole under the influence of magnetic and electric fields. v = 1 kHz, E || H

Similar experiments involved LC compounds with negative and positive anisotropy of dielectric permittivity. The following fundamental conclusion was made: degree orientation is proportional to field strength squared and, therefore, is caused by dielectric anisotropy of a substance. The following equation was derived:

$$aH^2 + \beta E^2 = \frac{1}{z_0^2}; a = \frac{\Delta \chi}{\pi^2 K}; \beta = \frac{\Delta \varepsilon}{\pi^2 K}.$$

This equation was verified by experimental data (Fig. 27).

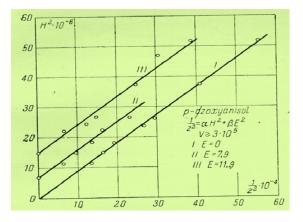


Fig. 27. Dependence of  $H^2$  vs.  $1/z^2$ 

When 
$$H = 0$$
, we obtain  $E_0 z = \pi \cdot \left(\frac{K}{\Delta \varepsilon}\right)^{\frac{1}{2}}$ .

Besides, it was demonstrated that when frequency of electric field exceeds 300 kHz, there is virtually no motion of LC molecules. The existence of a critical frequency was stated. The obtained results also allowed the authors to determine elastic constants of the studied nematics.

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The last experimental work of Freedericksz devoted to LC physics was co-authored with Repieva and included the results of the studies of smectic LC in electric field [34]. This work is undoubtedly interesting, although it contains only qualitative data.

Analysis of the works by Freedericksz allows us to trace changes in his opinions about the nature of liquid crystalline state. In the beginning, he followed the swarm theory, but later supporting the continuum theory. In his early works, Freedericksz believed that internal field in LC is caused by dipoles (according to the Born theory). But in subsequent papers he emphasized that «there are no reasons to assume the presence of internal dipole field». All these ideas were further developed in the works of his students, which, unfortunately. were conducted without him. Altogether there are 18 papers on LC published by Freedericksz.

### Last years of life

We are coming now to the most tragic period of Freedericksz' life. In the night of the twenty first of October 1936 he was arrested. Freedericksz was charged with «Participation in fascist terroristic organization created in 1932 by German intelligence service and aimed at overthrow of Soviet system and establishment of a fascist dictatorship within the territory of USSR». The «members of the organization» were also charged with preparation for attempt on Stalin' life. Naturally, all these charges were completely groundless. However, in the period of political repressions, similar incriminations were frequent. There were no formal investigation, and evidence was obtained by force.

Freedericksz was on trial in May 1937 during closed visiting session of military procuracy of Supreme Court of USSR without the defense and witnesses. The court announced the following sentence: «V.K. Freedericksz is sentenced to 10-year imprisonment, deprivation of political rights for 5 years, confiscation of all property. The sentence is final and without appeal».

Freedericksz spent first several years of imprisonment in Tayshet Corrective Labour Camp and was engaged in timber cutting. It was a hard manual labor, especially for elderly prisoners. Colleagues and friends tried to seek his release. Vavilov, Krylov, Ioffe, Muskhelishvili, Fock, Kapitsa wrote a letter to L. Beria in 1939 (this letter remained). Kurchatov, Baikov and Frenkel also applied for a release of Freedericksz from custody. D.D. Shostakovich wrote many letters to authorities. Freedericksz also wrote to higher authorities and asked to «give him a job according to his profession». In 1939 Freedericksz was transferred to the Oryol prison (probably, as a result of efforts of his relatives and friends). In the autumn of 1940 he was moved to the Ukhta-Izhma Corrective Labour Camp situated in Komi Republic in the Izhma River basin. He worked as a laboratory assistant at a refinery. The climate of Komi is very harsh. In winter the weather is intensely cold, and temperatures of 50 degrees of frost are reached. However, the conditions for prisoners were better than before. At the beginning of war, Freedericksz became a watchman at a brick factory. This new work saved his life, since all prisoners sentenced for treason were executed or transferred to maximum security camps.

Even in these hard conditions, Freedericksz retained his interest in physics and continued research work. He wrote a paper in collaboration with L. Polak which was titled «On the theory of anisotropic liquid», although it was not published. In this theoretical work, properties of LC were described with the aid of tensors and local coordinate systems.

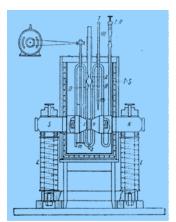
In the winter of 1943, authorities offered Freedericksz transition to closed military research institution. According to another version, Kurchatov (who knew Freedericksz well) was going to give him a position in nuclear program. There are no arguments for one or another version. Freedericksz was sent to Moscow. Along the way he fell ill with pneumonia and died on the 6<sup>th</sup> of January in a hospital in Nizhny Novgorod. The place of his burial is unknown. In 1956 the Military Board of the Supreme Court of the USSR completely rehabilitated Freedericksz. The sentence of 1937 was recalled for absence of a criminal act.

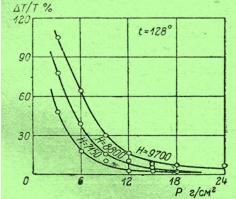
### Scientific school, early work

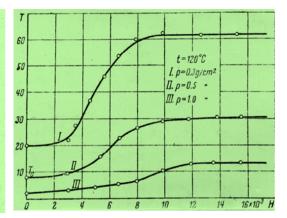
After Freedericksz was arrested, the research works on LC physics were continued only in the Leningrad State University (by V.N. Tsvetkov, G.M. Mikhailov and V.A. Marinin).

A series of works devoted to anisotropy of viscosity of LC was performed by Tsvetkov in collaboration with Mikhailov. The papers were published in 1937–1939 [35–36]. The authors discussed the experiments reported by Neufeld [37] and Miesowiez [38]. In the works of Tsvetkov and Mikhailov, it was noted that as a result of fast flow in a capillary, *p*-azoxyanisole molecules become oriented along the direction of the flow. The influence of magnetic field is not sufficient for reorientation. In order to achieve the desired effect, they used small rate of outflow of liquids from a capillary. The authors also developed a special viscometer with flattened capillary which was placed between poles of an electromagnet and thermostated air bath (Fig. 28).

It was demonstrated that the change in viscosity (outflow rate) of liquid crystals occurs and depends greatly on the pressure difference at the capillary ends (Fig. 29) and the field strength (Fig. 30). Thorough analysis of the obtained results was performed. It was revealed that the effect is caused by orientation of LC molecules in magnetic field (normal with respect to flow direction). At the same time, flow orients molecules along its direction. The influence of electric field on flow of LC in a capillary was also studied.







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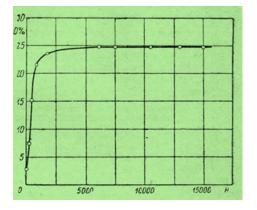
Fig. 28. Scheme of setup

*Fig. 29.* The dependence of outflow rate on the pressure difference at the capillary ends

*Fig. 30.* The dependence of outflow rate on the magnetic field strength

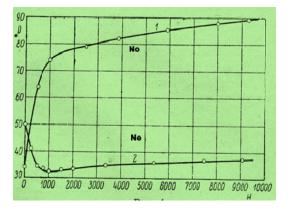
Several works of Tsvetkov were devoted to light scattering in LC [39–40]. The influence of magnetic field on transparency of LC substances (*p*-azoxy-anisole) was studied. Both planar-oriented and homeotropic samples were used.

When magnetic field was applied in the direction of orienting action of cell glass, transparency of a sample increased rapidly and reached saturation (Fig. 31).



*Fig. 31.* Transparency of a sample vs. magnetic field strength. Parallel *H* 

Different pattern was observed when the field was applied perpendicularly to orienting direction of surfaces (Fig. 32). At first transparency of the sample changed significantly, and then grew slowly with increase in field strength.



*Fig. 32.* Transparency of a sample vs. magnetic field strength. Normal *H* 

The authors believed that this phenomenon was caused by the following fact. When layer thickness is lower than critical, orienting action of glass cell is very strong, and the field cannot reorient LC molecules. In fact, here the authors dealt with the correlation length. This concept was introduced by de Gennes 35 years after. The influence of magnetic field on depolarization of scattered light in LC was also studied and discussed.

«The method of rotating magnetic field» was developed by Tsvetkov in 1939 and described in [41]. Depending on experimental conditions, it allows measuring rotational viscosity of a LC compound and its diamagnetic anisotropy. Homeotropic layer of LC is exposed to rotating magnetic field applied along the planar side of a sample (Fig. 33).



Fig. 33. Direction of magnetic field in the cell

The sample is subjected to magnetic field and frictional moment. These two moments compensate each other:

 $C\eta \cdot d\phi / dt = C\eta \omega = (1/2) \cdot VH^2 \cdot \Delta \chi \cdot \sin 2\alpha$ ,

where V is the «volume» of a particle;  $\Delta \chi$  is its diamagnetic anisotropy,  $\alpha$  is the angle between the director and magnetic field strength H.

The solution of the equation is of the following form:

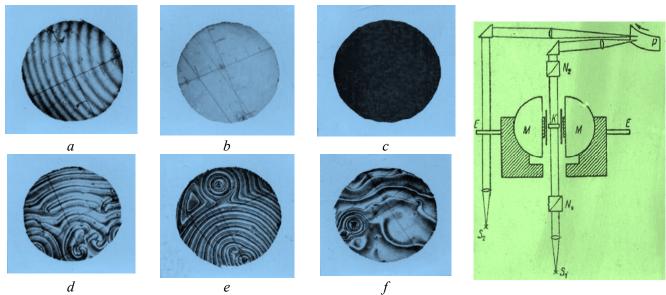
$$2t = \int \frac{dx}{\omega - a \cdot \cos x} + const; \qquad a = \frac{VH^2 \Delta \chi}{2C\eta}$$

Two cases are possible:

1)  $\omega^2 < a^2$ . Stationary mode:  $\alpha \le \pi/4$ . The sample follows the field and remains homogeneous. The  $\alpha$  value is constant.

2)  $\omega^2 > a^2$ . Non-stationary mode. The  $\alpha$  value changes with time. Turbulent motion of LC is observed.

The pattern was studied by optical method in white and monochromatic light. The sample was observed through crossed analyzer and polarizer. When the sample was homogeneous, field of view was dark 4 times per period and reached the highest illumination intensity 4 times. Different LC compounds were used (acetoxybenzalazin among them). Images obtained at various rotation rates are presented in Fig. 34.



*Fig. 34.* The observed images in monochromatic (*a*) and white light (b-c). The sample was homogeneous. Turbulence appeared at higher frequencies (*d*) and increased with increasing rotation rate (e-f)

Fig. 35. The setup for measuring phase difference  $\alpha$ . Here, M is the rotating electromagnet, N are the crossed polarizers, P is the photo film

A new setup for measuring phase difference  $\alpha$  was developed and implemented (Fig. 35). In the stationary mode, the image became dark four times per period. In order to measure phase difference, additional light beam was used. It was intercepted with 4 narrow screens. These screens were attached to the

electromagnet in such a way that they intercepted light beam in the moments when the direction of magnetic field coincided with the direction of polarizers. It was proved experimentally that the phase shift value depends on rotation rate and magnetic field strength. Viscosity of the LC sample was also determined; the result agreed well with the values obtained by other methods.

In addition, the authors measured the value of angular momentum M of magnetic field which affects LC sample. The special device was developed for this purpose (Fig. 36).

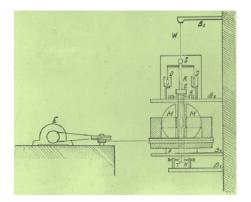
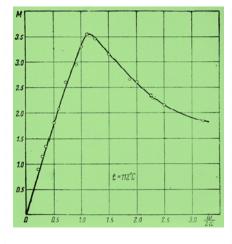
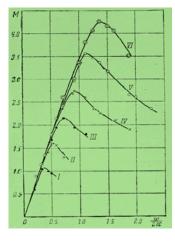


Fig. 36. Scheme of setup for determination M

LC sample was put into a glass cylinder 45 mm in length and 11 mm in diameter and suspended on a



*Fig. 37.* The dependences of *M* versus rotation rate  $\omega$ 

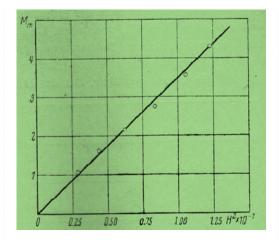


*Fig. 38.* The dependences of M versus  $\omega$  at different H

tungsten filament (300 mm in length and 0.1 mm in diameter). Elasticity of the filament was determined previously. The electromagnet was rotated. The twist angle of the filament was measured.

- 1. In isotropic phase of LC no angular momentum *M* was detected.
- 2. In nematic phase high angular momentum was observed and measured. Its value depended on rotation rate  $\omega$  and field strength *H* (Fig. 37–39).

The higher point corresponds to the transition from stationary mode to turbulent mode. The maximum value of angular momentum is proportional to magnetic field strength squared (Fig. 39). So it was possible to determine the value of diamagnetic anisotropy of a nematic  $\Delta \chi$ . The result was in good quantitative agreement with the data obtained by other methods. Later this method was used (in collaboration with Sosnovsky) in measurements of diamagnetic anisotropy of a series of nematic LC compounds [42]. Similar experiments were performed using rotating electric field [43].



*Fig. 39.* The dependences of M versus  $H^2$ 

The next important paper by Tsvetkov was published in 1942 [44], although the work has been completed earlier. In this work the authors introduced the main characteristic of a LC compound, that is, the orientation order parameter. It was emphasized that this parameter characterizes long-range orientation order. The order parameter discussed in this paper is now well-known:

$$S = \frac{3\overline{\cos^2 \vartheta} - 1}{2}$$

where  $\vartheta$  is the deviation angle of molecule axis from the director. It was demonstrated that the *S* value is proportional to diamagnetic anisotropy of nematic LC and its birefringence. Further, the first «correct» theory of liquid crystalline state of matter was proposed. The «ordering energy» was introduced. This is the energy necessary to transfer one molecule from the ordered to disordered state:

$$V = \frac{1}{2} a \overline{\vartheta_{max}^2} \,.$$

The maximum angle value corresponds to the completely disordered state and can be estimated as  $\overline{\vartheta_{max}^2} = 0.9$ . The a coefficient can be expressed as  $a = 3K\pi r$ , where K is the elasticity constant, r is the average radius of a molecule. Thus, we obtain  $V = 1.35K\pi r$ .

Degree of ordering is a function of ordering energy *V*:

$$S = 1 - \frac{3}{2}\overline{\sin^2 \vartheta} \approx 1 - \frac{3}{2}\overline{\vartheta^2}, \ \overline{\vartheta^2} = \frac{kT}{3\pi Kr}$$
  
Then we can write:

$$S(V) = 1 - 0.675 \frac{kT}{V}$$

On the other hand, the value of ordering energy depends on degree of orientation order (S). The following empirical relationship was suggested:  $V = V_{\alpha}e^{\beta s}$ , where,  $\beta \approx 3.1$ .

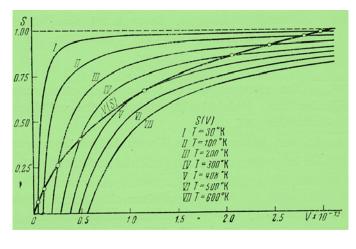


Fig. 40. The dependences of S versus V and V versus S

The last work which was performed in the beginning of the 1940s should be mentioned. This work is devoted to the study of pre-transition effects in isotropic phase of LC using magnetic and dynamic (Maxwell effect) birefringence. The results were published in [45]. The authors quantitatively reproduced the experiment carried out by Zadoc-Kahn in 1930 [46–47]. Not only *p*-azoxyanisole (1), but also

This relationship was obtained on the basis of the available experimental data.

Then the equation can be obtained:

$$S(V) = 1 - 0.675 \frac{kT}{V_{o}e^{\beta s}}.$$

Figure 40 presents the S(V) and V(S) dependences. It can be seen that existence of LC phase is possible only at temperatures not above 408 K. The minimum possible value of the order parameter for LC (*S*) turned out to be rather high (0.67 instead of 0.44 for *p*-azoxyanisole) (Fig. 41). This discrepancy was explained by the fact that the used relationships for energy were approximate.

However, it is important to note that the authors in fact offered the first self-consistent field theory. It was assumed that energy of molecules depends on squared angle of deviation of molecule axis from its director. These main ideas were developed by G. Meier and A. Saupe in the theory of LC state of matter more than 20 years later. These research works were the basis of doctoral thesis of Tsvetkov which was defended in 1940.

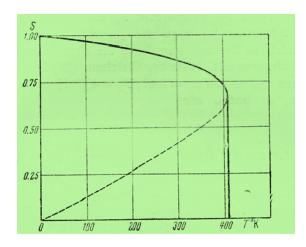


Fig. 41. The dependences of S versus temperature

two other nematics (*p*-azoxyphenetole (2), anizal-*p*-aminoazobebzene (4)) and one smectic compound (ethyl ester of azoxybenzoic acid (3)) were studied. It was emphasized that pre-transition effect is manifested much more clearly for nematics than for smectic LC compounds (Fig. 42). Pre-transition effect for *p*-azoxyanisole was observed for the first time in flow birefringence experiments (Fig. 43).

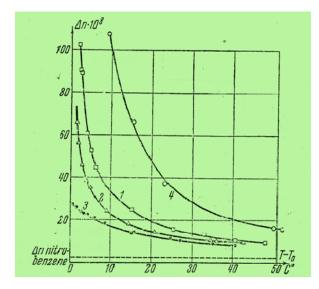


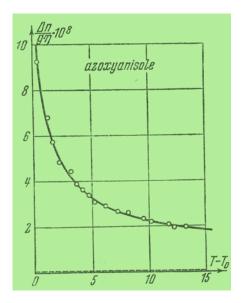
Fig. 42. Magnetic birefringence versus temperature

The obtained data were interpreted within the framework of the Frenkel theory of heterophase fluctuations. The effects were explained by the formation of LC-order fluctuations in isotropic phase; their order parameter is close to that of LC state. With decreasing temperature, scale of these fluctuations (a number of molecules in them) increased. The term «swarm» was used in these papers to describe a volume in which nematic order appeared.

After the beginning of war, the Leningrad State University was evacuated and these studies were carried out in Yelabuga (the town near Kazan in Tatarstan). Since 1943 Tsvetkov and his colleagues were engaged in polymer physics. The studies of liquid crystals were not ceased, but were not at the main activities.

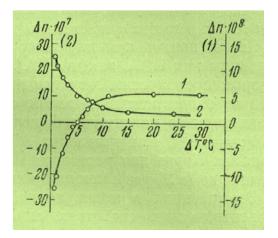
### Scientific school, from 1960s up to our days

In the 1960s LC compounds were intensively studied all over the world. This interest in LC was caused mainly by the work of a prominent chemist George William Gray. He suggested new approaches to the synthesis of LC materials. These approaches allowed reducing manufacturing cost of LC and it was possible to prepare LC which demonstrate mesophase at ambient temperatures. LC was considered as promising materials for practical applications. Since the 1960s, large-scale studies of LC were conducted at the Leningrad State University.



*Fig. 43.* Dynamic (Maxwell effect) birefringence versus temperature

The studies of pre-transition processes in isotropic phase of LC (which were started in 1940s) were continued. In these works, electric birefringence (Kerr effect) was used. The studies involved various LC compounds. It was demonstrated that the Kerr constant increases sharply near the phase transition temperature. However, one unexpected result was obtained. The Kerr constant for well-known *p*-azoxyanisole changed sign from positive (at high temperatures) to negative (near isotropization point) [48–49] (Fig. 44). Remember that dielectric anisotropy of *p*-azoxyanisole nematic is negative.



*Fig.* 44. Electric birefringence  $\Delta n$  versus  $\Delta T = T - T_c$ in isotropic melts of *p*-azoxyanisole (1) and anizal-paraaminoazobenzene (2)

Thus, the obtained results indicated that electrooptical effect in isotropic phase of LC at decreasing temperature is related to fluctuation of LC order in melt. Within these fluctuations axes of *p*-azoxyanisole molecules are oriented normally to electric field (due to negative dielectric anisotropy of this compound). However, the question is why dielectric anisotropy of *p*-azoxyanisole is negative. Its Kerr constant is positive in isotropic melt and solutions. This result

gave impulse to numerous further works, and these studies are still continued. The work was devoted to investigating dielectric properties of nematics and molecular mechanisms of dielectric permittivity of LC. It was shown that every component of dipole moment contributes both to longitudinal ( $\epsilon_{\parallel}$ ) and transverse ( $\epsilon_{\perp}$ ) components of dielectric permittivity of a nematic.

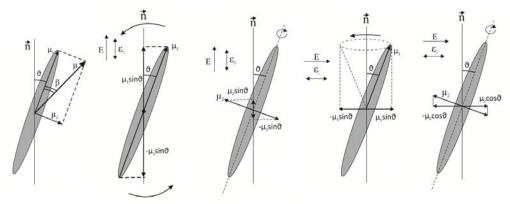


Fig. 45. Molecular mechanisms of dielectric permittivity [50]

It should be kept in mind that rotation of molecules is limited by nematic potential. That's why factors of limited rotation ( $x_1$  and  $x_2$ ) were introduced.

However, one type of rotation (coning motion) can be considered as isotropic (number 4 at fig. 45). In the end, the following expressions were obtained:

$$\sigma_{\parallel} = \frac{(\varepsilon_{\parallel}' - 1) \cdot M}{4\pi\rho} = PQN_{A} \left[ (a + \frac{2}{3}\Delta aS) + Q\mu^{2}\cos^{2}\beta \cdot \frac{1 + 2S}{3kT}(1 + x_{1}) + Q\mu^{2}\sin^{2}\beta \frac{1 - S}{3kT}(1 + x_{2}) \right],$$
  
$$\sigma_{\perp} = \frac{(\varepsilon_{\perp}' - 1) \cdot M}{4\pi\rho} = PQN_{A} \left[ (a - \frac{1}{3}\Delta aS) + Q\mu^{2}\cos^{2}\beta \cdot \frac{1 - S}{3kT} + Q\mu^{2}\sin^{2}\beta \frac{(S + 2)}{6kT}(1 + x_{2}) \right].$$

These relationships were successfully validated in a large number of experiments and used for calculation of limitation parameters x.

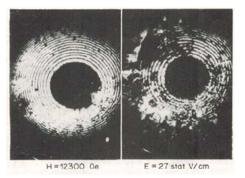
The next numerous series of papers was devoted to the studies of LC polymers which were synthesized and actively studied in the 1980s. Various LC polymers were investigated (Main chain synthesized by A.Yu. Bilibin and S.S. Skorokhodov at St. Petersburg State University and Institute of Macromolecular compounds; comb-like polymers synthesized by V.P. Shibaev, N.A. Plate at Moscow State University, combined structure synthesized by H. Ringsdorf and R. Zentel in Germany). The first paper was published in 1988 [51]. In the case of polymeric LC the classic geometry used by Freedericksz (planar-convex nematic layer) is very convenient. It allows obtaining good orientation of LC (which is difficult to achieve in the case of polymers) [52].

Micrographs of initial and deformed LC layer in magnetic and electric fields of Main chain aromatic polyester are presented at Fig. 46–47. Of course, the quality of obtained polarization patterns was lower than that in the case of low molecular weight LC. However, they allowed the authors to plot temperature dependences of optical anisotropy, elastic constant, dielectric anisotropy of nematic polymers.



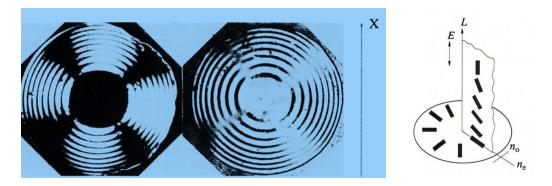
*Fig. 46.* Micrograph of initial LC layer of aromatic polyester [51]

The «Maltese cross» can be clearly seen in these photographs. Similar pattern was observed for low molecular weight LC. Indeed, for homeotropic layers of nematics with negative dielectric anisotropy the socalled «degenerate» transition occurs.



*Fig. 47.* Micrographs of deformed LC layer in magnetic and electric fields of aromatic polyester [51]

Analysis of polarization pattern with the use of additional birefringent plate with the predominated direction of optical axis leads to unambiguous conclusion about appearance of conoscopic texture in the sample (Fig. 48).

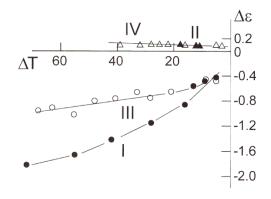


*Fig. 48.* Homeotropic nematic layer of AE deformed by an applied electric field (left) and AE with an additional  $\lambda/4$  plate (positive direction of the optical axis x is indicated). Scheme of conoscopic texture [53]

The following main results were obtained in the studies of polymeric nematic LC during this period.

1) It was demonstrated that elastic constants, equilibrium dielectric and optical properties of polymeric nematics are almost similar to the corresponding values for their low molecular weight structural analogs. The observed differences are not crucial. Transitions in LC polymers proceed much slower than in low molecular weight LC because of very high viscosity of their melts. These facts can be illustrated by (Fig. 49) for some nematic compounds [54].

2) The new approach to analysis of properties of polymeric LC was proposed and tested. This approach was based on comparison between characteristics obtained in experiments with diluted solutions and nematic melts.



*Fig. 49.* Dielectric anisotropy  $\Delta\epsilon$  versus temperature  $\Delta T$  for: polymer I (APE 1), II (APE 2), and low-molecular-weight III (AE 1), IV (AE 2) nematics

Interesting results were obtained in the studies of nematic «Siamese twin» dimers and trimers.

Dimers (4,4'-bis-cyanobiphenyloxyalkanes, BCBOA):

# 

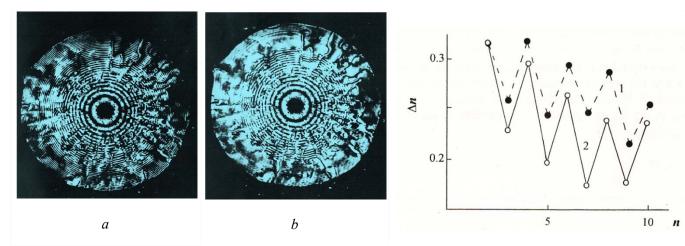
Trimers (*bis*-(4-cyanobiphenyl-oxyalkaneoxy)4,4'-biphenyls, BCBOAOB):

# $N = C - \bigcirc - \bigcirc - \bigcirc - (CH_2)_n - O - \bigcirc - \bigcirc - \bigcirc - \bigcirc - O - (CH_2)_n - O - \bigcirc - \bigcirc - C = N$

Their molecules consist of rigid anisotropic cyanobiphenyl fragments linked by flexible cores. These compounds demonstrate dramatic odd-even effect in thermal characteristics, degree of orientational order, entropy and enthalpy of isotropic liquid – LC

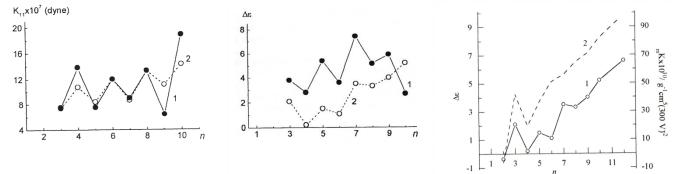
transition when the spacer length in the molecules is varied [55–56]. Using the classical Freedericksz geometry, it is possible to obtain well oriented planar layers of nematics and study their deformations in magnetic and electric fields. As an example, we present polarization photograph of planar layer of the dimer and photo of the same layer deformed by magnetic field (Fig. 50) [57].

The pronounced odd-even effect in optical properties of nematic dimers and trimers was found (Fig. 51) [58]. The odd-even effect was also observed for splay elastic constant (Fig. 52) [57–59] and dielectric anisotropy (Fig. 53–54) [59–60].



*Fig. 50.* Planar layer of nematic dimer with n = 10 (*a*) in the absence and (*b*) in the presence of magnetic field H = 5 kG at  $\Delta T = 30$ °C

*Fig. 51.* Birefringence  $\Delta n$  versus number of CH<sub>2</sub> groups in the oxyalkane chain for (1) dimers and (2) trimers at relative temperature  $\tau = 0.04$ 



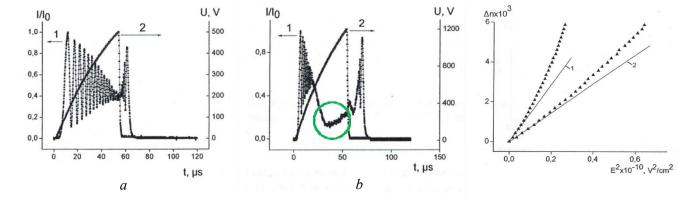
*Fig. 52.* Splay elastic constant  $K_{11}$  versus number of CH<sub>2</sub> groups in the oxyalkane chain for (1) trimers and (2) dimers at relative temperature  $\tau = 0.04$ 

*Fig. 53.* Dielectric anisotropy  $\Delta \epsilon$  versus number of CH<sub>2</sub> groups in the oxyalkane chain for (1) trimers and (2) dimers at close relative temperatures  $\tau$ 

*Fig. 54.* Dielectric anisotropy  $\Delta \varepsilon$  in nematic state (1) and the molar Kerr constant  $K_{\rm m}$  (2) in dilute solutions versus number of CH<sub>2</sub> groups in the oxyalkane chain for dimers

In addition, electro-optic properties of dimers were studied in diluted solutions using the Kerr effect [61-62]. It was shown that electro-optical properties in solutions and dielectric properties in melts of these substances are almost similar [61-64]. However, oscillations of dielectric anisotropy in nematic phase appear even at the *n* values which correspond to the absence of the odd-even effect in the Kerr constant. This fact leads to the conclusion that intramolecular orientational-polar order in these compounds increases in the mesophase due to the existence of the nematic potential.

Very interesting results were obtained in the studies of nematic LC in isotropic phase in the vicinity of the isotropization point using electric birefringence. It was found that strong impulse electric field may initiate transition of LC from isotropic to mesomorphic state. This phenomenon is illustrated by the data obtained for strongly polar 6-cyanobiphenyl presented in Fig. 55.



*Fig.* 55. Time dependences of reduced intensity I/I<sub>0</sub> of light flux (1) and electric pulse amplitude U (2) for 6 CB isotropic melts at  $\Delta T = T - T_c = 0.2$  °C and  $U_{max} = 500$  (*a*) and 1200 V (*b*)

*Fig.* 56. Birefringence  $\Delta n$  versus the square of the electric field  $E^2$  for 6 CB isotropic melts at  $\Delta T = T - T_c = 0.1 \text{ °C} (1)$  and 0.8 °C (2)

Electric field strength increases with time (curve 2). Optical response is presented by curve 1. It is seen that at high field strength (Fig. 55, b) the system becomes opaque due to transition to LC state. After switching off electric field, the system returns to isotropic state. It becomes transparent and undergoes relaxation in the same way as in Fig. 55, a. Similar result was observed in experiments with nematic polymers. However, the system which acquired LC state did not return to isotropic state after switching off field due to high viscosity of polymer melts.

Besides, deviation from the Kerr law near the isotropisation point was observed (Fig. 56). Theoretical interpretation of this effect was given within the framework of the Landau – de Gennes phenomenological theory. The results were published in [65-67].

A number of very interesting studies were carried out to create various devices for the practical use of LC.

In particular, linear prism liquid-crystal polarizers were intended [68] for replacement of Glan-Thompson and Glan-Taylor polarizing prisms in laser optics. It was necessary since large-aperture, high transmission and high threshold of laser radiation induced damage. These polarizers are presented in the image (Fig. 57). The principle of their operation is illustrated in Fig. 58. Note that the quality of the polarizer depends mainly on homogeneous orientation of LC layer.

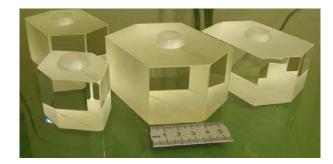
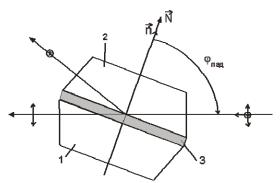


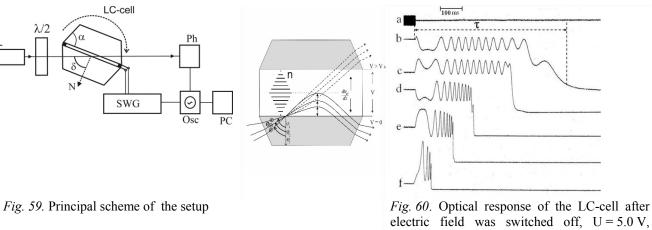
Fig. 57. LC polarizers



*Fig. 58.* Optical scheme of prism LC polarizer. 1, 2 – glass prisms, 3 – liquid crystal layer, N – normal to the LC layer, n – optical axis of LC layer

Also the original method for the determination of LC tilt angle was suggested [69–70]. Correct determination of this angle is important in development of LC optical devices. The experimental setup was also implemented.

At present, local dynamics of director reorientation under electric field in helical LCstructure is studied (Fig. 59–60). These experiments are carried out together with theoretical calculations and are of great interest due to practical applications of LC-materials [71–72].



*Fig. 60.* Optical response of the LC-cell after electric field was switched off, U = 5.0 V, f = 1000 Hz. a – voltage pulse, b, c, d, e, f – optical responses for  $z = 8.7, 7.4, 5.1, 3.0, 1.7 \mu m$ 

remarkable achievements in the field of LC science (Fig. 61). The first award winners were George William Gray and V.N. Tsvetkov, awarded for major contributions into LC chemistry and physics, respectively. The medal was also given to Dmitry Vsevolodovich Freedericksz (son of V.K. Freedericksz) (Fig. 62).



*Fig. 62.* The laureates after the award ceremony (from the left: G.W. Gray, D.V. Freedericksz, V.N. Tsvetkov)

### The memory of V.K. Freedericksz

Surely, a scientist is best remembered for his works, and the works of Freedericksz were continued by his disciples and their students. Besides, the Freedericksz medal was instituted by the Russian Liquid Crystal Society «Sodruzhestvo» as a prize for



Fig. 61. Freedericksz medal

There are two portrait galleries at the Faculty of Physics of Saint-Petersburg State University. These galleries contain portraits of prominent scientists who studied or worked at the Faculty. Both galleries hold portraits of Freedericksz (Fig. 63, 64).

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*Fig. 63.* Portrait of V.K. Freedericksz in the gallery of Physical faculty of SPbU

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*Fig. 64.* A part of the portrait gallery in Winter Garden of the V.A. Fock Institute of Physics (hall near the Fock lecture room). The portrait of Freedericksz is near the portrait of his colleague Friedmann

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