LIQUID CRYSTALS

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1. INTRODUCTION. BASIC CONCEPTS AND TERMINOLOGY

THE state of matter termed liquid-crystalline (or mesomorphic) has structural properties intermediate between those of a solid crystal and a liquid. Many scientific discoveries have had an interesting fate. However, the situation was apparently unprecedented that, for about twenty years after the discovery of liquid crystals, many scientists doubted the very fact of existence of matter in this form. Furthermore, this is not amazing: the term "liquid crystals" sounds unusual and contradictory even as viewed by many physicists and chemists of the beginning of this century; such a word combination bordered on the absurd.

The first to encounter the liquid-crystalline state of matter was the Austrian botanist F. Reinitzer,[1] who found very interesting properties in cholesteryl benzoate, which he had synthesized. Crystals of this substance melted at 145°C to a liquid of turbid appearance. Upon further heating, a second melting ensued, as it were, for the turbid liquid transformed at 179°C into an ordinary transparent melt. If then the melt was cooled, a bluish color appeared at 179°C, which rapidly disappeared, and the liquid mass became turbid. Coloration appeared again upon approaching 145°C, and the substance immediately began to crystallize. Struck by the unusuality of the phenomenon, F. Reinitzer sent his preparation for study to the German physicist O. Lehmann. By studying the substance with a polarizing microscope, O. Lehmann[2] determined that the turbid phase is optically anisotropic. The specimen became turbid because it was an aggregate of many microscopic regions of spontaneous optical anisotropy oriented at random with respect to one another (Fig. 1). Light scattering at the boundaries of these regions explained the nontransparency of the specimen. Later O. Lehmann found analogous properties in a series of other compounds, such as p-azoxyanisole, p-azoxyphenetole, ethyl p-azoxybenzoate, ammonium oleate, etc. A characteristic feature of all these substances was the fact that, over a certain temperature range, they possessed simultaneously the properties of a liquid (high fluidity, ability to form droplets, coalescence of drops upon contact, etc.) and those of most solid crystalline substances (optical anisotropy). O. Lehmann suggested that they are a new state of aggregation of matter. Without vacillating, he called this state "liquid-crystalline".

FIG. 1. The liquid-crystalline phase of cholesteryl benzoate between crossed Nicols of a polarizing microscope. Dark circle— air bubble. Magnification 540×.

O. Lehmann's communications aroused incredulity among many scientists, and doubt that such a state of matter could exist. Apparently, O. Lehmann's first notions on liquid crystals played a certain role here. He viewed them then as being ordinary crystals in which the three-dimensional space lattice is highly mobile (this later proved false). Certain scientists tried to prove that liquid crystals are nothing but an emulsion strongly scattering light, so that a specimen looks turbid. Others thought that they were tiny solid crystallites surrounded by a liquid film, and hence coalescing on contact, or conversely, they were droplets of an ordinary liquid that had a very thin crystalline film on their surfaces. However, numerous studies by O. Lehmann,[3,4] R. Schenk,[5] and others showed irrefutably that the liquid-crystalline state is an independent thermodynamic state of matter. They found that liquid crystals are anisotropic not only in their optical properties, but in their electrical, magnetic, and other properties. Further, O. Lehmann showed that two types of liquid crystals exist. He called the first type "liquid crystals proper"; they had about the same viscosity as water. The second type, which had a viscosity about ten times that of the first type, he called "fluid crystals." About one out of every two hundred substances synthesized in laboratories shows liquid-crystalline properties. It turned out that liquid crystals are formed mainly by organic compounds whose molecules have elongated, rodlike shapes.[6-8]

G. Friedel[10] proposed a classification of the states of matter based on their structural differences.

G. Friedel distinguishes two types of liquid crystals, just as O. Lehmann does. He introduced new terms to denote them: the "smectic state" and the "nematic state," which are combined under the general term, the "mesomorphic state." In the smectic state the elongated molecules form layers that easily slide on one another. The name "smectic" comes from the Greek $\sigma\mu\eta\gamma\mu\alpha$, or soap. It was chosen because the first liquid crystals of this type were found among the soaps. The name "nematic state" comes from the Greek $\nu\eta\mu\alpha$, or thread: nematic liquid crystals under the microscope show thin mobile filaments (or disinclinations). In the nematic state the elongated molecules are oriented in a single definite direction. The term "mesomorphic state" indicates that the nematic and smectic states are characterized by a molecular structure intermediate in degree of molecular order between solid crystals and amorphous liquids. As a whole, Friedel's classification of the states of matter appears as follows:

1. The amorphous state (Fig. 2a) is characterized by disordered arrangement and motion of the molecules. The molecules can rotate about any arbitrarily chosen axes.

2. The nematic state (Fig. 2b). The centers of gravity of the elongated molecules are arranged at random. The long axes of the molecules are oriented in a certain direction. Rotation about the long axis of the molecules is allowed.

3. The smectic state (Fig. 2c). The centers of gravity of the elongated molecules are arranged in equidistant planes, and are mobile in two dimensions (in the smectic planes). The molecules can rotate about their long axes.

4. The crystalline state (Fig. 2d). It is characterized by arrangement of the molecules on a three-dimensional crystal lattice.

We note that there is still another type of liquid crystals, the cholesteric liquid crystals, which G. Friedel[10] assigns as a variety of the nematic type. Their structure is the same as for nematic liquid crystals, but has an additional twist about an axis perpendicular to the long axes of the molecules. Cholesteric liquid crystals have especially interesting properties, which will be discussed in detail below.

We should also note that the literature also uses other terms besides "liquid crystals," "fluid crystals," and the "mesomorphic state" (of the smectic and nematic types), e.g.: "anisotropic liquids" and "paracrystals." The most commonly used terms are "smectic liquid crystals" and "nematic liquid crystals." We shall adhere to this terminology in this article.

Liquid crystals that are obtained by heating a solid have been called "thermotropic." However, heating is not the only way to obtain liquid crystals. Their formation can be observed when solid crystals of certain substances are dissolved in certain solvents.
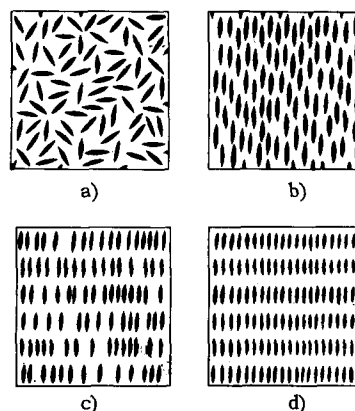

FIG. 2. Schematic arrangement of molecules in: (a) an amorphous melt, (b) a nematic liquid crystal, (c) a smectic liquid crystal, and (d) a solid crystal.

These liquid crystals have been called "lyotropic."

A number of reviews and monographs[3-16] have been devoted to the problem of the liquid-crystalline state. The symposia in Germany[17] in 1931 and in England in the Faraday Society[18,19] in 1933 and 1958 were definite high points for summing up the results of the study of liquid crystals. An International Conference on Liquid Crystals was held in 1965 at Kent State University (USA).

About a thousand papers have been published on the liquid-crystalline state. Nevertheless, the problem of the nature and properties of liquid crystals is still far from final solution. The data of many studies often contradict one another. However, there is no doubt that the renewal of intensive studies of liquid crystals in America, Germany, France, England, and in our country, due to the unexpectedly widened perspectives of applying them in new fields of technology, has ensured progress in this field of knowledge in the immediate future.

2. TEXTURE AND OPTICAL PROPERTIES OF LIQUID CRYSTALS

a) Smectic Liquid Crystals

The classic example of a substance giving liquid crystals of the smectic type is ethyl p-azoxybenzoate:

$$C_2H_5OOC - \langle \rangle - N = N - \langle \rangle - COOC_2H_5.$$
$$O$$
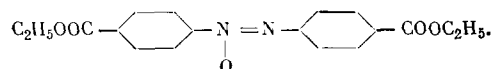
Solid crystals of this substance melt at 114°C and form liquid crystals of the smectic type. The latter melt at 120°C to an ordinary isotropic liquid. If the isotropic melt is cooled, then at 120° individual nuclei of the liquid-crystalline phase appear at first. They have the shape of elongated rods (Fig. 3). Then the rods coalesce to form a so-called confocal (or focal conic) texture, which can be conveniently studied in the polarizing microscope between crossed Nicols (Fig. 4). We note that an ordinary isotropic liquid is
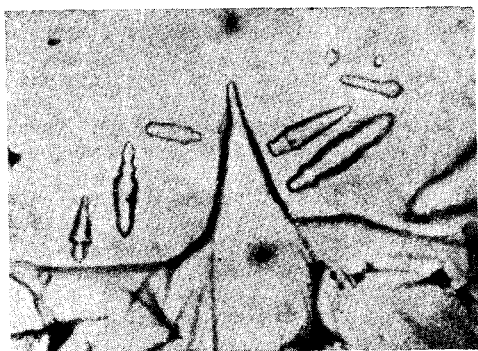
FIG. 3. Nuclei of a smectic phase in the form of rods suspended in the isotropic melt. At the bottom of the micrograph, the rods have coalesced into a confocal texture. Natural light. Magnification 200×.
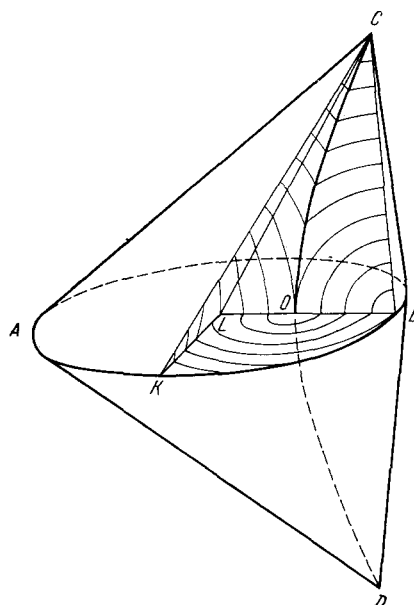

FIG. 5. Diagram of the structure of a confocal domain. The smectic layers form series of cyclides of Dupin. The arrangement of the molecules is shown in one of the layers.

invisible between crossed Nicols. In this case the field of view of the microscope remains dark. However, if we bear in mind that the birefringent smectic texture shown in Fig. 4 has a clearly marked regular structure, then it becomes evident that smectic liquid crystals are something completely different an ordinary liquid (although they are mobile!).

The texture shown in Fig. 4 consists of distinct regions, or confocal domains. The geometry of each domain is rather complex. The differing degree of binding of the molecules to the glass surfaces (the slide and the cover glass) causes the smectic layers to be twisted to form a family of surfaces, or the so-called cyclides of Dupin.[10,13,20] The arrangement of the smectic layers in each domain is clearly visible in Fig. 5. The basis for generating the family of cyclides is the confocal pair of the ellipse AB and the hyperbola COD. At any point in the domain, the direction of the long molecular axes coincides with the direction of a straight line drawn through three points: the center of the given molecule, a point on the ellipse, and a point on the hyperbola. For example, such a line might be BL, BC, or KC in Fig. 5). These straight lines are also the directions governing the arrangement of the optic axes in the domain. This structure of confocal domains is the reason for the optical pattern that one observes under the micro-

scope (see Fig. 4). We note that the ellipse and hyperbola are the sites of breaks in the optical continuity of the medium, and hence are quite noticeable even in natural light. Study of the geometry of the smectic texture and the dynamics of its growth from an isotropic melt makes it possible to draw a set of interesting conclusions on the structure of the smectic phase.[10,20,21] From among the many curious peculiarities of structure of smectic liquid crystals, we shall mention here only one, which most clearly illustrates their unique nature. This is the formation of terraced drops. If one puts a little of the substance on a very clean and flat surface, e.g., a flake of mica freshly cleaved on its cleavage plane, then on heating, the smectic phase appears in the form of terraced flattened drops. Figure 6 gives a diagram of their structure. The formation of terraced drops results from the layered nature of the smectic liquid crystal. The thickness of each terrace is a multiple of the thickness of an individual smectic layer. When the surface of the drop is vibrated mechanically, one can see the individual layers freely sliding on one another. Motion of the layers can also be observed when the

FIG. 4. The smectic confocal texture of ethyl p-azoxybenzoate. Crossed Nicols. Magnification 400×.
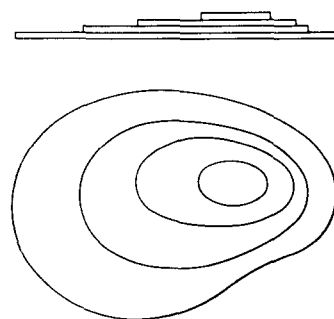

FIG. 6. Diagram of the structure of terraced smectic drops in two projections.

drop is spreading on the surface at the instant when the solid crystals melt to form the smectic drop.

Study of uniformly-oriented regions of a smectic specimen in convergent light has shown that the conoscopic pattern is analogous to that obtained from a uniaxial crystal plate. All known liquid crystals of the smectic type are uniaxial, and have a positive birefringence.

According to A. V. Shubnikov,[22] a uniformly-oriented smectic specimen or an individual "monocrystalline" domain can be assigned a symmetry symbol m·∞:m. This is the same symmetry as the family of indicatrices of uniaxial crystals. This is the limiting symmetry group, which has a single symmetry axis ∞ of infinite order, an infinite number of longitudinal symmetry planes m, an infinite number of twofold axes, and a center of symmetry. We note that most studies of smectic liquid crystals have been only qualitative in nature. This is apparently due to certain experimental difficulties involving the preparation of uniformly oriented smectic media, the need of strict temperature control, and finally, the mobility of the medium. In turn, this explains the almost total lack of a theory of the physical phenomena observed in liquid crystals of this type. Evidently, only the design of quantitative experiments can ensure success along this line, and as a final result, in the practical application of smectic liquid crystals as well.

b) Nematic Liquid Crystals

We recall that the molecules in a nematic liquid crystal are oriented in a certain definite direction (see Fig. 2b). There are two varieties of nematic liquid crystals: the nematic liquid crystals proper and the cholesteric. The cholesteric variety has a structure twisted like a screw. Bearing in mind the very unique properties of cholesteric liquid crystals, we find it convenient to discuss them in a separate section. Now we shall take up the nematic liquid crystals proper.

A typical example of a substance giving nematic liquid crystals is p-azoxyanisole:

$$CH_3-O-\langle\ \rangle-N=N-\langle\ \rangle-O-CH_3.$$
$$\overset{|}{O}$$
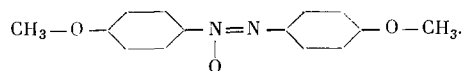
Liquid crystals of p-azoxyanisole exist over the temperature range from 116° to 136°C. A specimen exhibits a multitude of dark filaments (from which the name nematic came). The filaments are mobile, and quite visible in natural light (Fig. 7). They are sites of breaks in the optical continuity of the medium, at which the orientation of the elongated molecules abruptly changes. By analogy with the dislocations in ordinary crystals, one can call the filaments disinclinations.[23] If the specimen is prepared as a thin layer between a slide and a cover glass, then the disinclination lines often lie perpendicular to the glass.
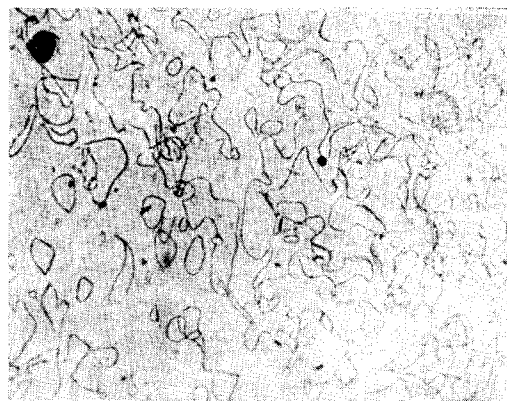

FIG. 7. Filaments in a nematic liquid crystal. Natural light. Magnification 200×.

The sites of emergence of the disinclinations at the surface of the specimen are well marked. They look like dark spots, or "nuclei."[10] Between the crossed Nicols of a polarizing microscope, one notes dark branches extending from the nuclei. These are the regions of the specimen in which the directions of the long axes of the molecules coincide with the vibration directions of the polarizer and analyzer, and are hence extinguished (Fig. 8).

The nature of the arrangement of the molecules along the disinclination lines can vary.[4,23] The possible cases of mutual arrangement near the nuclei (in transverse sections through the disinclinations) are shown in Fig. 9. The different configurations of arrangement of the molecules are described by the parameters n and Φ, which play a role in the theory of elasticity of liquid crystals.[23,24]

In addition to the disinclinations observed as filaments or nuclei, one also distinguishes surface disinclinations, which occur only at the surface of the specimen in contact with the slide or cover glass.[25] By using special methods of treating the glass surfaces between which the substance is enclosed, one can obtain oriented "monocrystalline" nematic layers free from disinclinations.[25-30]

Studies in convergent light have shown that nematic crystals are uniaxial positive. The magnitude of the

FIG. 8. Nuclei and dark branches proceeding from them. Liquid-crystalline texture of p-azoxyanisole. Magnification 120×.

$$n=-1,\ \Phi=+\tfrac{1}{2}\Psi \qquad n=-1,\ \Phi=-\tfrac{1}{2}\Psi \qquad n=+2,\ \Phi=+\Psi$$

$$n=+2,\ \Phi=+\Psi+\tfrac{\pi}{4} \qquad n=+2,\ \Phi=+\Psi+\tfrac{\pi}{2} \qquad n=-2,\ \Phi=-\Psi$$

$$n=+3,\ \Phi=+\tfrac{3}{2}\Psi \qquad n=+4,\ \Phi=+2\Psi$$
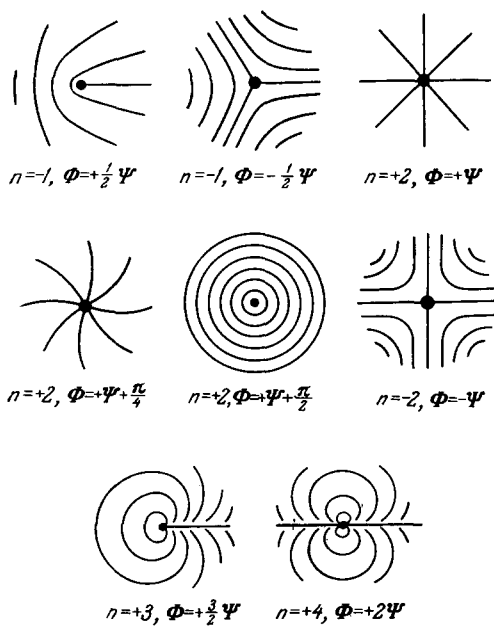
FIG. 9. Diagram of the arrangement of molecules about the nuclei. The lines indicate the directions of the long axes of the molecules.

birefringence of a nematic phase is rather high. Thus, for p-azoxyanisole at 117°C, the difference between the refractive indices of the ordinary and extraordinary rays $\Delta n = (n_e - n_o) = 0.268$. The value of the birefringence of liquid crystals varies with the temperature. The refractive index of the extraordinary rays decreases with rising temperature, while that of the ordinary rays increases. The value Δn of the birefringence falls, and at the temperature of transition of the liquid crystal to an isotropic liquid it becomes zero (Fig. 10).[151]

Many liquid crystals show very marked dichroism. Thus, p-azoxyanisole shows dichroism from dark yellow to white. If one looks at an unoriented specimen of p-azoxyanisole with the polarizer alone (with
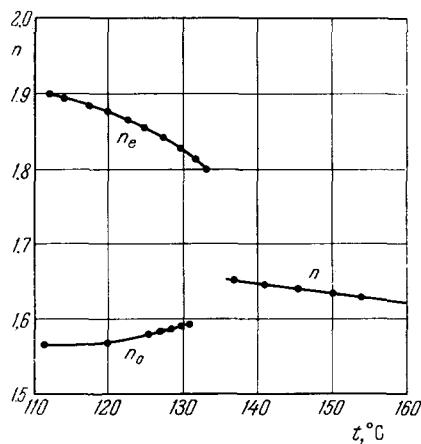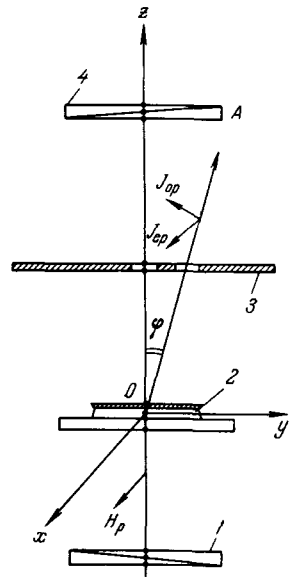
FIG. 11. Diagram of an apparatus for measuring the light scattering of a liquid crystal. 1—Polarizer; 2—oriented liquid-crystalline specimen; 3—screen with apertures; 4—analyzer.

the analyzer out), one can see that the differently-oriented regions whose optic axes coincide with the vibration direction of the polarizer or are perpendicular to it show different colors (dark yellow and white). When the microscope stage is rotated through 90°, the color of each region changes to its opposite. As will be discussed below, the phenomenon of pleochroism of liquid crystals is used in technology for preparing polaroids.

An extremely important fact is that nematic liquid crystals scatter light (and hence look turbid), not only when unoriented, but even when prepared as "monocrystalline" films. Using the apparatus illustrated in Fig. 11, one can measure the intensity of the scattered light at the angle φ to the incident light beam.[28] The intensity of the scattered rays decreases with increasing angle φ. It has been shown that the scattered light vibrates mainly in the direction perpendicular to that of the incident light (H_p). Thus, for example, for $\varphi = 9°$, the depolarization coefficient is

$$K = \frac{J_{op}}{J_{ep}} \approx 8.$$

Here J_{op} refers to the vibrations lying in the yz scat-

FIG. 10. Graph of the temperature-dependence of the refractive index n_o of the ordinary rays and n_e of the extraordinary rays for p-azoxyanisole.
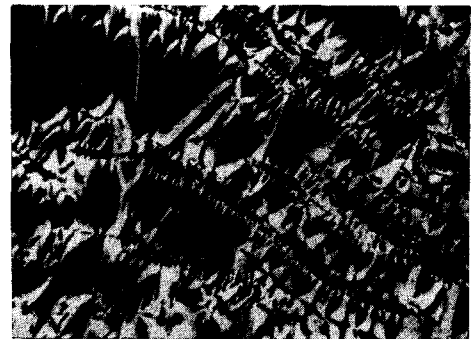

FIG. 12. The cholesteric confocal texture of cholesteryl cinnamate. Crossed Nicols. Magnification 270×.

tering plane, and J_{ep} to the vibrations in the xz plane.

Measurements of the scattered light, together with study of the temperature-dependence of the refractive indices, provide valuable material for creating an optical theory of liquid crystals. One must suppose that a basis will be laid for refinement and development of this theory as optical data are amassed for a larger number of substances than have been treated as yet.

Spectroscopic studies on liquid crystals also show promise. We note that the visible and ultraviolet spectra for the liquid-crystalline and isotropic phases of a given substance differ little. A substantial difference has been found in the Raman spectra of p-azoxyanisole in its different phases.[31] Here the spectra of the solid substance and the nematic phase contain a line at 1247 cm^{-1}, which is lacking in the spectrum of the isotropic melt of p-azoxyanisole. This shows that the structure of the nematic phase resembles the solid phase more than it does the isotropic.

Recent studies of Maier and Englert[32,33] on the infrared dichroism of p-azoxyanisole are of great interest. They used plane-polarized light. In one case the vibration direction coincided with the major axes of the molecules, and in the other case they were perpendicular. The data obtained here could be used to estimate the degree of orientation of the molecules in the nematic specimen.
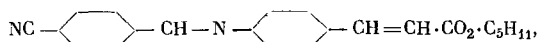
c) Cholesteric Liquid Crystals

As we see from the name itself, liquid crystals of the cholesteric type are given by the derivatives (esters) of cholesterol. For example, cholesteryl cinnamate, which has the structural formula
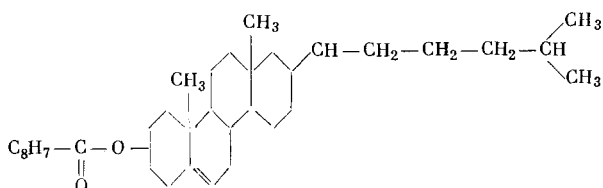
gives a liquid-crystalline phase over the temperature range 156—197°C.

As an example of cholesteric liquid crystals not belonging to the compounds of cholesterol, we can mention act-amyl p-(4-cyanobenzylideneamino)-cinnamate

$$NC-\langle\quad\rangle-CH-N-\langle\quad\rangle-CH=CH\cdot CO_2\cdot C_5H_{11},$$

which forms a cholesteric phase over the temperature range 95—105°C. When an isotropic melt is cooled, the cholesteric liquid crystals form a confocal texture (Fig. 12). Hence we can conclude that the substance exists in layers. It would seem that we could classify the given substance by this criterion as being smectic. However, many facts convince us that this is not the case. First of all we note that not a single substance is known which gives both a cholesteric and a nematic phase (over the appropriate temperature ranges). At
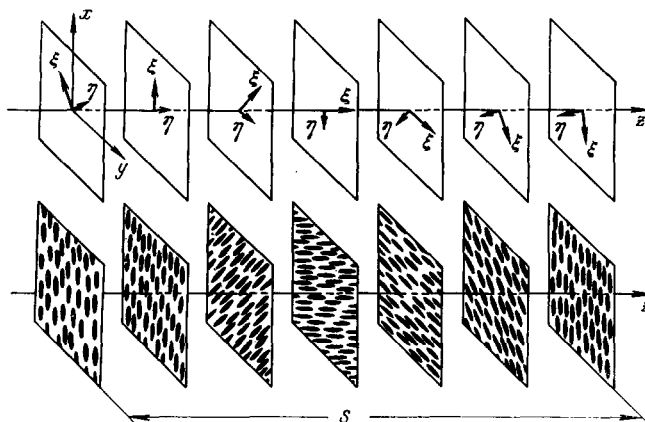

FIG. 13. Diagram of the arrangement of molecules in a cholesteric liquid crystal. ξ and η are the molecular axes. The lower diagram shows the arrangements of the set of molecules for the cases in which the molecular axes lie in the directions shown in the upper diagram.

the same time, we know at present many substances that give a cholesteric phase at higher temperatures, but form a typical smectic phase at lower temperatures. The transition from a cholesteric phase to a smectic one involves a latent heat of transition. Many facts indicate that a cholesteric phase is a variety of nematic phase, but in contrast to the latter, has a structure twisted in screw-like fashion. Figure 13 shows a diagram illustrating the arrangement of the molecules in a cholesteric structure. Here X, Y, and Z are a Cartesian coordinate system, and ξ and η are the principal axes of the molecules. In the OZ direction, the molecular axes are twisted in such a way that their positions are given by the equations

$$\xi = X \cos \frac{2\pi Z}{P} + Y \sin \frac{2\pi Z}{P}, \qquad \eta = Y \cos \frac{2\pi Z}{P} - X \sin \frac{2\pi Z}{P}.$$

As a whole, ξ, η, and Z form a helical system of coordinates.

The pitch of the helix is P = 2S, and this determines the layered character of the structure. In distinction from the layers of a smectic phase, whose layer thickness equals the length of the molecule (20—40 Å), the thickness of the layers in a cholesteric phase is of the order of 2000 Å. Correspondingly, the diagram shown in Fig. 14 may serve as a possible explanation of the formation of confocal domains in a cholesteric phase. The helical twist of the arrangement of molecules giving rise to the layered structure of the substance is shown in this diagram only along the generating cones AC, BC, and BD. In contrast to smectic domains, the molecules are arranged here with their long axes always perpendicular to a straight line drawn through the hyperbola and the ellipse. This explains why the domains of a cholesteric phase are always optically negative (while in a smectic phase they are always positive). If one moves the cover glass slightly, the cholesteric confocal texture is disrupted, and a planar texture is formed. In essence, the latter is a "mono-
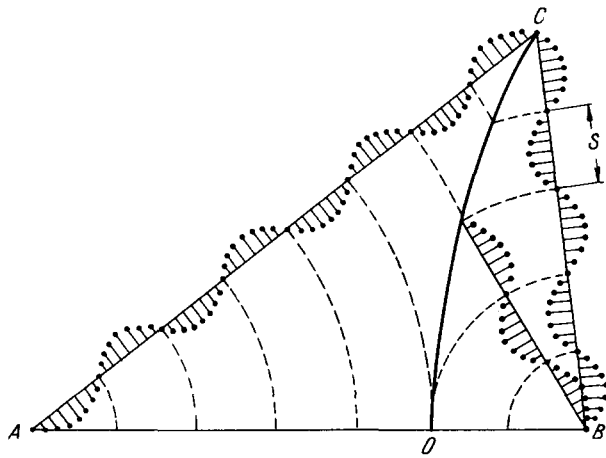
FIG. 14. Arrangement of molecules in a cholesteric confocal domain.

crystalline" cholesteric film. Here also a layered structure exists, but not in the physical sense, which would presuppose the existence of molecular layers that could slide on one another as happens in smectic terraced drops. Rather, it is due to the helical twisting of the arrangement of molecules (Fig. 15). The thickness of these layers (Grandjean layers) increases as the temperature of the cholesteric phase rises. When one observes a planar texture between crossed Nicols, it appears colored, and the color does not vary as the stage is rotated. This indicates that the texture is optically active. In certain liquid-crystalline substances and mixtures, the rotation is as much as 60,000—70,000°/mm. Perhaps this is one of the most amazing properties of liquid crystals, since the specific rotation of the plane of polarization for ordinary organic crystals or liquids rarely exceeds 300°/mm.

Such a strong optical activity cannot be explained by the intrinsic rotatory power of the molecules. Apparently, it is due to the twisted nature of the structure of cholesteric liquid crystals, i.e., by the regular "rotation" of the molecules in their mutual packing.

The following is a first approximation of a theoretical optical model of the cholesteric structure permitting explanation of its optical properties.[34] Let us suppose that a planar cholesteric texture consists of birefringent laminae having refractive indices n_e and

n_0. These laminae are stacked on one another in such a way that their median lines describe a helix of pitch P. In such a case, application of the electromagnetic theory of light leads to an expression for the value of the optical activity of cholesteric liquid crystals:

$$\alpha = -4.5 \cdot 10^4 n^2 \frac{P}{\lambda^2} ;$$

Here α is the optical activity in a direction parallel to the axes of the helical structure, n is the birefringence of the medium in the untwisted form, and P is the pitch of the helix (2S = P in Fig. 13). This equation gives results in good agreement with the experimental data.[35,36] The same theory predicts that there is a certain wavelength λ_0 at which one will observe intense selective reflection by a cholesteric substance of circularly polarized light having λ_0 = Pn, where n = $(n_e + n_0)/2$ is the mean refractive index. This reflection is strong in the range from $\lambda_0(1 - \frac{1}{2}\alpha)$ to $\lambda_0(1 + \frac{1}{2}\alpha)$, but weak outside this range; $\alpha = (n_e - n_0)/n$ is the relative birefringence. Indeed, the sign of the rotatory power of a cholesteric liquid crystal inverts as the wavelength varies, and the curve of the specific rotation of the plane of polarization has the form shown in Fig. 16. The inversion wavelength λ_0 differs for different substances, and depends on the temperature.[32] It can occur not only in the visible, but also in the infrared or the ultraviolet regions of the spectrum.

Strong reflection (scattering) of light passing through a planar cholesteric texture occurs in a narrow spectral band $\Delta\lambda$ about λ_0 (e.g., $\Delta\lambda$ = 0.02 μ for cholesteryl propionate). The wavelength of the scattering depends not only on the substance and the temperature, but also on the angle between the scattered and incident light rays. The scattered rays will have shorter wavelength as this angle increases. Hence, if one observes a planar cholesteric texture in white light (even with the naked eye), it will show varying colors, depending on the angle to the surface at which the observation is made.[10]

If one makes the observation at a constant angle of view, but at varying temperatures, then one will also observe a color change in the specimen. An especially convenient way to make the observation is to cool the specimen in the air. Then a temperature gradient arises, since the substance cools fastest at the edges
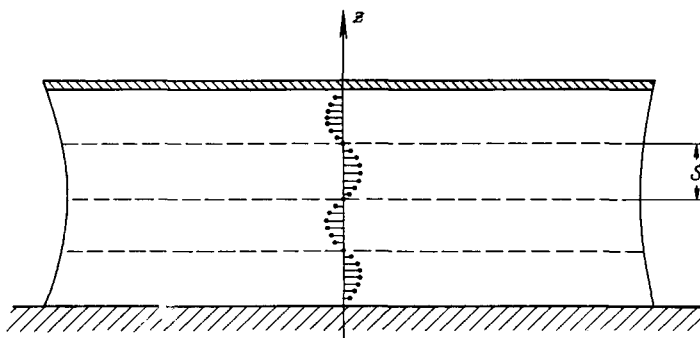

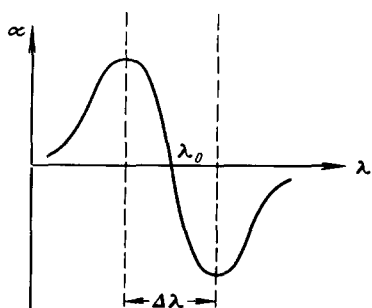FIG. 15. Arrangement of molecules in a planar cholesteric texture.

FIG. 16. The wavelength-dependence of the specific rotation of the plane of polarization of a cholesteric liquid crystal.

of the cover glass. Then one can see an isotropic melt existing in the center of the specimen, solid crystals beginning to grow along the edges of the cover glass, and a cholesteric liquid crystal in the interval between these phases. If the structure of the liquid crystal is planar, one can observe it brilliantly flashing in all the colors of the spectrum. In the warmer regions, the color is blue-violet, and in the cooler regions adjoining the solid phase it is red.

There is a definite relation between the structure of the molecules and the sign of rotation of the plane of polarization. As we know, every cholesteric liquid crystal can rotate the plane of polarization either to the right or to the left, depending on the wavelength of the light. If the compound consists of molecules of right-handed structure, and the wavelength of the incident light is shorter than that scattered with maximum intensity, the liquid crystal will rotate the plane of polarization to the right. However, if the wavelength of the incident light is gradually increased, then when it passes through λ_0, where maximum scattering is observed, the rotation will become left-handed. The converse holds for substances having left-handed molecules.

Another interesting fact is that light scattered by a planar cholesteric texture is circularly polarized (to the left or right). When a specimen is illuminated by light that is also circularly polarized, the following effect can be observed. If a dextrorotatory liquid crystal is illuminated by light that is also circularly polarized to the right, the light will be scattered without change of sign (likewise circularly polarized to the right). This phenomenon is opposite to the normal effect occurring when polarized light falls on other substances (not liquid crystals). If the incident circularly-polarized light is of opposite sign ("left-handed" light and right-handed substance), then it will pass through the specimen without change of sign or appreciable scattering. In other words, a dextrorotatory cholesteric substance scatters the right-handed circular components of the indicent beam, and transmits the levorotatory components.

Other important information on the nature of cholesteric liquid crystals has been obtained by studying

mixtures of substances.[38-40] If one prepares a mixture of 2.4 parts by weight of amyl p-(4-cyanobenzylideneamino)-cinnamate, a right-handed cholesteric liquid crystal, and 2.7 parts by weight of cholesteryl benzoate, a left-handed liquid crystal, then below a certain temperature t_0 this mixture will be dextrorotatory, but levorotatory above t_0. As t_0 is approached, the optical activity declines. At the point t_0 the optical activity is zero, the optical sign becomes positive, and the mixture acquires all the characteristic properties of nematic liquid crystals. This fact favors the idea that cholesteric liquid crystals are actually a variety of nematic liquid crystals having a twisted structure.

Another important example of the study of mixtures is: if one mixes the dextrorotatory liquid crystal amyl p-(4-cyanobenzylideneamino)-cinnamate (A) with the nematic (not rotating the plane of polarization) liquid crystal isoamyl p-(4-cyanobenzylideneamino)-cinnamate (B), this mixture will show paradoxical properties. As the percentage of the cholesteric substance A is increased, the optical activity falls.

Analogous data are obtained also in mixtures of other substances, e.g., nematic p-azoxyanisole and cholesteric cholesteryl acetate. The optical activity increases as the content of the dissymmetric cholesteryl acetate molecules is lowered, and that of the more symmetric p-azoxyanisole molecules is increased. Above all, this indicates that the rotation of the plane of polarization by cholesteric liquid crystals depends on the structure of the aggregate of molecules, rather than on the structure of the molecules themselves. This conclusion is borne out very convincingly also by the fact that a nematic liquid crystal can be easily transformed into a cholesteric phase by introducing a small amount of an optically-active admixture that doesn't give liquid crystals by itself. An example of such a mixture is p-azoxyanisole containing a small amount of rosin.[41] The liquid-crystalline drops precipitating from the isotropic melt have a layered structure (Fig. 17a). Individual regions of the specimen form a periodic texture (Fig. 17b). Apparently, this texture is caused by a helical twisting of the structure of the substance.

We note in conclusion that cholesteric liquid crystals or twisted nematic phases have a lower symmetry in their optical properties than smectic and nematic phases, namely, $\infty : 2$. This symmetry group coincides with the symmetry of the rotation of the plane of polarization, and is a subgroup of $m \cdot \infty : m$.

d) Lyotropic Liquid Crystals

Many colloidal systems give formations resembling nematic, cholesteric, and smectic liquid crystals. For example, they include aqueous systems of many soaps, of tobacco mosaic virus, and of certain peptides, etc. Such formations are called lyotropic liquid crystals,
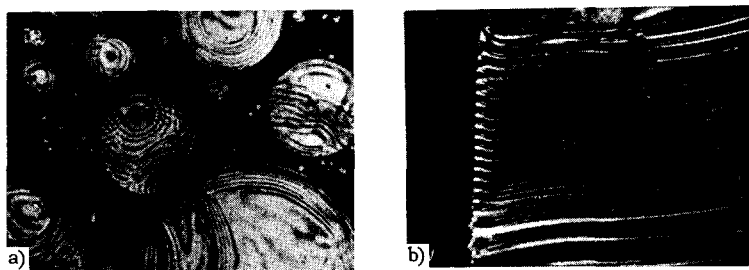
FIG. 17. Liquid crystals of a mixture of p-azoxyanisole and rosin. a) Liquid-crystalline spherulites in an isotropic melt; b) a periodic texture at the edge of the liquid-crystalline specimen. Crossed Nicols. Magnification 75×.

which are produced in the process of dissolving a solid crystalline substance. [42] As the amount of solvent is increased, the system becomes first smectic, then nematic, and finally is transformed into an isotropic liquid. We note that many substances give liquid crystals of only one type. For example, poly-γ-benzyl-L-glutamate at a certain concentration in dioxane gives only a cholesteric phase. [35,36]

A very convenient substance for studying the texture of lyotropic liquid crystals is potassium oleate.[43] Water-alcohol solutions of potassium oleate are sold under the name of "tincture of green soap." If we put a drop of such a solution between a slide and a cover glass, then smectic lyotropic liquid crystals will begin
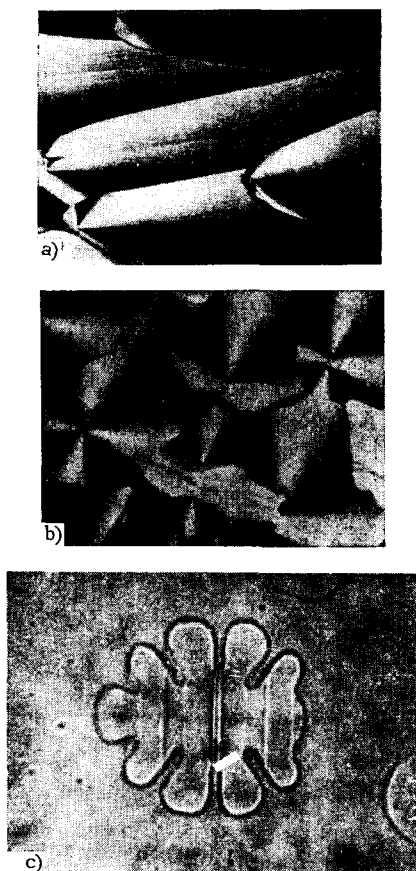

FIG. 18. Lyotropic smectic liquid crystals of potassium oleate. a) Texture at the edges of the specimen; b) texture at the center of the specimen (magnification 300×); c) a single domain in the form of a figure of rotation (magnification 800×).

to grow after several hours at the edges of the cover glass (Fig. 18a). The texture shown in Fig. 18b will be formed nearer the center of the specimen. When a single domain of this texture grows freely (when its growth is not hindered by neighbors), it has the shape of a figure of revolution (Fig. 18c). After the domain has increased in diameter in the growth process, and has come into contact with the glass walls, the smectic layers perpendicular to the axis of the domain are twisted into cyclides of Dupin, and form a more complex texture (see Fig. 18b). Aqueous solutions of thiazine dyes (in particular, new methylene blue) also give lyotropic liquid crystals. [44]

The "solvent-smectic liquid crystal" system often gives rise to a unique texture in the form of the so-called myelin forms. One can observe the growth of myelin forms with greatest ease in the system cholesterol-glycerol. If one heats this system, then at a certain temperature t_1 the cholesterol combines with the glycerol to give liquid crystals of smectic type. On further heating, the liquid crystals melt at a temperature t_2, and decompose into the original components, cholesterol and glycerol. This phenomenon, which was discovered by A. B. Mlodzeevskiĭ, [45] is called the dissociation of liquid crystals, since the liquid crystals are stable only in the definite temperature range t_1–t_2. They decompose below t_1 or above t_2, dissociating into their original components. If one heats a cholesterol-glycerol system between a slide and a cover glass, then the smectic liquid crystals absorb the excess glycerol, resulting in growth of the myelin forms (Fig. 19). Here the glycerol plays the role of solvent for the liquid crystals, and hence a texture in the form of myelin forms is classified as a liquid-crystalline formation of lyotropic nature. In their growth, the myelin forms move and interweave like the coils of snakes. Between crossed Nicols, the centers of the myelin tubes always prove to be extinguished,
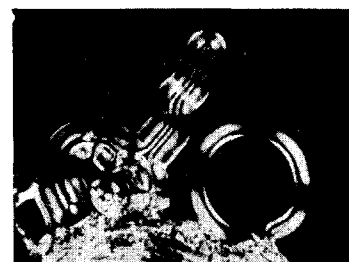
FIG. 19. Myelin forms of liquid crystals of a mixture of cholesterol and glycerol. Crossed Nicols. Magnification 800×.

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whereas the edges show strong birefringence. The sign of elongation of the tubes is positive. Myelin tubes of 0.01—0.02 mm diameter show strong interference colors.

Lyotropic liquid crystals can be formed in three-component systems.[46-51] As is known, some organic substances insoluble in water become soluble in water-soap solutions (solubilization). Such three-component "soap—water—water-insoluble substance" systems exist in the liquid-crystalline state in a certain region of the phase diagram. Thus, for example, cholesterol, which has a melting point of 148.5°C, exists at room temperature in a stable liquid-crystalline state in a soap-water solution at a concentration of one mole cholesterol per mole of soap. Liquid-crystalline spherulites and myelin forms are produced during the process of dissolving the solid substance.

3. THE STRUCTURE OF LIQUID CRYSTALS

The first studies of the structure of liquid crystals were made right after the discovery of the phenomenon of x-ray diffraction.[52-54] We note that the x-ray diffraction patterns of unoriented liquid-crystalline specimens hardly differ from those of an ordinary isotropic melt. The most valuable information on their structure can be obtained by studying oriented specimens.[55,56] One can use as orienting factors an external electric or magnetic field, or achieve orientation by special treatment of the surfaces enclosing the liquid-crystalline substance. Under these conditions, the x-ray diffraction pattern of a liquid crystal is a set of more or less diffuse equatorial and meridional arcs (Fig. 20). This is not observed in ordinary isotropic melts. Recently, the studies of B. K. Vaĭnshteĭn[67,68] have made possible a definitive, quantitative evaluation of liquid-crystalline structures.

It has proved possible to apply statistical distribution functions of the particles in describing the structures of liquid crystals. We note that substances capable of occurring in a liquid-crystalline phase usually
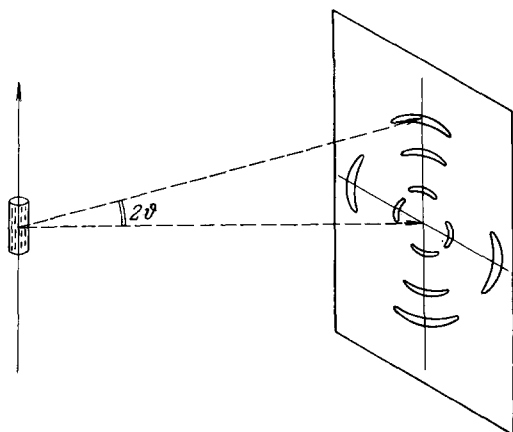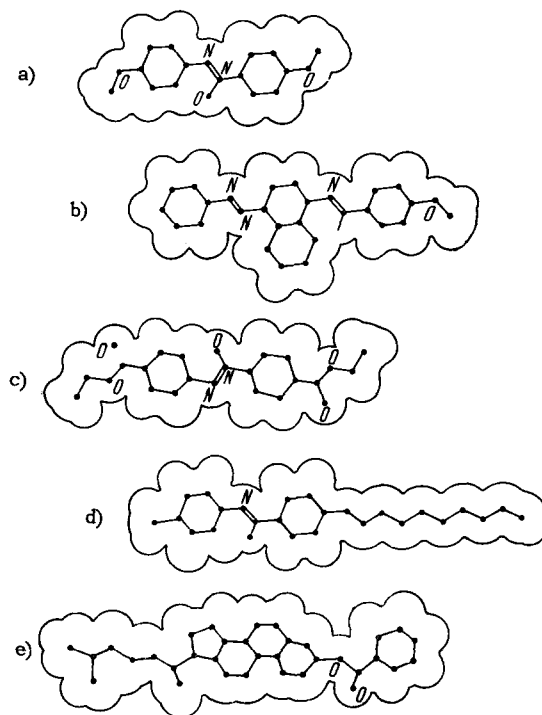

FIG. 21. The shapes of the molecules of certain substances that give liquid crystals: a) p-Azoxyanisole (nematic); b) a-benzeneazo-(anisol-a'-naphthylamine) (nematic monotropic); c) ethyl p-azoxybenzoate (smectic); d) p-(n-nonoxy) benzal-p'-toluidine (nematic and smectic); e) cholesteryl benzoate (cholesteric).

have elongated, highly anisometric molecules (Fig. 21). This raises grounds for considering them to have a mutually parallel arrangement and thus to form a denser molecular packing than would exist with a chaotic molecular orientation. Thus, certain additional minima in the packing energy become possible, intermediate between the values corresponding to true liquids and true crystals. These additional minima in the packing energy are realized in nematic liquid crystals or in layered smectic liquid crystals. In both types of uniformly-oriented liquid crystals, the long axes of the molecules are oriented along the principal z axis (and if the texture is unoriented, this is true in the individual domains). In the lateral (x,y) directions, short-range order is maintained in the arrangement of the molecules (Fig. 22a). This short-range order can be characterized by a so-called statistical distribution function $W(x,y)$ of the second kind. To derive it, one does the following. One plots about the coordinate origin the positions of the centers of gravity of the molecules surrounding any given molecule. Then one does the same for another, and a third, and so on for all the molecules. Thus one essentially obtains a superposition of the patterns of distribution of the molecules shown in Fig. 22a, with the center of each molecule successively shifted to the coordinate origin. Thus, we obtain the distribution function $W(x,y)$ of neighbors in the given molecular aggregate (Fig. 22b). This function clearly reveals the distribution of nearest

20. Diagram of the x-ray diffraction pattern of an oriented liquid-crystalline specimen.
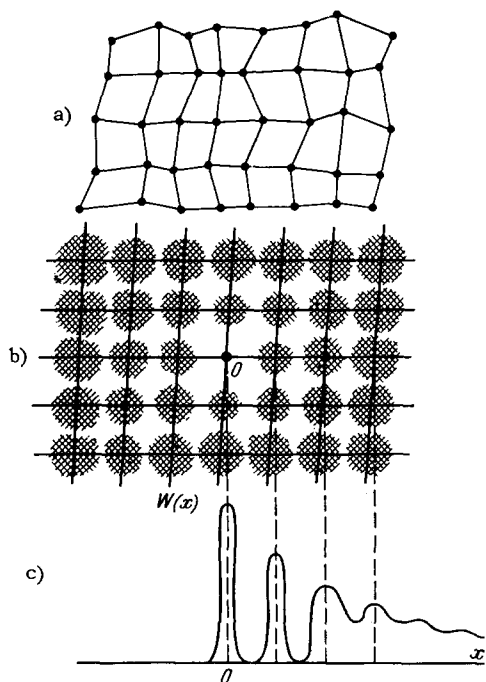
FIG. 22. a) Net disturbances of the second kind; b) the distribution function of the second kind; c) a graph of the distribution function in the Ox direction. [67]

neighbors surrounding the given molecule. Short-range order is manifested, arising from the existence in the aggregate of minimum distances within which molecules cannot approach one another, and also from the existence of a certain first maximum distance, since large cavities between the molecules also cannot exist. Evidently, in this structure the distances to the second-nearest neighbors will vary over broader ranges. The further away a neighbor is, the more diffuse its distribution function becomes. At a certain distance, it becomes constant. That is, the probability of finding the molecule anywhere is the same. If we graphically plot the distribution function W(x) for a certain direction Ox, it will have the form shown in Fig. 22c. Its peaks become more diffuse with increasing distance from the origin, and disappear at a certain distance from O, as the curve becomes flat.

As was said above, the molecules in a liquid crystal exhibit short-range order in the xy plane. Hence, this order can be characterized by the two-dimensional distribution function W(x, y) or W(r), which gives the probability of finding molecules having the vector r as the distance between their long axes. The function W(r) shows periodic, but declining maxima (just like W(x)). If the cross-section of the molecules varies greatly along their height, then a statistical periodicity that can be described by a function W(r) becomes impossible. In this case, the mutual arrangement of the molecular axes can be described by a cylindrically-symmetric function Z(r), which gives the probability of finding distances r between the molecular axes. The averaging of this function gives the projection of the

cylindrical distribution function of the molecular axes $2\pi r Z(r)$ on the xy plane. Thus, the statistics of the arrangement of the molecules, both in smectic and in nematic crystals, can be characterized in the lateral direction (perpendicular to the long molecular axes) by the functions W(r) or Z(r).

How can we characterize the structure of a liquid crystal in the z direction? In nematic liquid crystals there is no correlation between the projections of the centers of gravity on the z axis. The translation function $\tau(z)$, which is obtained by transferring all the centers of gravity of the molecules to the z axis (in a way analogous to the construction of the function W(x, y)), will have a constant value everywhere without showing either maxima or minima. We might say in this case that the structure possesses infinitesimally small statistical translations $\tau_\infty(z)$, or continuous-translation axes. Consequently, the symbol for the structure (symmetry) of nematic liquid crystals can be written as $\tau_\infty W(r)$. In smectic liquid crystals the molecules are arranged in layers, and the translations of the molecules along the z axis are mutually correlated. The correlation can be described by a periodic translation function $\tau(z)$. The layers are arranged with a certain period C, which is close to the length of the molecule. In addition, for smectic liquid crystals, one can speak with a greater degree of certainty about an antiparallel arrangement of the molecules in the layers, so as to achieve closest packing. [68] Hence, we must add "statistical" twofold axes "2" to the structural symbol of the smectic liquid crystals to account for the antiparallel arrangement of the molecules. Thus we can write the symbol as a whole as $C\tau(z)W(xy):2$. The symbol ":" here means that the axes 2 lie in the plane of the layers, and are perpendicular to the z axis. Of course, detail can be added to these symbols by adding further statistical symmetry elements as the concrete structures become studied. Thus, for example, for cholesteric structures (which we have assigned as a variety of nematic), we must take into account the twist, and introduce a screw axis of infinite order σ_∞ as a symmetry element, etc.

We can get information on the nature of the distribution functions by x-ray diffraction. Substances that give liquid crystals consist mainly of carbon atoms with a small amount of nitrogen and oxygen atoms, which have similar scattering powers (we can neglect the hydrogen atoms). Hence, to a certain degree of approximation, we can consider the specimens to be made of carbon atoms, and use the formula [67,68]

$$4\pi r^2 \varrho\,(r) = 4\pi r^2 \varrho_0 + \frac{2r^2}{\pi} \int s^2 I\,(s)\,\frac{\sin sr}{sr}\,ds;$$

Here, $4\pi r^2 \rho(r)$ gives the number of atoms in a spherical shell at distances from r to r + dr from the original atom,

$$I\,(s) = \frac{I_n}{f^2} - 1, \qquad s = \frac{4\pi\sin\vartheta}{\lambda}, \qquad \varrho_0 = \frac{\varrho}{A\cdot1.65};$$
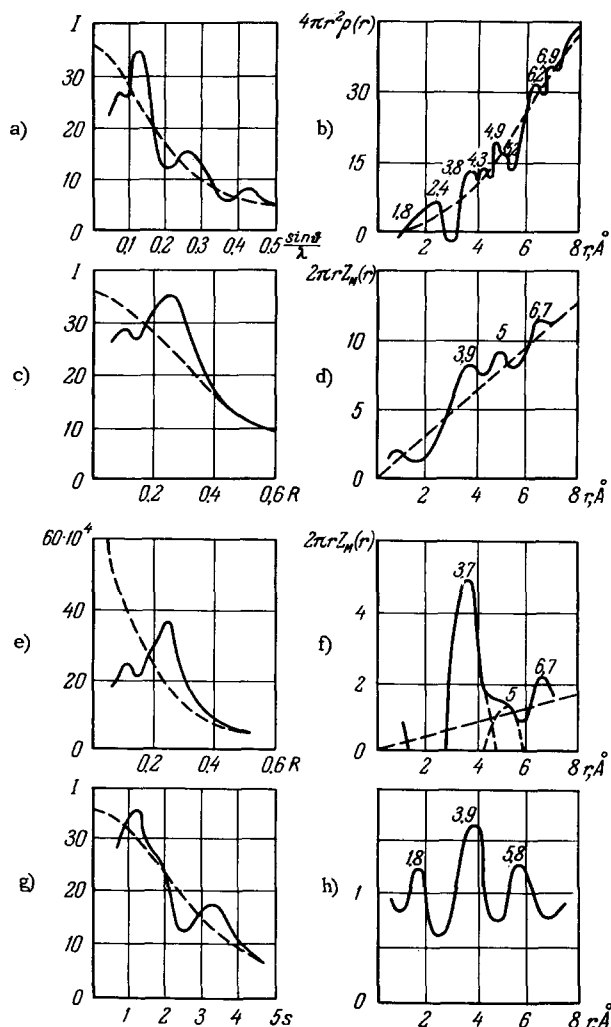
FIG. 23. Normalized curves of the intensity distribution (left) and the distribution function for liquid-crystalline BAN enclosed in glass (see text for details).[70]

ρ_0 is the mean density of the substance, which is equal to the number of atoms per cubic Ångström; ρ is the density expressed in g/cm^3; and A is the atomic weight (of carbon).

As an example, we shall give the results of a study of α-benzeneazo-(anisal-α'-naphthylamine) (BAN).[70] The corrected and normalized intensity curve I(s) for unoriented liquid-crystalline specimens of BAN enclosed in glass is shown in Fig. 23a. The curve is drawn as a function of (sin θ)/λ. The dotted line gives the value of the atomic form factors as f^2. The ordinates of the intensity curve and the atomic form factors have been made to match at (sin θ)/λ = 0.5, where

the intensity curve shows neither maxima nor minima. The spherical Fourier integral can be calculated by the strip method,[71] and the radial distribution curve drawn (Fig. 23b).

We should bear in mind the fact that the radial distribution does not depend on whether the atoms belong to the same or different molecules. No "sensitivity" to the presence of molecules is built into it. Hence, the assignment of peaks as being "intramolecular" or "intermolecular" must be based on other data.[67] In particular, one can build a model of the molecule (see Fig. 21b) by using the known values of covalent and intermolecular radii, bearing in mind the principle of directionality of covalent bonds. One can compare the interatomic intermolecular distances in the molecule with the positions of peaks on the radial distribution curve. This comparison is given in Table I.

Undoubtedly, the greatest contribution to the intensities of the peaks in the radial distribution curve comes from the indicated interatomic distances in the molecule. However, this curve also contains peaks due to intermolecular scattering. From considering models we can assume, e.g., that the 3.8 Å peak on the radial distribution curve (Fig. 23b) is due to intermolecular interference. However, whenever one can orient a liquid crystal, one can directly distinguish the peaks due to intermolecular interference by using the intensity distribution along the equator and the meridian of the pattern obtained from the oriented specimen.

Figure 20 shows how the reflections from an oriented specimen are produced on the film. Since an oriented specimen has a statistical cylindrical symmetry, the intensity distribution along the equator of the photograph can be used to construct the cylindrical distribution of the projections of atoms on the base plane perpendicular to the axis of the specimen. In order to construct this function, the x-ray diffraction pattern is photometered along the equator of the photograph. The intensity curve is corrected and normalized, just as for the radial distribution. The normalized intensity curve along the equator for BAN is shown in Fig. 23c. The distribution functions $2\pi r Z(r)$ of the atomic projections on the base plane are calculated by the Fourier-Bessel integral:

$$2\pi r Z(r) = 2\pi r Z_0 + 4\pi^2 r \int I(R)\ J_0(2\pi rR)\ R\ dR;$$

$2\pi r Z(r)$ is equal to the number of atoms within an annulus of radii r and r + dr; R = S/2π; $J_0(2\pi rR)$ is the

Table I

a, Å	1.4	2.46	—	4.26	4.31	4.38	4.92	—	5.57	5.78	—	6.98
b, Å	1.8	2.4	3.8	—	4.3	—	4.9	5.2	—	—	6.2	6.9

a —interatomic distances in the BAN molecule,
b —peak positions on the radial distribution curve.

zero-order Bessel function of R; and Z_0 is the number of atoms per Å^2.

It is clear from simple geometric considerations that $Z_0 = \rho_0^{2/3}$. The function $2\pi r Z(r)$ for BAN is shown in Fig. 23d. The areas under the peaks on this curve indicate the number of close neighbors around the initial atom. For the 3.9 Å peak, this number is eight, and for the 5 Å peak it is 10.5. The numbers of neighbors determined from models proved to be 8 and 12, respectively. The greatest number of atoms in the projection along the molecule fall on the major axis. The size of the peaks in the distribution function is proportional to the product of the numbers of atoms in the projection. Thus it is evident that the major contribution to the $2\pi r Z(r)$ curve is due to the projections of these "axial" atoms in particular. Consequently, if we take their position as the axis of the molecule, we can interpret the curve in Fig. 23d as being a function mainly involving intermolecular interference. This is confirmed by comparing the possible intermolecular distances (from the model representation) with the positions of the peaks on the $2\pi r Z(r)$ curve. This comparison is given in Table II.

Table II

a, Å	3.6	5	6.7
b, Å	3.9	5	6.7

a—possible intermolecular distances,
b—peak positions on the $2\pi r Z(r)$ curve.

The fact that the $2\pi r Z(r)$ curve involves mainly intermolecular interactions is confirmed by another treatment of the equatorial intensity curve of the pattern of an oriented specimen. It can be used to construct the cylindrical distribution function $2\pi r Z_M(r)$ of the molecular axes on the base plane. To calculate this function, one uses the same Fourier-Bessel integral as before. However, one must take into account the fact that the scattering unit is no longer the atom, but the molecule. In this case, the integrand $I(R)$ will correspondingly have a different form:

$$I(R) = \frac{I_n - \overline{|F_M|^2}}{|\overline{F_M}|^2}.$$

If we average cylindrically, the expressions for $|\overline{F_M}|^2$ and $|\overline{F_M}|^2$ have the form

$$|\overline{F_M}|^2 = \Big[\sum_{i=1}^{n} f_0(R)\, J_0(2\pi r_i R)\Big]^2,$$

$$\overline{|F_M|^2} = \sum\sum f_i f_k J_0(2\pi r_{ik} R).$$

To calculate $|\overline{F_M}|^2$ and $\overline{|F_M|^2}$, we must project the atoms of the molecule on the base plane, take into account the weights of the interatomic distances in the projection, and sum the terms of the expressions for $|\overline{F_M}|^2$ and $|F_M|^2$ over all the existing combinations of i and k. The experimental intensity curve is normalized here by ratio to the $\overline{|F_M|^2}$ curve (indicated by the dotted line in Fig. 23e). The quantity Z_0 occurring in the first term of the Fourier-Bessel integral is the number of molecular centers of gravity per square Ångström.

The $2\pi r Z_M(r)$ curve constructed upon calculating the Fourier-Bessel integral is shown in Fig. 23f. The peaks on this curve (at 3.7, 5, and 6.7 Å) agree well with the intermolecular distances derived from a model (3.6, 5, and 6.7 Å). A calculation of the area under the peaks on the $2\pi r Z_M(r)$ curve gives the number of neighbors surrounding the molecule. For the 3.7 Å peak, this number turned out to be approximately six.

Studying the intensity distribution along the meridian gives the interatomic intramolecular distances. The corrected and normalized intensity curve for this case is shown in Fig. 23g. The linear atomic distribution was calculated by a one-dimensional Fourier integral:

$$\varrho_l\,(r) = \varrho_{0l} + \frac{1}{\pi}\int I(s)\cos(sr)\,ds;$$

Here $\rho_l(r)$ is the linear distribution function of the atoms along the axis of the specimen; $\rho_{0l} = \rho_0^{1/3}$ is the number of molecules per Å along the axis.

The $\rho_l(r)$ curve for BAN is shown in Fig. 23h. As we see, the positions of the peaks are somewhat shifted toward the most probable interatomic distances calculated from the model of the molecule (see Table I). This is apparently explained by the fact that the peak intensities also contain a contribution from the reflection due to intermolecular interference. As a whole, however, the interatomic distances within the molecule lie near the peaks obtained from the $\rho_l(r)$ curve. Thus, by using the Fourier-analysis method, one can obtain definite information on the structure of a liquid-crystalline specimen. The example given here of the study of a liquid-crystalline specimen of BAN belonging to the nematic type shows the possibilities of this method. The probable type of molecular packing for BAN is shown in Fig. 24. This structure has the symmetry $\tau_\infty W(x, y)$. Study of smectic phases, e.g., cholesteryl caprate or p-(n-nonoxy)benzal-p'-toluidine,[72] has shown that their x-ray diffraction patterns contain reflections corresponding to the distance between adjacent smectic planes. The period corresponding to this distance proved for both substances to be somewhat less than the length of the molecule. This permits us to assume that the molecules are tipped (at random or in concert) with respect to the plane of the layer. Analysis of the shape of the molecules shows that the most probable packing of the molecules in the smectic layers is antiparallel (Fig. 25). Hence, we must introduce "statistical" twofold axes into the symmetry symbol of these substances. As a whole, the symmetry symbol of a smectic liquid crystal (cholesteryl caprate or p-(n-nonoxy)benzal-p'-toluidine is:
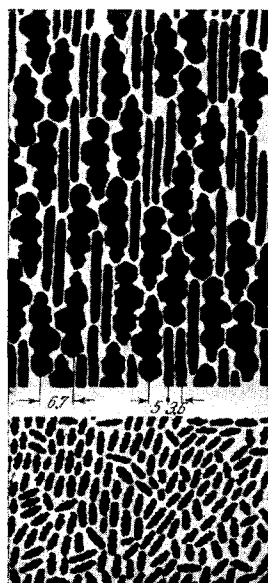
$$C\tau\,(z)\,W\,(x,\,y):2.$$
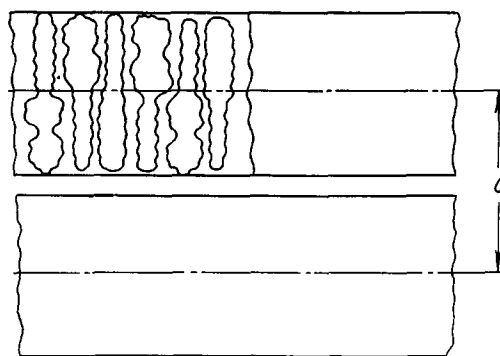
FIG. 24. Structure of a nematic liquid crystal of BAN.

FIG. 25. Layered smectic structure of p-(n-nonoxy)benzal-p'-toluidine.

Thus, experimental investigations bear out the theoretical conclusions [67,68] given above on the structure of liquid crystals. The structures of some lyotropic liquid crystals have also been studied by the x-ray diffraction method. [74-76] One can get definite information on the structures of molecules and of the liquid-crystalline phase by nuclear magnetic resonance (NMR). [116-127]

It has been shown [116] that the isotropic liquid phase of p-azoxyanisole in a magnetic field H = 7300 gauss shows a resonance-line width of 0.1 gauss. When the temperature is dropped below 135.8°C and the specimen transforms to the liquid-crystalline state, the amplitude of the signal declines, and the line splits into three components. The spacing between adjacent peaks amounts to about 3.3 gauss, and their intensities are in the ratio 2:3:2. This line structure disappears when the specimen transforms to the solid crystalline state.

Figure 26 [118] gives comparative NMR data for three compounds. For 4,4'-methoxyazoxybenzene (p-azoxyanisole, or PAA), the line contour in the

liquid-crystalline region remains approximately constant, but the separation of the peaks declines with increasing temperature: 4,4'-methoxy(D_3)-azoxybenzene (DPAA) is the same compound as PAA, but with the protons of the end groups replaced with deuterons. Hence, the protons on the benzene rings are the source of the signals. The signal from this compound consists of a strong doublet and a relatively weak central peak. The shape of the signal remains constant over the entire liquid-crystalline temperature range, but the separation of the peaks declines with increasing temperature. However, 0.5°C below the transition point of the liquid crystal to an isotropic liquid, the central peak rapidly increases, attaining 3/2 times the size of the neighboring peaks, which vanish at the transition point itself. Only a single narrow line remains. At the highest temperatures, p-azoxyphenetole (PAP) gives a line shape similar to that of PAA (Fig. 26). With decreasing temperature, the central peak becomes smaller, and two additional peaks appear (Fig. 26). We can conclude from this that the replacement of the methyl groups of PAA by the ethyl groups of PAP gives rise to a more highly oriented liquid-crystalline phase. Apparently, the shape of the NMR signals is explained by the rotation of the end groups in the molecules. Smectic substances, such as sodium oleate and sodium stearate, give simple lines having a width in the liquid-crystalline state intermediate between those in the iso-

PAA 4,4'-methoxy- azoxybenzene (p-azoxyanisole)		
DPAA 4,4'-methoxy (D_3)-azoxy- benzene		
PAP 4,4'-ethoxy- azoxybenzene (p-azoxyphene- tole)		

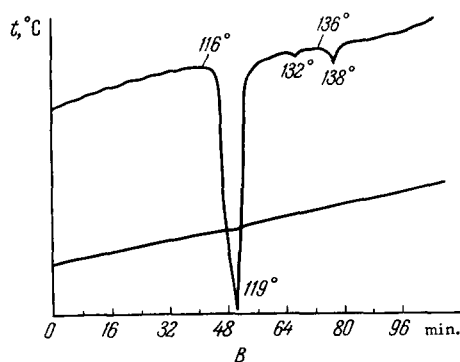FIG. 26. Molecular structure and shape of NMR signals of certain nematic liquid crystals.[118]

FIG. 27. Thermogram of p-azoxyanisole.

tropic and solid-crystalline states.[118] Pretransitional phenomena have been studied by NMR.[119] It turned out that pretransitional phenomena are not symmetrical with respect to the transition point, and depend on the thermal history of the specimen. These data are explained by the Frenkel' theory of heterophase fluctuations, with account taken of the role of impurities arising from the thermal decomposition of the substance.

4. SOME PROPERTIES OF LIQUID CRYSTALS

a) Thermal Properties

We recall that a substance can exist as a liquid-crystalline phase within a definite temperature range from t_1 to t_2. This temperature range is called the region of existence of the liquid crystal. This region can be rather broad for some substances. Thus, n-propyl p-azoxycinnamate exists in the liquid-crystalline state between 123° and 243°C. The range of existence of the liquid crystal in this case is 120°C. Substances are also known whose regions of existence of the liquid-crystal form are only a few degrees. Thus, for methylbenzal-p-aminobenzene-p-hydroxybenzoate the region of existence of the liquid crystal is only 3°C (from 174° to 177°C).

One can use the method of thermography[77-80] to study phase transitions in liquid-crystalline compounds. As an example, we give the thermogram of p-azoxyanisole (Fig. 27). The differential heating curve shows two clearly marked peaks beginning at 116° and 136°C. These points correspond to the temperature of melting of the solid crystal to give a liquid crystal (116°C) and that of the liquid crystal to give an isotropic liquid (136°C). The maxima at 119° and 138°C correspond to the maximum thermal effects of the stated transitions. In addition, we observe a poorly marked endothermic effect having a maximum at 123°C. The latter is probably due either to thermal decomposition of the substance or to pretransitional thermal phenomena. One can also detect phase transitions by measuring the light transmission of the specimen.[81] Changes in the texture of the substance being studied (growth of domains, rearrangement of a confocal texture into a monocrystalline layer, etc.) can also be

detected by this method. Thermography and study of light transmission in combination with polarizing-microscope analysis make it possible to decipher in full the nature of the transitions in a specimen upon varying the temperature.

Just like the transition of a solid crystal into a liquid crystal, the transition of the latter into an isotropic liquid involves a latent heat of transition.[82-84] Thus, for p-azoxyanisole the heat of fusion of the solid crystal to give a nematic liquid crystal is 29,570 joules/mole, while the heat of fusion of the nematic liquid crystal to an isotropic liquid is 574 joules/mole. As we see, the latter is a very small quantity. Indeed, we find that various investigators give also some other values of the heat of transition to the isotropic liquid somewhat different from that given here. Apparently, this involves errors in measuring the small heat effect. We also note that very few of such measurements have been made, and that the design of precision measurements of heats of transition for liquid-crystalline substances would be very useful, and might give valuable information on the nature of the phase transitions of this class of substances. There is even less information in the literature on the variation of the specific volume of liquid crystals as a function of temperature.[85] This relation has been studied most precisely for p-azoxy-phenetole (Fig. 28). As we can see from Fig. 28, the volume varies discontinuously at the liquid crystal-isotropic liquid transition. Thus we are dealing with a first-order phase transition in the liquid crystal-isotropic liquid transition. That is, it is a transition involving absorption of latent heat, with a change in the specific volume.

However, to test the generality of this hypothesis undoubtedly requires setting up experiments along this line on a broader scale. While speaking of phase transitions in substances forming liquid crystals, we should
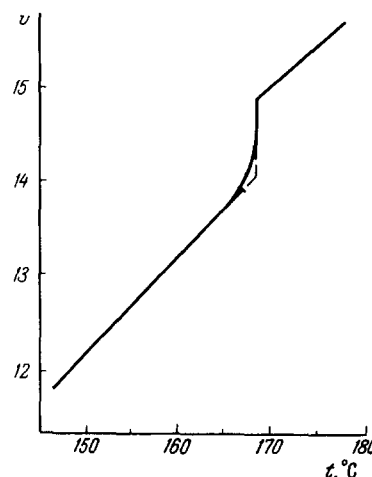

FIG. 28. Temperature-dependence of the volume (on a relative scale) of p-azoxyphenetole. A discontinuity in the volume is observed at the transition point to an isotropic liquid (165°C).[85]

note that not all liquid crystals are stable over a definite temperature range. If liquid crystals are formed both on cooling and heating the substance, then the liquid-crystalline phase is termed enantiotropic. The pattern of phase transitions in this case is:

$$SC \rightleftarrows LC \rightleftarrows IL.$$
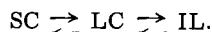
Here SC denotes the solid-crystalline phase, LC the liquid-crystalline phase, and IL the isotropic liquid. The arrows indicate that the liquid-crystalline phase is produced both while heating and cooling the substance. Examples of such substances are p-azoxyanisole, p-azoxyphenetole, anisaldazine, ethyl p-azoxybenzoate, and many others. Besides these substances, there are others that give liquid crystals only when the substance is supercooled. In this case, the liquid-crystalline phase is called monotropic with respect to the solid state. The pattern of phase transitions in this case is:

$$SC \rightleftarrows IL$$

LC
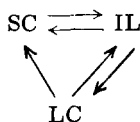
An example of such a substance is cholesteryl acetate. Solid crystals of cholesteryl acetate melt directly to an isotropic liquid at 114°C. If the isotropic melt is cooled very slowly, liquid crystals may not be formed, but solid crystals will begin to grow directly. However, if supercooled (the specimen being cooled rapidly), the sample transforms to a liquid-crystalline phase at about 90°C. When heated, the liquid crystals melt again at 114°C to an isotropic liquid, while if the cooling is prolonged, then the sample begins to crystallize eventually.

It has been shown recently for the example of cholesteryl acetate that phase transitions can be studied by the positron-decay method.[86]

Some substances possess several liquid-crystalline phases. Thus, p-(n-nonoxy)benzal-p'-toluidine gives smectic liquid crystals over the temperature range 70—73°C, but nematic liquid crystals in the range 73—76°C. The pattern of phase transitions for such substances is:

$$SC \rightleftarrows SLC \rightleftarrows NLC \rightleftarrows IL.$$
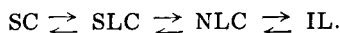
Here SLC denotes the smectic liquid crystal, and NLC the nematic liquid crystal.

b) Magnetic Properties

Liquid crystals are anisotropic in their magnetic properties.[87,88] Figure 29 shows a graph of the temperature-dependence of the specific diamagnetic susceptibility of p-azoxyanisole. For liquid-crystalline p-azoxyanisole (as for all nematic liquid crystals), the diamagnetic anisotropy is normally positive.

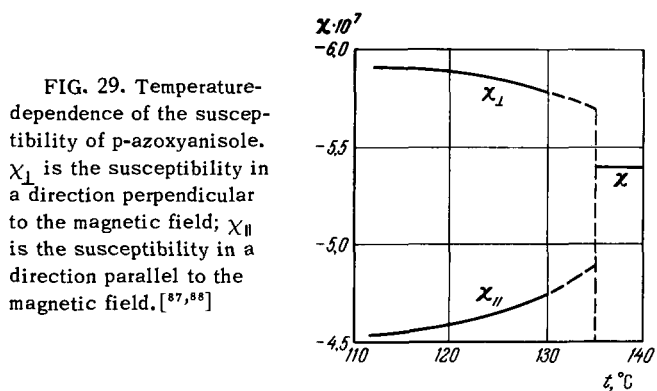When nematic liquid crystals are placed in strong enough magnetic fields, the long axes of the molecules

FIG. 29. Temperature-dependence of the susceptibility of p-azoxyanisole. $\chi_\perp$ is the susceptibility in a direction perpendicular to the magnetic field; $\chi_\parallel$ is the susceptibility in a direction parallel to the magnetic field.[87,88]

orient themselves parallel to the lines of force, and thus the specimen becomes monocrystalline. The orienting effect of the field on the layers of the substance adjacent to the walls of the vessel in which the liquid crystal is being studied interferes with the action of the forces of adhesion of the molecules to the walls. Thus, e.g., when p-azoxyanisole is enclosed between plane glass surfaces with overall specimen thicknesses up to 2 mm, the thickness of the layers adjacent to the walls in which the molecules do not line up parallel to the field amounts to:

0.01 mm for a field H = 1260 gauss, and
0.002 mm for a field H = 10,000 gauss.

Smectic liquid crystals are not oriented by a magnetic field (up to 30,000 gauss), owing to their high viscosity. However, one can orient a smectic substance by cooling the isotropic melt in a magnetic field. In this case the smectic phase proves to be oriented. The optic axis of the liquid monocrystal proves to lie in the direction of the field, i.e., in the same way as for a nematic substance. If the field is then turned off, the orientation persists, in contrast to nematic specimens.

As Frederiks[89,90] has shown, when nematic liquid crystals are put between a slide and a watch glass, then for every value of H there is a certain limiting critical layer thickness Z_C. For lesser thicknesses, the optic axes maintain their original direction (owing to the action of the glass surfaces) (Fig. 30). There is a relation between H and Z_C:

$$Z_C H = K,$$

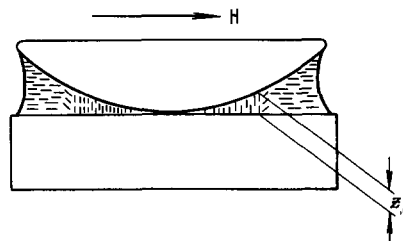where K is a constant. We should note that the limit-

FIG. 30. Diagram of an apparatus for studying the critical thickness of a liquid-crystalline at which the magnetic field begins to orient the liquid crystal.

ing layer thickness Z_C does not depend on the type of glass nor on whether it has been coated with a thin film of metal.

V. N. Tsvetkov[91] has discovered a highly interesting phenomenon in which a liquid-crystalline specimen is placed in a rotating magnetic field. Here the substance of the liquid crystal begins to rotate with the field. Tsvetkov explained the existence of a torque acting on the liquid-crystalline particles in terms of the phase shift between the field vector and the magnetization vector of the substance.

Determination of the torque in a rotating magnetic field makes it possible to measure the diamagnetic anisotropy of a liquid crystal.

FIG. 31. Temperature-dependence of the dielectric constant of p-azoxyanisole. ϵ_1 and ϵ_2 are the principal dielectric constants of the liquid crystal, and ϵ_0 is that of the isotropic melt.[98]

c) Electric Properties

The dielectric anisotropy of various substances[92-98] capable of occurring in the liquid-crystalline state can be either positive or negative. This depends on the size and direction of the dipole moments of the molecules. The dielectric properties of p-azoxyanisole are shown in Fig. 31. As we see from Fig. 31, the size of the dielectric anisotropy declines with increasing temperature of the nematic phase. This involves a decrease in the degree of order of the molecules.[98]

Many contradictory viewpoints have existed with regard to the orientation of liquid crystals in electric fields. On the one hand, Zocher and Birstein[99] have concluded that the optic axes of liquid crystals having symmetrical molecules and negative dielectric anisotropy orient in a direction perpendicular to the field, but substances with asymmetric molecules have positive anisotropy, and their optic axes orient along the field. On the other hand, Jezewski[100] studied the variation in the dielectric constants of p-azoxyanisole and p-azoxyphenetole (substances having negative dielectric anisotropy) in an electric field. He found that, when a field was turned on perpendicular to the plates of the condenser in which the substance was placed, the capacity of the condenser, and hence also the dielectric constant, declined. This meant that the optic axes of the molecules were aligned parallel to the field. V. N. Tsvetkov[12] has explained the contradiction between these results with the idea that the electric field gives rise to flow in the liquid-crystalline substance, as well as orienting the molecules of the liquid crystal. Together with his students, Tsvetkov showed that liquid-crystalline substances in which the molecular dipole moment forms a large angle α with the optic axis of the molecule show negative dielectric anisotropy, and they orient with their optic axes perpendicular to the field. Substances whose molecules have small values of α orient in the direction of the field.

We should note that study of the behavior of liquid crystals in electric and magnetic fields shows much promise with respect to using them in various electro- and magnetooptic devices.
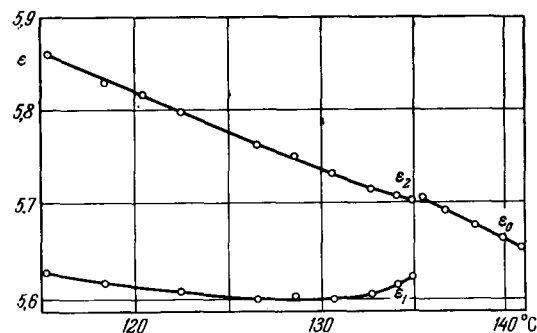
d) Action of Ultrasound on Liquid Crystals

Irradiation with ultrasound (f = 1.8 Mc) substantially changes the texture of a nematic liquid crystal.[104,105] When the ultrasound is applied, the nematic filaments are set in motion. Some of them join with one another, and others are broken apart. A cellular texture appears in a thin liquid-crystal layer when acted on by high-intensity ultrasound. The layer of the nematic substance (p-azoxyphenetole) is divided into cells in which the material is motionless. An important finding in these studies is that one can obtain thin layers of liquid crystals of varying light transmission by varying the intensity of the ultrasound.

Interesting data have been obtained on the velocity and absorption of ultrasound in liquid crystals.[104,106] It has been shown that these quantities vary anomalously at the transition point of the isotropic liquid to the liquid crystal (Fig. 32). As we see from this graph, the anomalous variation in the velocity and absorption of ultrasound in p-azoxyanisole becomes noticeable even 2—3°C before the transition point (135°C) is reached. This phenomenon can be explained by the appearance of heterophase fluctuations near the tran-
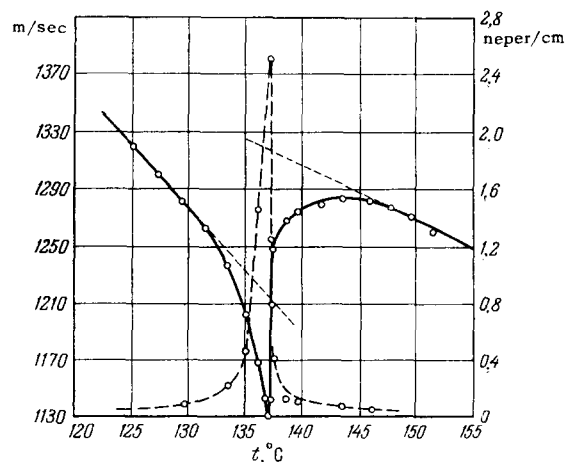

FIG. 32. Temperature-dependence of the velocity of ultrasound (solid line) and its absorption (dotted line) for p-azoxyanisole. These quantities attain their extreme values at the transition point of the liquid crystal to an isotropic liquid.[106]
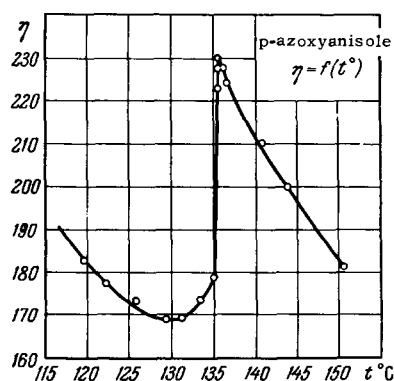
FIG. 33. Temperature-dependence of the viscosity of p-azoxyanisole. The viscosity shows a discontinuity at the transition point of the liquid crystal to an isotropic liquid. [¹⁰⁶]

FIG. 34. Temperature-dependence of the surface tension for p-azoxyanisole. a) Ring method of du Nouy; [¹¹⁵] b) capillary method. [¹¹³]

sition point. An analogous trend is observed in the curves for absorption and velocity of ultrasound in the cholesteric liquid crystals of cholesteryl benzoate.

e) Viscosity and Surface Tension

Figure 33 shows the temperature-dependence of the viscosity of p-azoxyanisole found by G. M. Mikhaĭlov and V. N. Tsvetkov. [¹⁰⁸] As we see from Fig. 33, the viscosity depends linearly on the temperature both in the isotropic liquid and in the liquid-crystalline phase. An abrupt change in the viscosity is observed at the transition point of the isotropic melt to the liquid crystal (135°C). [¹⁰⁷⁻¹¹⁰]

G. M. Mikhaĭlov and V. N. Tsvetkov [¹⁰⁸⁻¹¹⁰], as well as a number of other authors, have measured the viscosity of liquid crystals in magnetic and electric fields. As it turned out, application of a magnetic field in a direction perpendicular to a capillary through which a nematic liquid crystal (p-azoxyanisole) was flowing increased the flow time. When a longitudinal magnetic field was applied, the flow time was decreased. This indicates that the viscosity of the liquid crystal is anisotropic. In particular, the viscosity is less in the direction of the long axes of the molecules. The viscosity anisotropy measured in magnetic fields proves to be very considerable. [¹¹¹] Thus, for p-azoxyanisole at 122°C, the viscosity proved to be:

$\eta_1 = 0.024$, when the molecules are parallel to the flow direction of the liquid crystal through the capillary;

$\eta_2 = 0.092$, when the molecules are parallel to the velocity gradient of flow;

$\eta_3 = 0.034$, when the molecules are perpendicular to both the velocity vector and the velocity gradient vector of flow.

Study of the viscosity anisotropy of smectic and cholesteric liquid crystals is difficult, since these mesophases are hard to orient by external influences.

The study of the viscosity, especially near the "liquid crystal–isotropic liquid" transition, and the theoretical interpretation of the viscosity anomaly at
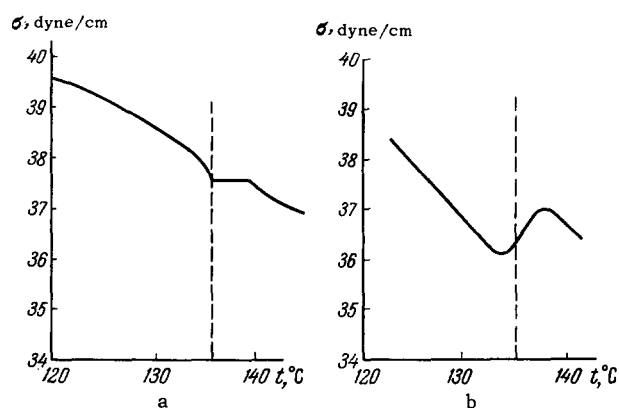
this point are a very important problem. To solve it will permit us to penetrate deeper into the nature of the liquid-crystalline state.

A problem even less studied than the viscosity is that of the surface tension of liquid crystals. Here there exist only studies of the surface tension of nematic p-azoxyanisole. [¹¹²⁻¹¹⁵]

Figure 34 shows the temperature-dependence of the surface tension of p-azoxyanisole as determined by different methods. As we see from Fig. 34, the data are contradictory. This indicates the necessity of further studies along this line.

5. THEORIES OF THE LIQUID-CRYSTALLINE STATE

At present no general theory of the liquid-crystalline state has been developed. There are only a number of special theories, each of which explains to some extent only certain of the properties of liquid crystals.

a) "Swarms" in Nematic Liquid Crystals

Most of the theories of nematic liquid crystals start with the assumption that "swarms" exist in them.

Bose [¹²⁹] was the first to introduce the swarm concept. According to this theory, the molecules gather into parallel groups or swarms, owing to forces of mutual attraction. The concept of a "swarm" must be distinguished from that of a "liquid-crystalline domain." An unoriented liquid-crystalline specimen is an aggregate of variously-oriented domains having transverse dimensions of the order of 0.1 mm. If one applies an orienting influence, then the specimen can become in essence a nematic monocrystal, or a single big domain. If the optic axis of this domain is vertical, then it is extinguished between crossed Nicols in a polarizing microscope. In thick enough layers of a nematic monocrystal at a temperature not very far from the transition point of the liquid crystal to an isotropic liquid, one can observe a multitude of twinkling bright points on the extinguished dark field of the domain.

This phenomenon has been explained by the idea that a monocrystalline nematic domain consists of molecular swarms. The swarms fluctuate, owing to thermal motion, and when the optic axis of a swarm deviates from the normal to the specimen surface (the direction of the optic axis of the whole domain), the swarm is observed as a luminous point. By photographing this pattern on movie film, the mean diameter of a scintillating swarm has been calculated. It proved to be 4×10^{-5} cm.

The existence of swarms in a nematic liquid crystal has made it possible to explain its magnetic properties. As is known, the molecules of a liquid crystal orient with their long axes along the magnetic lines of force. One can determine the magnetic moment of a particle which is being oriented by a magnetic field. For liquid-crystalline p-azoxyanisole, this quantity amounts to 9.48×10^{-17} i.e., 10^4 times as large as a Bohr magneton. This compelled Ornstein[130-132] to suggest that the magnetic field acts not on individual molecules, but on swarms, each of which contains 10^4 molecules. According to these notions, a swarm is an aggregate consisting of parallel molecules. A rather great independence is ascribed to the swarm, and it can be considered as a particle taking part in the Brownian movement.

In fact, Ornstein's proposals that a swarm has a constant magnetic moment have not been borne out (see above).

Chatelain's light-scattering study[28] is a very strong proof of the existence of swarms. In order to explain the light scattering by a nematic monocrystal, he had to assume that it consists of swarms of diameter 2×10^{-5} cm, and hence containing 10^7 molecules. However, as the author himself notes, even here the concept of a swarm is very approximate, and undoubtedly the actual structure of a liquid crystal is more continuous than is supposed in the swarm concept.

Studies to prove the existence of swarms in the isotropic-liquid phase of substances capable of forming liquid crystals are of great interest. It has turned out that all these substances show a very high magnetic birefringence Δn in the isotropic-liquid phase. Here Δn increases anomalously as the melt is cooled and the temperature approaches the transition point of the isotropic liquid to a liquid crystal.[133]

According to Frenkel's theory,[134] near the transition point from the one phase to the other, nuclei of the new phase are formed even before the transition point is reached. Local and temporal fluctuations, called heterophase fluctuations, arise in the old phase.

Tsvetkov[136,150] has extended the theory of heterophase fluctuations to transitions of the "nematic liquid crystal–isotropic liquid" type. According to this theory, swarms, or nuclei of the liquid-crystalline phase, are formed in the isotropic phase. Magnetic birefringence studies[150] confirm the existence in the isotropic phase of swarms containing from several tens to several hundreds of molecules. Analogous conclusions have been drawn from a study of dynamooptical phenomena in p-azoxyanisole.[135]

Thus, there are grounds for assuming the existence of swarms even in the isotropic phase for substances that form liquid crystals.

Nevertheless, there is no direct proof of the existence of swarms in nematic liquid crystals (e.g., by x-ray diffraction). Furthermore, as Zocher[137-139] has convincingly shown, it is not at all necessary to assume the existence of swarms in liquid crystals to explain many phenomena in liquid crystals, in particular, the nature of the action of a magnetic field on liquid crystals. Zocher considers that the direction of orientation of the molecules of a liquid crystal varies continuously from point to point, and this orientation changes abruptly only near the disinclinations (filaments). The equations for explaining the action of a magnetic field on a liquid crystal in this case have exactly the same form as in the swarm theory, with only the physical interpretation of the coefficients differing.

Thus, the problem of the existence of swarms in nematic liquid crystals is still open.

b) The Molecular-statistical Theory of Liquid Crystals

According to a new theory of nematic liquid crystals developed by Maier and Saupe,[140-142] the main reason for the formation of the nematic liquid-crystalline state is the dispersion forces between the molecules. This theory is based on the following hypotheses. The interaction between the constant dipole moments of the molecules is defined only for a definite arrangement of the centers of gravity of the molecules and a definite value of the energy for an isotropic distribution of the molecular axes in space. Nematic order in the distribution of the molecular axes arises by way of the dipole-dipole part of the dispersion interaction of the molecules existing in the ground state.

The initial expression for the energy of nematic ordering is:

$$\varepsilon = \frac{A}{V^2} S \left(1 - \frac{3}{2} \sin^2 \vartheta \right);$$

Here ϑ is the angle between the long axes of the molecules and the optic axis of the domain, A is a constant, V is the molecular volume, and S is the degree of order of the molecules of the liquid crystal.

One of the important consequences of this theory is the conclusion on the temperature-dependence of the fundamental elastic moduli of liquid crystals. The bend modulus has the form

$$K_{33} = \frac{S^2}{V^{7/3}} C_{33}.$$

For the moduli of the two other fundamental deformations, splay K_{11} and twist K_{22}, the same relations are obtained, but with different constants: C_{11} and C_{22}, re-

spectively. The elastic constants of a liquid crystal
can be measured by optical methods, the liquid crystal
being deformed by a magnetic field.[12,90] When the
temperature is varied over a range of about 30°C, the
values of the moduli vary by a factor greater than two,
but the temperature-independent coefficients of the
moduli are practically constant: $C_{11} = 0.64$ dyne·cm[7],
and $C_{22} = 0.39$ dyne·cm[7] (for p-azoxyanisole). This
is a good corroboration of the molecular-statistical
theory of nematic liquid crystals.

We note that it would take an experimental test on
a larger number of substances than has yet been made
to confirm the universality of this theory. Still, we
should not minimize the value of this new molecular
theory of nematic liquid crystals. Apparently it cor-
rectly takes the reason for nematic ordering to be the
dispersion interaction of the molecules; this is the
major point in the theory. We should also note that a
number of the physical assumptions of this theory, in
particular the concept of the degree of order S, had
also been formulated in V. N. Tsvetkov's study.[136]

c) The Theory of Elasticity of Liquid Crystals

A phenomenological theory of the elasticity of liquid
crystals and the rheology of liquid crystals has been
developed in a series of papers.[23,24,143,144] In order
to describe the possible deformations of a liquid crys-
tal, let us set up a Cartesian coordinate system x, y, z
at some arbitrary point O within the material. Near
the coordinate origin, the unit vector L of the molec-
ular orientation varies gradually within a certain re-
gion. At the point O the vector L lies along the z
axis. Under these conditions, the deformation of the
liquid crystal is characterized by six components
(Fig. 35):

splay:

$$\frac{\partial L_x}{\partial x} = a_1, \qquad \frac{\partial L_y}{\partial y} = a_5;$$

bend:

$$\frac{\partial L_x}{\partial z} = a_3, \qquad \frac{\partial L_y}{\partial z} = a_6;$$

twist:

$$\frac{\partial L_y}{\partial x} = a_4, \qquad \frac{\partial L_x}{\partial z} = a_2;$$

Then,

$$L_x = a_1 x + a_2 y + a_3 z + O(r^2),$$

$$L_y = a_4 x + a_5 y + a_6 z + O(r^2),$$

$$L_z = 1 + O(r^2), \qquad r^2 = x^2 + y^2 + y^2 + z^2.$$

In this notation, the free-energy density of the
liquid-crystalline specimen takes on the form

$$g = K_1(a_1 + a_5) + K_2(a_1 - a_4) + \frac{1}{2} K_{11}(a_1 + a_5)^2$$

$$+ \frac{1}{2} K_{22}(a_2 - a_4)^2 + \frac{1}{2} K_{33}(a_3^2 + a_6^2)$$

$$+ K_{12}(a_2 - a_4)(a_1 - a_5) - (K_{22} + K_{24})(a_1 a_5 - a_2 a_4);$$
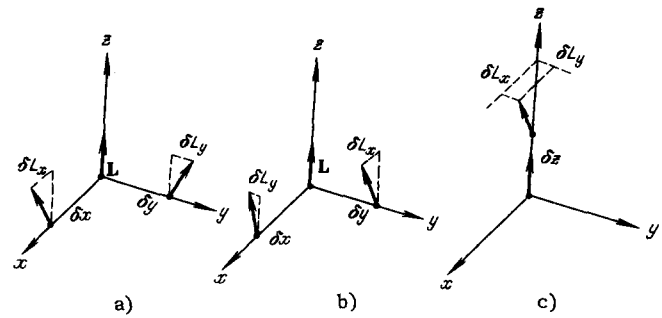

FIG. 35. Compounds of the molecular-orientation vector L.
a) Splay deformation; b) twist deformation; c) bend deformation.

Here the K_{ik} are the strain moduli. The values of the
K_{ik} specify the particular type of liquid crystal that
we are treating.

Smectic liquid crystals are characterized by the
fact that

$$a_2 - a_4 = 0 \text{ and } a_3 i + a_b j = 0;$$

under these conditions the free energy is a minimum.
All the coefficients K_{ik} are very small in comparison
with K_{22} and K_{33}, which are fundamentally what char-
acterizes a smectic specimen. K_{22} is the strain mod-
ulus for twist, and K_{33} for bend.

Nematic liquid crystals are characterized by the
fact that

$$\frac{K_1}{K_{11}} = \frac{K_2}{K_{22}} = K_{12} = 0,$$

and only four moduli remain non-zero: K_{11}, K_{22}, K_{33},
and K_{24}, $K_{24} = 0$ if the liquid crystal forms a planar
texture.

For cholesteric liquid crystals, the characteristic
fact is that $K_{22} \neq 0$, $K_2 \neq 0$, and $K_2/K_{22} \neq 0$. If the
specimen is uniformly oriented, then only twist exists,
characterized by K_{22}. The rotation has a pitch of
$\pi K_{22}/K_2$. If $K_1 \neq 0$ and $K_1/K_{11} \neq 0$, then there is a
uniform splay within a three-dimensional region of
space.

The theory provides an explanation for the exist-
ence of disclinations in nematic specimens. The
configuration of the molecules near the disclinations
is calculated for the case in which $K_{11} = K_{33}$ and K_{12}
= 0. If the vector L is parallel to a plane, then the
free energy is a minimum in the absence of a torque,
when

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0,$$

where Φ is the azimuth of the vector L in the plane.
The solution of this equation gives an expression for
the various types of disclinations:

$$\Phi = \frac{1}{2} n\psi + \Phi_0, \qquad \tan \psi = \frac{x_2}{x_1},$$

where n = 1, 2, 3, ... (see Fig. 9).
Thus, the discussed theory encompasses the char-
acteristics of the different types of liquid crystals.

6. PRACTICAL APPLICATION OF LIQUID CRYSTALS

One of the most prominent chemists, D. Vorländer, who has synthesized a large number of substances giving liquid crystals and established the basic features of the molecules characteristic of liquid crystals, wrote in his well-known monograph[6] that liquid crystals are of interest only with respect to the theory of structure of matter, and could hardly be put to practical use at any time. However, at present the situation has changed radically. Liquid crystals are beginning to be used in technology, medicine, biology, etc.

a) Liquid Crystals in Technology

As we have shown above, many substances in the liquid-crystalline state possess valuable electrooptic properties, which are usually strongly dependent on the temperature, the wavelength, external influences, etc. Undoubtedly, many of these properties are of practical interest. Some of them have already been applied in practice. We shall give a set of examples.

The properties of nematic lyotropic liquid crystals can be used to prepare polaroids.[145] If one puts nematic lyotropic liquid crystals of a dichroic substance between two transparent films that have been previously rubbed in one direction, then one obtains a monocrystalline nematic layer. The solvent eventually evaporates, and a thin film of oriented dichroic molecules remains between the covers. That is, one obtains a polaroid. By combining various substances, one can obtain polaroids of requisite colors.

Liquid-crystalline infrared-visible transformers have been developed,[147] and have been applied to make visible the radiation of a gas laser at wavelength $3.3\,\mu$. The transformer is a film of a cholesteric liquid crystal. Here they used the property of a cholesteric liquid crystal to reflect spectral colors when illuminated by white light. Thus, the use of complex and expensive electronic circuits that had been used for this purpose was eliminated here completely.

Cholesteric liquid crystals have begun to be used to measure temperature gradients.[146] Here one uses the property of cholesteric liquid crystals that they have a definite color at a definite temperature. Use of various mixtures of cholesteric liquid crystals makes it possible to use them to measure temperatures over a rather broad range: from $-20°$ to $+250°C$. The substances are prepared in the form of flexible films that can be applied to a solid surface to record the temperature gradients in different directions. They can be used to study opaque parts to find structural defects, which would conduct heat inhomogeneously and give rise to a color pattern in the applied film.

The color of a cholesteric liquid crystal depends not only on the temperature, but also on other factors. As is known, a trace of vapors in the environment can affect the structure of the substance and change its color. Thus one can determine the presence of vapors in the environment in a concentration of $1:1,000,000$.

The mobility of the structure of a liquid crystal and its rapid change when acted on by external forces is also a very valuable property. For example, the action of an electric or ultrasonic field produces a change in the light transmission of a liquid-crystalline specimen which can be used to modulate light.

b) Liquid Crystals in Medicine and Biology

Many structural formations of cells and even of organs can occur in a liquid-crystalline state. Without error, one can say that the brain is in essence a complex architectural construction that is liquid-crystalline in nature. The gray matter of the brain consists mainly of cerebrosides, phosphatides, and glycerides occurring in a lyotropic liquid-crystalline state. In the white matter of the brain and the conducting pathways of the nervous system, liquid crystals play the role of dielectrics. They form the myelin sheath about the nerve fibers (neurons). The myelin sheath plays an important role in the transmission of the information-bearing electric impulse. Evidently, a deepening of our knowledge of the properties of biological liquid crystals will permit us to gain much information on biological objects.

A large role in the vital activity of organisms is played by the esters of cholesterol, which can form liquid-crystalline phases. As is known, liquid crystals of the esters of cholesterol occur in the organism both in the normal state and in the pathological state, arising from the course of a number of diseases.[148,149]

These few examples sufficiently illustrate the practical importance of studies on liquid crystals, and explain the increasing interest in the problem of the liquid-crystalline state.

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Translated by M. V. King.